Pure Appl. Chem., Vol. 75, No. 6, pp. 683–800, 2003.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON ATOMIC WEIGHTS AND ISOTOPIC ABUNDANCES*

ATOMIC WEIGHTS OF THE ELEMENTS: REVIEW 2000

(IUPAC Technical Report)

Prepared for publication by
J. R. DE LAETER[1], J. K. BÖHLKE[2,‡], P. DE BIÈVRE[3], H. HIDAKA[4], H. S. PEISER[2],
K. J. R. ROSMAN[1], AND P. D. P. TAYLOR[3]

[1]Department of Applied Physics, Curtin University of Technology, Perth, Australia; [2]United States Geological Survey, 431 National Center, Reston, VA 20192, USA; [3]Institute for Reference Materials and Measurements, European Commission – JRC B-2440, Geel, Belgium; [4]Department of Earth and Planetary Systems Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

---

*Membership of the Commission for the period 2000–2001 was as follows:

***Chairman*:** L. Schultz (Germany); ***Secretary*:** R. D. Loss (Australia); ***Titular Members*:** J. K. Böhlke (USA); T. Ding (China); M. Ebihara (Japan); G. I. Ramendik (Russia); P. D. P. Taylor (Belgium); ***Associate Members*:** M. Berglund (Belgium); C. A. M. Brenninkmeijer (Germany); H. Hidaka (Japan); D. J. Rokop (USA); T. Walczyk (Switzerland); S. Yoneda (Japan); ***National Representatives*:** J. R. de Laeter (Australia); P. De Bièvre (Belgium); C. L. do Lago (Brazil); Y. K. Xiao (China/Beijing).

‡Corresponding author

Atomic weights of the elements: Review 2000

(IUPAC Technical Report)

Abstract: A consistent set of internationally accepted atomic weights has long been an essential aim of the scientific community because of the relevance of these values to science and technology, as well as to trade and commerce subject to ethical, legal, and international standards. The standard atomic weights of the elements are regularly evaluated, recommended, and published in updated tables by the Commission on Atomic Weights and Isotopic Abundances (CAWIA) of the International Union of Pure and Applied Chemistry (IUPAC). These values are invariably associated with carefully evaluated uncertainties. Atomic weights were originally determined by mass ratio measurements coupled with an understanding of chemical stoichiometry, but are now based almost exclusively on knowledge of the isotopic composition (derived from isotope-abundance ratio measurements) and the atomic masses of the isotopes of the elements. Atomic weights and atomic masses are now scaled to a numerical value of exactly 12 for the mass of the carbon isotope of mass number 12. Technological advances in mass spectrometry and nuclear-reaction energies have enabled atomic masses to be determined with a relative uncertainty of better than 1×10^{-7}. Isotope abundances for an increasing number of elements can be measured to better than 1×10^{-3}. The excellent precision of such measurements led to the discovery that many elements, in different specimens, display significant variations in their isotope-abundance ratios, caused by a variety of natural and industrial physicochemical processes. While such variations increasingly place a constraint on the uncertainties with which some standard atomic weights can be stated, they provide numerous opportunities for investigating a range of important phenomena in physical, chemical, cosmological, biological, and industrial processes. This review reflects the current and increasing interest of science in the measured differences between source-specific and even sample-specific atomic weights. These relative comparisons can often be made with a smaller uncertainty than is achieved in the best calibrated "absolute" (= SI-traceable) atomic-weight determinations. Accurate determinations of the atomic weights of certain elements also influence the values of fundamental constants such as the Avogadro, Faraday, and universal gas constants. This review is in two parts: the first summarizes the development of the science of atomic-weight determinations during the 20th century; the second summarizes the changes and variations that have been recognized in the values and uncertainties of atomic weights, on an element-by-element basis, in the latter part of the 20th century.

CONTENTS

PREFACE

PREFACE

Purpose of the review

This review describes the gradual evolution of knowledge, understanding, and detailed information on the atomic weights of the chemical elements and their isotopic compositions in normal materials, as evaluated regularly by IUPAC. Atomic weights at the start of the 20th century were a well-recognized part of chemistry, but are now interdisciplinary, both in their measurements and their applications. Under these circumstances, such a review has clear purposes and aims at:

- tracing the history of concepts, such as that of “atomic weights” once believed to be constants of nature;
- describing the methods of atomic-weight determinations;
- giving current knowledge of the best values of the atomic weights based on the elements’ isotopic compositions;
- indicating the estimated uncertainties of all these data in accord with methods of measurement science, as established during the century;
- adopting scales of measurements in accord with the modern system of units as also developed during the century;
- warning of known limitations of the above data for exceptional materials; and
- exploring applications for the differential measurement of isotopic composition to all branches of materials science.

This review is not primarily concerned with definitions and technical terms, as this matter is the responsibility of IUPAC’s Interdivisional Commission on Nomenclature and Symbols (IDCNS), recently renamed Interdivisional Committee on Terminology, Nomenclature and Symbols (ICTNS). Questions of semantics generally, when derived by logic or based on historic use, or in accord with conventions in related fields, are vigorously debated. Even CAWIA, whose very name includes the much-disputed term “atomic weight,” has not been able to avoid involvement. When Tomas Batuecas, President of the Atomic Weights Committee, persuaded the authorities in the IUPAC Bureau in 1963 to change the term to “atomic mass”, traditional chemists revolted, “atomic weights” was retained, and

Edward Wichers, who had previously been Commission President, was quietly reinstalled in the chair of the Atomic Weights Commission. Other substitute terms, such as "relative atomic mass" and "mean relative atomic mass", have since found strong backing, and the International Organization for Standardization (ISO) *Standards Handbook on Quantities and Units* lists "relative atomic mass" with the annotation "formerly called atomic weight". CAWIA members, however, have rationalized the retention of the use of "atomic weight" when clearly defined. The principal value of the work of CAWIA and this review, however, does not hinge on that or any other term. Whereas in this review we have retained the use of "atomic weight", we have for other terms tended to use those advocated by the Bureau International des Poids et Mesures (BIPM), which makes recommendations for all measurements and for the use of the International System of Units of Measurement (SI).

Acknowledgments

This review has only been made possible because of those who have contributed to our knowledge of atomic weights and isotope abundances over the past 100 years. As we move into the 21st century, we acknowledge all those individuals who have worked in the field during the 20th century. In particular, we express our appreciation to the members of CAWIA and its predecessors, who have given so much of their time and talents to advance the discipline to the authoritative status it enjoys today.

The authors are indebted to their colleagues on CAWIA under the chairmanship of Prof. Ludolf Schultz, who authorized the preparation of this review at the 1997 meeting of CAWIA in Geneva, and have given advice and encouragement over the intervening period of time. The help of CAWIA members in reviewing sections has been of great value. In particular, we acknowledge substantial advice and assistance from Dr. T. B. Coplen, Prof. N. N. Greenwood, Dr. N. E. Holden, and Dr. E. Roth, including the discovery by Holden of several errors in a previous review.

In compiling this review, the authors have drawn extensively on articles written by past and current members of CAWIA who have kindly permitted their material to be used without restriction. In particular, the framework of the previous element-by-element review was used as the basis for the present review. Its basic philosophy was maintained, and some CAWIA members are coauthors of both reviews. We also thank CAWIA's parent organization IUPAC, through its Division of Inorganic Chemistry, for supporting this initiative.

The support of Curtin University of Technology in Perth (Australia), the Institute of Reference Materials and Measurements (IRMM) of the European Commission—Joint Research Centre in Geel, Belgium, the United States Geological Survey (USGS) in Reston, Virginia, USA, and the University of Hiroshima, Japan, is gratefully acknowledged. Prof. H. Hidaka acted as host to a preliminary meeting of the element-by-element review team in Hiroshima in October 1998. A second meeting was held in Berlin, Germany in August 1999, at the time of the IUPAC General Assembly, and a final meeting with a subset of members was held in June 2000 at IRMM, in Geel. Dr. T. B. Coplen and Mr. Jaroslav Keybl (USGS) provided important editorial assistance.

List of acronyms

BIPM	Bureau International des Poids et Mesures
CAWIA	Commission on Atomic Weights and Isotopic Abundances
CBNM	Central Bureau for Nuclear Measurements (European Community)
CGPM	General Conference on Weights and Measures (BIPM)
CEA	Commissariat à l'Énergie Atomique
CIPM	International Committee for Weights and Measures (BIPM)
CODATA	Committee on Data for Science and Technology (ICSU)
EC	European Commission
GISP	Greenland ice sheet precipitation

IAEA	International Atomic Energy Agency
ICP-MS	inductively coupled plasma-source mass spectrometry
ICSU	International Council of Scientific Unions
ICTNS	Interdivisional Committee on Terminology, Nomenclature and Symbols (IUPAC)
IDCNS	Interdivisional Commission on Nomenclature and Symbols (IUPAC)
IDMS	isotope dilution mass spectrometry
IMGC	Istituto di Metrologie "Gustavo Colonnetti" (Italy)
IRMM	Institute of Reference Materials and Measurements (EC)
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
IUPAP	International Union of Pure and Applied Physics
LSVEC	lithium-svec (a lithium carbonate)
NBL	New Brunswick Laboratory
NBS	National Bureau of Standards (USA)
NGS	natural gas standard
NIST	National Institute of Standards and Technology (USA)
NML	National Measurement Laboratory, CSIRO (Australia)
NRLM	National Research Laboratory for Metrology (Japan)
NSVEC	nitrogen-svec (a gaseous nitrogen)
PTB	Physikalisch-Technische Bundesanstalt (Germany)
SAIC	Subcommittee on the Assessment of the Isotopic Composition of the Elements
SI	Système International d'Unités, the International System of Units
SIAM	Subcommittee on Isotope Abundance Measurements
SIMS	secondary ion mass spectrometry
SLAP	standard light Antarctic precipitation
SRM	standard reference material
SUN-AMCO	Commission on Symbols, Units, Nomenclature, Atomic Masses and Fundamental Constants (IUPAP)
TICE	Table of Isotopic Compositions of the Elements (CAWIA)
TSAW	Table of Standard Atomic Weights (CAWIA)
USGS	United States Geological Survey
VSMOW	Vienna standard mean ocean water

PART 1: HISTORY, ASSESSMENT, AND CONTINUING SIGNIFICANCE OF ATOMIC-WEIGHT DETERMINATIONS

Introduction

The 20th century was the stage on which impressive advances in scientific knowledge were achieved. This is well illustrated by the development of the science of atomic-weight determinations (see Table 1). At the beginning of the 20th century, some elements had not yet been isolated, but the discovery of Ga, with predicted mass and properties, convinced chemists of the usefulness of the periodic listing of the elements. Becquerel [1] had just announced the discovery of radioactivity, and Thomson was still to discover stable isotopes. By contrast, at the end of the 20th century, the science of atomic weights has attained a high level of sophistication and international recognition. In recent decades, the experimental comparison of the abundance ratios of two given isotopes in two materials has attained remarkably small uncertainties even when applied to very small samples, and especially when comparisons are made with synthetic mixtures of materials with enriched isotopes. Nevertheless, there is every indication that further improvement in instrumental performance and measurement precision will greatly benefit isotope science in the future. The detection of small variations in atomic weight of some elements in natural terrestrial materials has yielded many important opportunities for application of isotope-abundance measurements and a never-ending demand for improvements in measurement techniques.

Many of these achievements are due to the work of the committees concerned with atomic weights and isotopic compositions. Some such national committees existed as early as in the last years of the 19th century [2]. Then, at the very beginning of the 20th century, the International Committee on Atomic Weights was formed. In 1920, it was reconstituted as part of IUPAC and has so continued ever since. The Committee, and its variously renamed Commissions, has issued at regular intervals reports on progress in the science relating to atomic weights [3–19]. In 1979, the Commission on Atomic Weights received a new name Commission on Atomic Weights and Isotopic Abundances (CAWIA) and formally undertook the responsibility for evaluating new isotopic-composition data through its Subcommittee on the Assessment of the Isotopic Compositions of the Elements (SAIC), now titled the Subcommittee of Isotope Abundance Measurements (SIAM), and for examining the implications of these and other measurements on the values of the atomic weights. In its reports, CAWIA has provided the results of such investigations to the scientific community on a regular basis.

Table 1 Important events in the history of atomic weights.

1892	The American Chemical Society forms a Committee on Atomic Weights.
1896	H. A. Becquerel discovers radioactivity.
~1900	T. W. Richards develops the “Harvard method” for determining atomic weights.
1902	The International Committee on Atomic Weights is formed.
1912	J. J. Thomson discovers isotopes of Ne by a mass-spectrometric technique.
1913	The International Committee is affiliated with the International Association of Chemical Societies.
1919	F. W. Aston demonstrates the effectiveness of the first mass spectrograph. E. Rutherford demonstrates nuclear transformations by impact between nuclei.
1920	The International Committee on Atomic Weights is affiliated with IUPAC at its formation. A. J. Dempster calculates the atomic weight of Mg by using the relative isotope abundances together with the whole number masses of the stable isotopes of Mg. F. W. Clarke publishes the last version of his major element-by-element review of atomic weights based solely on the chemical method.
1921	The International Committee on Atomic Weights becomes the Committee on Chemical Elements with responsibility for radioactive and stable isotopes.
1929	W. F. Giauque and H. L. Johnston discover that O has three isotopes, which leads to IUPAP using a mass scale based on $m(^{16}O) = 16$ atomic mass units, whereas IUPAC continues to use $A_r(O) = 16$.
1930	The Committee on Chemical Elements is subdivided into three parts, one of which becomes the Atomic Weights Committee.
1932	H. C. Urey and colleagues discover the isotope ^2H.
1938	O. Hahn, F. Strassmann, and L. Meitner discover nuclear fission.
1940	A. O. Nier designs a magnetic sector mass spectrometer for isotope-abundance ratio measurements.
1947	H. C. Urey summarizes the thermodynamic properties of substances in relation to their isotopic composition.
1950	A. O. Nier carries out the first “absolute” isotope-abundance measurement for Ar by calibrating two mass spectrometers by means of synthetic mixtures of Ar isotopes.

(*continues on next page*)

Table 1 (*Continued*).

1954	The NBS introduces a mass spectrometer-based program to certify isotopic reference materials and to measure the “absolute” isotope abundances of selected elements.
1957	A. O. Nier and A. Ölander independently suggest that $A_r(^{12}C) = 12$ and $m(^{12}C) = 12$ u be adopted to replace the $A_r(O) = 16$ and $m(^{16}O) = 16$ atomic mass units.
1959/1960	IUPAC and IUPAP agree to unify the two existing scales to a $A_r(^{12}C) = m(^{12}C) / u = 12$. Everling, König, Mattauch, and Wapstra publish isotope mass values.
1962	Cameron and Wichers publish a comprehensive element-by-element review, presenting the atomic weights of the elements on the scale of $A_r(^{12}C) = 12$ exactly. The CBNM commences a similar program to that established by NBS in 1954.
1969	The renamed Commission of Atomic Weights associates every recommended $A_r(E)$ value with an estimated expanded uncertainty, $U[A_r(E)]$, of restricted magnitude of either 1 or 3 in the last digit of $A_r(E)$.
1979	The Commission receives the name CAWIA and publishes for the first time a Table of Isotopic Compositions of the Elements.
1984	CAWIA publishes a comprehensive element-by-element review, updating the values for atomic weights that had occurred since 1962, largely as the result of isotope-abundance determinations.
1985	CAWIA permits $U[A_r(E)]$ to be stated as any single value in the last digit of $A_r(E)$.
1993	Audi and Wapstra publish their 1993 Atomic Mass Table, which is accepted by CAWIA to calculate atomic weights.
2003	CAWIA publishes a comprehensive element-by-element review of the atomic weights, with an overview of the achievements of sciences related to atomic-weight determinations during the 20th century.

For each of the chemical elements, E, CAWIA compiles atomic weights, $A_r(E)$, with estimated uncertainties, $U[A_r(E)]$. Abundances of isotopes, ^iE, can be represented as mole fractions, $x(^iE)$, where i is the mass number of the isotope. $A_r(^iE)$ is its relative mass. $\Sigma[x(^iE)] = 1$ for a given E. CAWIA (and its predecessors) has reviewed the status of atomic-weight determinations from time to time. Several notable atomic-weight compilations were done in the 19th century, followed by a landmark review published in 1920 by Clarke [20], who recalculated the atomic weights of all known elements from evaluated measured mass ratios of stoichiometric compounds and elements on the scale of $A_r(O) = 16$. In contrast with later reviews, Clarke’s review was based principally on the so-called chemical (or Harvard) method. Clarke’s review remained the definitive work on atomic weights for the next 20 years or more. In 1953, A. O. Nier carried out an early evaluation of some relative isotope-abundance measurements by mass spectrometry for the Atomic Weights Committee [21]. The comprehensive review by Cameron and Wichers [22], was the direct result of the decision by IUPAC and the International Union of Pure and Applied Physics (IUPAP), to adopt a new atomic-weight scale based on $A_r(^{12}C) = 12$. It drew heavily on new values for atomic weights based on atomic masses [23], which have since been updated with encouragement by IUPAP and relied upon by CAWIA. Mass spectrometric measurements of the abundances of the isotopes were encouraged and evaluated by CAWIA. This combined method has since been accepted for measuring atomic weights for all but the monoisotopic elements. A subsequent review [24] critically examined, on an element-by-element basis, changes that had occurred in atomic weights since the 1962 review and also described changes in the methodology of reporting atomic-weight information. In a related publication, Peiser [25] pointed out that many IUPAC-recommended atomic weights were still based on experimental determinations that appeared to be short of the best state of the art.

In 1997, CAWIA decided to initiate another major review, which would be an attempt to describe the developments in atomic-weight determinations during the 20th century, and to present our knowledge of the field in a single volume. This review is the result of that decision. Another aim of this review is to summarize the current CAWIA-evaluated knowledge of the numerical values of all atomic weights $A_r(E)$ and their uncertainties $U[A_r(E)]$, their reliability and the limitations to their applicability. This may be of value to users who, on a given topic, might otherwise have to consult several of CAWIA's biennial reports. As explained in the Preface, this review is not primarily concerned with terminology, which is the responsibility of ICTNS within IUPAC. Nevertheless, the Commission in its 1973 report [6] found it necessary to explain its understanding of "normal" and "well-characterized" materials. Subsequent Commission reports for 1975 and 1977 [7,8] further amplified these definitions and recommended appropriate labeling of commercially available chemicals.

History

The ancient Greeks considered the idea some 2500 years ago that matter might be composed of atoms (Greek: *atomos*; uncuttable). They introduced the idea that all matter is not capable of infinite subdivision, and called the ultimate and indivisible constituents of matter "atomos." In the 17th century, the Irishman Robert Boyle developed chemical analysis—the technique for breaking down substances into their constituents. He defined an element as a material that could be identified by scientific experiment and could not be broken down by chemical means into still simpler substances. This is the definition that is still in use today.

The French scientist Antoine Lavoisier revolutionized chemistry in the 18th century by introducing accurate weighing of substances, including gaseous matter. He observed that a given amount of matter has a mass that remains the same when it is redistributed from one chemical combination to another, whether in the solid, liquid, or gaseous state. The analysis of the French chemist Joseph Proust showed that a particular chemical compound always contained the same elements united in the same proportions by mass ("weight").

The English schoolteacher John Dalton, at the start of the 19th century, tested Proust's hypothesis and noted that the same elements can sometimes combine in different proportions to produce different substances. In his atomic theory, all matter was made up of particles called atoms of various elements. Atoms of the same element were alike in every compound. Atoms of different elements differed in their mass ("weight"). In chemical reactions, atoms preserved their identity and were not destroyed. When Dalton published his atomic theory, he included tables of atomic weights [26].

The Italian physicist Amadeo Avogadro made a distinction between the chemical atom (smallest part of matter that can enter into chemical combination) and the physical molecule (smallest particle of a chemical compound), and suggested that equal volumes of all gases contain the same number of molecules under the same conditions of temperature and pressure, whereas a molecule (Greek: a small mass) may contain more than one distinguishable atom [27].

The English physician William Prout [28] noted that Dalton's atomic-weight values of elementary gases were nearly exact multiples of the atomic weight of H, $A_r(H)$, and suggested that H was the primordial matter from which all elements are formed. For a while, it appeared that a number of atomic-weight values agreed with this hypothesis, and testing it led to a major measurement effort of determining atomic-weight values over the remainder of the 19th century.

At the Karlsruhe Congress in September 1860, about 140 leading European chemists met to formulate an understanding of the nature of atoms and molecules and to reach a consensus with respect to an atomic-weight scale. The Italian chemist Stanislao Cannizzaro presented his "Sketch of a Course in Theoretical Chemistry" [29], in which he called attention to the value of Avogadro's distinction between atoms and molecules as an organizing device for the interpretation of chemical phenomena. The interchange of the terms "atoms" and "molecules" had led to confusion and to instances of two different atomic weights being assigned to the same element. Lothar Meyer and Dimitri Mendeleyev both attended this Congress and subsequently developed periodic tables of the chemical elements based on revised atomic weights. Mendeleyev left open spaces in places where no known element filled that space

[30]. He also predicted the properties of these unknown elements. When Sc, Ga, and Ge were discovered over the next 16 years and found to conform with Mendeleyev's predicted chemical properties, atomic weights became established in the periodic table and their usefulness more fully understood.

By the end of the 19th century, the atomic theory and its implications for the chemical elements had taken firm hold. Nature was seen to be using remarkably few types of elementary "building blocks" for all materials. With an understanding of simple number valences of these "elements", the stage was set for chemistry to emerge as a science based on measurement of the interactions between numbers of "atoms" of the elements in simple number proportions. Chemical reactions, energies, and products, could now all be represented by simple formulae and equations. With newly developed balances of high precision, the relative mass values of atoms of the elements could be determined. When these relative values were scaled to the mass of a H atom equal to one, or to the mass of an O atom equal to 16, chemists called them "atomic weights".

In the 19th century, quantitative chemical-composition measurements of materials with relative uncertainties a little smaller than 1 % became possible and widely practiced. In order to achieve that level of uncertainty, chemists needed ratios between constants called "atomic weights" to be determined to an even smaller uncertainty than they could achieve in chemical analysis. To determine atomic weights to best possible accuracies, Berzelius and others developed the quantitative gravimetric study of the known stoichiometric compounds and acquired knowledge of the characteristic reactions for each known element. Often, the compounds and reactions involved O, less frequently H, Cl, Br, or Ag. Atomic weights scaled to the mass of the H and O were mutually related through the O/H mass ratio in water, which was measured with great skill under carefully controlled conditions of purity.

At the end of the 19th century, this prodigious effort culminated in 1886 in the publication of an atomic weights table by Clarke [31], in which he relied heavily on the work of Berzelius, Brauner, and others. Although not all elements were known at that time, it is interesting to note that two-thirds of the atomic weights listed agreed to better than 1 %, and almost 40 % agreed to better than 0.1 % with those of the 1959 table of the Atomic Weights Committee [32]. The comparison between the two data sets is justifiable because the atomic-weight scale was then based on $A_r(\mathrm{O}) = 16$, whereas the current value is 15.9994. A comparison of the atomic weights of polyisotopic elements as determined by "absolute" physical and chemical techniques is given in Peiser et al. [24]. New and better atomic-weight determinations by classical chemical methods was a factor in enabling chemists to make the remarkable progress in the science in the 20th century, for instance, in purification and recovery methodologies. These chemists, among them Richards, Urbain, Hönigschmid, Brauner, and Baxter, who measured atomic weights with very small uncertainties, were accorded the highest honor by the scientific community.

Commission on Atomic Weights and Isotopic Abundances

As early as 1872 F. W. Clarke, chief chemist at the USGS, recognized that measurement comparability between laboratories made uniformly recognized atomic weights desirable. Under his leadership, the best contemporary knowledge of the atomic weights became the primary task of the American Chemical Society's Committee on Atomic Weights in 1892 [31].

An elaborate international election by 57 chemists from many nations was organized by W. Ostwald in 1902, and, as a result, an atomic-weights committee was initially entrusted to just three members who had obtained the highest number of election votes [2]: Clarke, K. Siebert from Germany, and T. E. Thorpe from England. There was a strong feeling that France, a leader in the promotion of rational unification in measurement science, had to be represented on the Committee. So, first H. Moissan and, after his death, G. Urbain of France were coopted to the Committee. This Committee preserved continuity through World War I, despite problems in contacting German colleagues through Switzerland as is documented in IUPAC's archives. In 1913, the International Committee on Atomic Weights joined the International Association of Chemical Societies.

After World War I, the Committee flourished. It became part of IUPAC when it was established in 1920. IUPAC saw the Committee's mandate at the heart of its own responsibilities to the world's scientific community. Indeed, no data set of science and technology has been involved more extensively or in as many disciplines, technologies, and commercial transactions, as is the IUPAC table of recommended atomic weights, now called the standard atomic weights.

In 1921, it was decided to reorganize and enlarge this Committee by giving it the responsibility of advising on the existence of radioactive and stable isotopes, as well as on atomic weights. It was renamed the Committee on Chemical Elements. Two members of the Committee were Francis Aston and Frederick Soddy, both of whom had received Nobel Prizes in Chemistry. Altogether six Nobel Prize winners have served on the Committee. In 1930, the Committee on Chemical Elements was subdivided into three parts, one of which became the Atomic Weights Committee. In 1969, after several further reorganizations, the IUPAC responsibility for atomic weights fell upon the Commission on Atomic Weights, renamed CAWIA in 1979, which has the role of evaluating new isotope-abundance data and publishing tables of Standard Atomic Weights and Isotopic Compositions of the Elements on a regular basis. Interesting historical accounts of the International Commission have been given by Holden [2,32].

In 1969, there was a serious move within IUPAC to eliminate the Atomic Weights Commission. Not that atomic weights were not needed—not that the Commission had performed badly—but because atomic weights were then thought to be so accurate that any further improvement was at most an "academic" exercise of no interest or relevance to professional chemists or chemical technology, and certainly not to commerce. The recognition that isotope-abundance variations would impair the "accuracy" of atomic weights was one of the arguments to continue the work of the Commission.

In the 1970s, it became clear that the very techniques that yielded accurate atomic weights could be employed to do chemical analyses and other chemical measurements to better accuracies than had previously been achieved. New applications came into prominence, among them the use of subtle differences in sample atomic weights and isotopic compositions to identify sources of materials and influences from manufacturing processes and mechanisms of biological reactions. From the classical emphasis on better atomic weights, we have come to the understanding that it is not simply the accuracy of atomic weights that is all-important, but of equal significance is the uncertainty associated with the standard atomic weights. The subtle differences in isotope abundances and atomic weights now drive mass spectrometrists to measure samples with as high precision as possible. Improvements in the values of the standard atomic weights aim to give scientists a reliable basis to evaluate what uncertainties are introduced into an analytical result when the standard atomic weights are used as reference values.

Urey [33], De Bièvre [34], and others have pointed out that variations in isotope abundances are a vast information source. Nature has provided over 300 stable and long-lived isotopes, which are of immense value to science by their ability to carry information through their "isotopic signatures." The ability of a mass spectrometer to measure isotope-abundance ratios with high precision enables it to act as instrument of choice for comparing amounts of isotopic substance, that is numbers of atoms, in two samples just like a conventional chemical precision "balance" compares the amounts of mass quantity in two material objects [35]. The mass spectrometer takes the particulate nature of matter fully into account in that it sorts out atoms on the basis of their mass, then counts them, thus leading to the direct measurement of ratios of numbers of atoms (i.e., ratios of amounts of substance). These two features make isotope mass spectrometry one of the most powerful analytical tools we have at our disposal [36,37].

While CAWIA made outstanding progress in assessments of atomic-weight determinations, the more universal art of measurement at the highest achievable accuracy also advanced. By the end of the 19th century, the field of measurement science, called metrology, became widely recognized as a fundamental aspect of the scientific method and an essential gateway to progress in technology. For metrological concepts to be conveniently used in science and industry, two major steps had to be taken:

(1) Magnitudes of the measured quantities had to be expressed in the familiar decimal system of numbers.

(2) Physics-developed laws of mathematical relationships between different quantities had to be involved so that most measurements could be expressed in terms of coherent units of a few base quantities.

A consistent system of measurement units thus became possible, and international agreement was needed.

The General Conference on Weights and Measures (CGPM) operates every four years under the Convention of the Metre, a diplomatic treaty concluded in 1875 and adhered to by most industrialized countries. In 1960, CGPM established the SI under the above concepts. Virtually all international bodies have adopted the SI and attempt to facilitate its almost universal application, especially in chemistry, with its prime interest in "amount of substance" (a base quantity in SI since 1971). Until recently, chemists had few methods of directly measuring "amount"—that is, counting "absolute" numbers of entities, or their ratios—but were limited to the use of an amount–related property of matter—"mass," the ratio of which could be measured by a remarkably accurate measuring device (i.e., a balance). For over a century, laboratory balances have been effectively used in comparing the masses of two similar objects to a relative precision of 1×10^{-6}. These mass ratios needed mass-to-number specific conversion factors in order to yield the desired ratios of numbers of entities, the true aim of measurement in chemistry. These factors involve atomic weights. The wide adherence to the SI by chemists thus appears to present at most minor hurdles in traditional semantics. One major task, however, remains for CAWIA: the development of agreed methods for the assignment of uncertainties, the essential quality assessments of all good measurements, under guidance by ISO [38].

Discovery of radioactivity and isotopes

The discovery of radioactivity by the French scientist H. A. Becquerel [1] caused a fundamental upheaval in the science of atomic weights, as it opened up the possibility that radioactive elements characterized by spontaneous emission of "rays", and their decay products, could have different atomic weights. One component of these "rays", called alpha particles, carried appreciable mass and were identified as He nuclei by W. Ramsey and F. Soddy [39]. Soddy [40] also demonstrated the chemical identity of mesothorium 1 (^{228}Ra) and Ra, and concluded that there were chemical elements with different radioactive properties and different atomic weights, but with the same chemical properties and therefore occupying the same position in the periodic table. Soddy coined the word "isotope" (Greek: *isos topos*: in the same place), to account for these radioactive species. The original definition of "isotope" referred to the fact that a second species could be inserted at the same place in Mendeleyev's tables. At that time, the phenomenon was thought to be a characteristic only of some radiogenic elements. The possibility of the existence of an isotope of H of mass 2 would have been judged pure speculation. The discovery of ^{2}H in nature had to wait for approximately another 20 years.

The study of the natural radioactive decay chains for Th and U led to the hypothesis that the radioactive parent isotopes, ^{232}Th and ^{238}U, would decay by loss of an integral number of alpha- and associated beta-particles, into different stable end isotopes of Pb—^{208}Pb and ^{206}Pb, respectively. Lead from radioactive minerals should therefore differ in atomic weight according to the proportion of U and Th in the mineral and with the age of the sample. That hypothesis proved to be correct. The measured atomic-weight value for "common" Pb (from a nonradioactive source material) was reported by Baxter and Wilson to be 207.2 [41]. Soddy and Hyman [42] reported that Pb in a thorium silicate mineral had an atomic-weight value of 208.3. Richards and Lembert [43] reported the atomic-weight value of Pb in U minerals to be as low as 206.4. It was concluded that Pb was made up of a mixture of stable isotopes, each having a different relative mass not differing appreciably from a whole number value when scaled to $A_r(\mathrm{O}) = 16$.

The second event that had a profound effect on the future of the determination of atomic weights was the discovery of the stable isotopes of Ne by J. J. Thomson [44], although Sir William Crookes had postulated the existence of isotopes based on the spectroscopic analysis of Yb some years earlier. Using a positive ray parabola technique, Thomson demonstrated that Ne exists in at least two isotopic forms, of mass numbers 20 and 22 in the approximate proportion 9 to 1. This provided an explanation for the measured atomic weight of naturally occurring Ne of 20.2, which differed appreciably from a whole number value. This discovery marked the advent of a new field in spectroscopy—the "spectroscopy of mass"—which, as Thomson foresaw, would have great applicability in chemistry.

Thomson encouraged F. W. Aston at the Cavendish Laboratory at Cambridge University to continue this work by building a mass analyzer that possessed the property of focusing as well as analyzing positive rays with a much higher resolution than Thomson's parabola method. Aston [45] was able to confirm the presence of ^{20}Ne and ^{22}Ne and showed that a third stable isotope at mass number 21 also existed, and confirmed that the masses of the isotopes were integrally related to each other and to that of H and O. The discovery that Cl possessed two stable isotopes provided further confirmation for fractional atomic weights and supported the concept of a whole number rule for the isotopes [46]. Aston analyzed a sample of Pb that yielded lines on the photographic plate at mass positions 206, 207, and 208 with relative intensities of 100, 10.4, and 4.5, respectively [47]. Aston concluded that mass 207 must be the end product of the actinium radioactive decay series and was probably derived from an isotope of U, which would have a mass of 235. Aston's outstanding work in developing increasingly sophisticated mass spectrographs enabled him to systematically survey the isotopic compositions of most elements and to establish an atomic-mass scale, which was to be essential to the determination of atomic weights by the "physical" method.

As one now thinks about the new insights thus provided by Aston, one is reminded of how, much earlier still, Prout had hypothesized, from partially confusing data, that there was a numeric pattern to atomic weights that had to be of significance. This integral value pattern could be fitted with far greater precision to the relative atomic-mass values of isotopes. The remaining much smaller departures from integral values are the result of the mass equivalence of binding forces affecting atomic masses, the subject of the next section.

Atomic masses

As important as the concept of atomic weights of the chemical elements in their normal occurrence is to chemists, so is the concept of atomic masses of individual isotopes to physicists. In nuclear physics, the atomic-mass values are linked directly to the binding energies of particles in the atomic nucleus and for the energy balance in nuclear reactions. Much of the early effort in designing and building new mass spectrometers, particularly double focusing mass spectrometers, was driven by the desire to measure atomic masses with the highest possible precision.

Masses of atoms in their atomic and nuclear ground states are important in many areas of science, such as in nuclear physics and technology, nuclear astrophysics, and mechanical resonances in crystals. In the context of this review, atomic masses (together with isotope abundances) contribute to the calculation of atomic weights of polyisotopic elements, and uniquely determine the atomic weights of the monoisotopic elements. They also play an important role in determining the values of some of the fundamental constants. The atomic masses are derived by a least-squares adjustment from data consisting predominantly of redundant mass-spectrometric measurements based on the "mass-doublet" technique (in which the masses of isotopes with identical mass number are compared) but also of nuclear-reaction data and spontaneous-fission information. Atomic-mass tables have thus been produced over an extended period of time by A. H. Wapstra and his colleagues [23,48–51]. IUPAC–CAWIA accepts these atomic-mass values in composing its Tables of Standard Atomic Weights (TSAW). Atomic masses are published with the support of the Commission on Symbols, Units, Nomenclature, Atomic Masses and Fundamental Constants (SUN-AMCO) of IUPAP. The Atomic Mass Table constitutes part of the basic data set of the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (ICSU), and is one of the most comprehensive sets of scientific data published to date [52].

The relative uncertainties associated with atomic masses are typically of the order of 1×10^{-8}, and little improvement in this level of uncertainty is expected through mass-spectrometric and nuclear-reaction data. A different approach has recently been developed to determine atomic masses, resulting in a reduction of up to two orders of magnitude in the uncertainties for the atomic masses of some isotopes (including ^{12}C and ^{28}Si). The technique involves a Penning Trap [53] in which an isolated ion's cyclotron motion in a magnetic field is compared to a reference ion's motion. The ratio of the cyclotron frequencies determines their relative masses, which are then converted to a scale based on the mass of the ^{12}C atom. The published uncertainties of the atomic masses measured by this method impose no significant constraints and, in their differences from the IUPAP values, introduce no significant additional uncertainties with which the atomic weights of polyisotopic elements are evaluated.

Determination of atomic weights

An obstacle to measurements of "atomic" weights during the 19th century was the disagreement over how to write chemical formulae. At that time, a number of chemists tried to use 100 for the atomic number of U. The best chemical atomic weights were those determined by the "Harvard method". T. W. Richards of Harvard University was largely responsible for the development of this method (pioneered by the Belgian chemist J. Stas), in which atomic weights were determined by the preparation of high-purity chlorides or bromides of the element followed by the measurement of the mass ratio to the corresponding silver halide. Solutions containing near-equivalent amounts of reactants were mixed, and the point of exact equivalence determined. This was often followed by the quantitative collection and weighing of the precipitated silver halide. These measurements often attained uncertainties better than 1×10^{-4} for some elements. The consistency between the set of atomic weights derived from chlorides and those from bromides depended on the atomic-weight ratio between Cl and Br, which was evaluated carefully [22].

Richards' work on atomic weights received worldwide recognition, and for it he was awarded the Nobel Prize for Chemistry in 1914. G. P. Baxter was Richards' principal associate and succeeded him as head of the Atomic Weights Laboratory at Harvard University. Baxter not only applied the Harvard method to additional elements, but also made highly precise determinations of the atomic (or molecular) weights of gaseous elements by gas density measurements. O. Hönigschmid came to Harvard to work with Richards and then returned to the University of Münich where he devoted the remainder of his career to atomic-weight determinations.

Richards, Baxter, Hönigschmid, and their associates achieved a remarkable record in atomic-weights research. Of the 194 independent determinations of atomic weights reported in the literature from 1883 to 1947 using the Harvard method, these three scientists and their associates accounted for 142 of them. The atomic weights of 65 elements were determined by this method, and, until recently, the IUPAC-recommended atomic weights of some elements were still based partly on these measurements.

Into this ordered measurement program for atomic weights by the Harvard method came the discovery of isotopes. Experimental investigations in nuclear physics began to require specialized instruments—one of which was the mass spectrometer. Thomson [44] and Aston [45–47] demonstrated that some elements were polyisotopic. Dempster [54] calculated the atomic weight of Mg using the relative abundances of their stable isotopes together with "whole number" mass values of the isotopes, and shortly afterwards made similar studies of Li, K, Ca, and Zn [55,56]. Thus began what would become the ultimate demise of chemically determined atomic weights. From this time until the late 1930s, Aston, Dempster, Nier, and others determined the isotopic compositions of most of the elements, so that the “physical” method of determining atomic weights became a superior alternative to the “chemical” technique, and later superseded it entirely.

The atomic weight of an element in a specific sample is currently defined as “the ratio of the average mass per atom of that element to 1/12 the rest mass of one ^{12}C atom with all atoms in their nuclear and atomic ground states”. Former definitions differed only by the scale-determining mass of the reference atoms, which included H and O. The establishment of a consistent and accurate set of atomic weights, especially one applicable to a wide range of normal terrestrial occurrences, has been a major ongoing task in science. TSAW is an important set of scientific data, as atomic weights are fundamental to convert two base quantities of the SI into each other, “mass” and “amount of chemically defined substance”—both of which are essential in analytical chemistry and to the understanding of chemical reactions. Atomic weights are not only fundamental to science and technology, but are also basic to trade and commerce, which are directly involved with “amount” of specified substances. In practice, a material property, mass, is used because of the general availability of balances (which measure mass ratios), and because many chemical measurements do not involve well-defined entities. Mass ratios thus remain a sometimes necessary and convenient alternative to amount-of-substance ratios. Nevertheless, the determination and continuing evaluation of atomic weights, which was one of the major tasks of chemistry in the 19th century, remains of key importance in the development of metrology of “amount of substance” at the close of the 20th century.

Avogadro’s realization that equal volumes of ideal gases under identical conditions contained equal numbers of atoms or molecules (with relative molecular mass equal to the sum of the atomic weights of all atoms composing a single molecule), led to a simple method of measuring atomic weights from measures of volume and mass of gaseous specimens. That method was the only choice for the nonreactive noble gases for which compounds were unknown until the last 15 years of the 20th century. Of this method’s other uses, the most important was the reaction between exactly equivalent amounts of gaseous H and O (to form water). The comparison provided their atomic-weight ratio and hence the relation between two historically important atomic-weight scales, based on $A_r(\mathrm{H}) = 1$, attractive for numeric simplicity, and that based on $A_r(^{16}\mathrm{O}) = 16$, derived from the element that has stoichiometrically reliable compounds with many other elements. The kinetic theory of gases, which describes the statistics of random molecular motions in gases, added greatly to the understanding and practice of this physicochemical method of atomic-weight determination. It is noteworthy that the instrumental realization of near-perfect conditions for inert gases in a mass spectrometer enables the kinetic theory of gases to be applied once again to atomic-weight measurements. Experimental values for mass fractionation through the pressure “pinhole” of the gas inlet system of the mass spectrometer can be compared to theoretical values resulting from the kinetic theory of gases [57]. Thus, one can measure the degree of imperfection of the primary measurement while the measurement is in progress. Values very close to the theoretical value of ½ in the exponent of the isotope mass ratio have been obtained [58,59]. This approach can be useful for any element that can be converted into an inert gaseous compound such as $\mathrm{Fe(PF_3)_5}$, $\mathrm{Ni(PF_3)_4}$, $\mathrm{Pt(PF_3)_4}$, and $\mathrm{WF_6}$ [60]. Measurements monitored in this way yield results identical to those that were calibrated by means of synthetic isotope-abundance ratios. The near-perfect disorder in the gas phase thus continues to contribute to atomic-weight measurements. By surprising contrast, the near-perfect order in the solid phase (i.e., in crystals), has only marginally added to our knowledge of atomic weights

Atomic-weight scale

By 1928, it seemed that most of the scientific issues surrounding atomic weights had been resolved. The discovery of isotopes had explained the existence of nonintegral atomic weights, and both chemists and physicists were in agreement that a common scale for atomic weights could be based on the assumption that O was monoisotopic and hence $A_r(\mathrm{O}) = 16$. Furthermore, the established chemical technique for determining atomic weights could be supplemented by independent mass-spectrometric data from physics. Then in 1929, an analysis of optical absorption bands in the earth's atmosphere revealed that O had three isotopes [61,62]. This led to the unsatisfactory state of affairs in which physicists used an atomic-weight scale based on $A_r(^{16}\text{O}) = 16$, while chemists continued to use an elemental $A_r(\text{O}) = 16$ scale. This difference in scale definition necessitated a factor of 1.000 275 to convert the physics-derived values into numbers consistent with the scale used by chemists. A further complication then arose when it was shown that the isotopic composition of O was not invariant in nature. Thus, the two mass scales were not even related by a fixed constant, but rather the conversion factor varied from 1.000 268 to 1.000 278, depending on the source of O. The situation is also difficult because, if the chemical community adopted the $A_r(^{16}\text{O}) = 16$ scale, a relative change of 275×10^{-6} would be required in all chemical amounts whose values depend on the size of the mole. Furthermore, with two sets of atomic weights there were two sets of values for the fundamental constants—the Avogadro, N_A, the Faraday, F, and the universal gas constant, R—and errors were made by failures to match mass values with the appropriate constant [63].

In 1957, A. O. Nier and A. Ölander independently proposed a new scale in which $A_r(^{12}\text{C}) = 12$, partly because C is used as a reference standard in atomic mass determinations [64], and partly because, for the sake of equity, both chemists and physicists would have to change their respective scales, albeit by small amounts. IUPAC and IUPAP agreed to unify the two scales in 1959 and 1960, respectively, which required increases of 318×10^{-6} and 42×10^{-6} in the corresponding physical and chemical atomic-scale units of mass respectively. It had taken 31 years to achieve a single scale for atomic weights. At the time of the Cameron and Wichers [22] review of the atomic weights based on the unified scale, 47 of the 62 polyisotopic elements had atomic weights that were based entirely or in part on physical measurements, the atomic weight of Ne was based on gas density measurements, and those of the remaining 14 polyisotopic elements were based on chemical measurements.

The Ninth CGPM in 1948 instructed the International Committee for Weights and Measures (CIPM) to make recommendations on "a practical system of units of measurement." In 1960, the CGPM adopted the thus recommended SI, and, in 1971, with the specific advice of IUPAC, IUPAP, and ISO, redefined the mole as an SI base unit for the measurement of the quantity of "amount of substance", which thus became a new SI base quantity designed specifically to facilitate measurements in analytical chemistry and to make them consistent with the SI. The new definition was:

> "The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. When the mole is used the elementary entities must be specified and may be atoms, ions, electrons, other particles or specified groups of such particles. In this definition, it is understood that unbound atoms of carbon 12, at rest in their ground state, are referred to."

That number of entities per mole is given the symbol N_A (the Avogadro constant). The linear scale for atomic weights (defined as dimensionless mean relative mass values), is given by $A_r(^{12}\text{C}) = 12$. When $m(\text{E})$ is the average mass of an atom of element E, we have:

$$A_r(\text{E}) = 12 \cdot m(\text{E}) / m(^{12}\text{C}) \tag{1}$$

Since the atomic weight of an element is the weighted sum of the relative masses of its isotopes, $A_r(^i\text{E})$, expressed on the identical scale of $A_r(^{12}\text{C}) = 12$, and the abundance (mole fraction) of isotope ^iE is $n(^i\text{E})/n(\text{E})$, or $x(^i\text{E})$:

$$A_r(\text{E}) = \Sigma\, [x(^i\text{E}) \cdot A_r(^i\text{E})]. \tag{2}$$

An equivalent equation applies for molar-mass values, but they are not dimensionless quantities and are usually expressed in units of gram per mole:

$$M(\text{E}) = N_A\, m(\text{E}) = 12 \cdot [M(\text{E}) / M(^{12}\text{C})]\ \text{g mol}^{-1}. \tag{3}$$

Since the molar mass of an element is also the sum of the fractional abundances of the isotopes multiplied by their molar mass values, one can also write:

$$M(\mathrm{E}) = \Sigma\,[x({}^{i}\mathrm{E})\cdot M({}^{i}\mathrm{E})], \tag{4}$$

for which, when expressed in numbers, the units must be given: g mol^{-1}. For instance:

$$M({}^{12}\mathrm{C}) = 12\ \mathrm{g\ mol}^{-1} = N_\mathrm{A}\ m({}^{12}\mathrm{C}). \tag{5}$$

The "unified atomic mass unit" u commonly is used for atomic-scale mass values and is defined by:

$$12\ \mathrm{u} = m({}^{12}\mathrm{C}). \tag{6}$$

The SI base unit of mass is the kilogram: kg = 1000 g and

$$\mathrm{g}/\mathrm{u} = N_\mathrm{A}\ \mathrm{mol}. \tag{7}$$

Whereas the above equations refer to abundances, in practice one measures abundance ratios $R_{i/j} = x({}^{i}\mathrm{E})/x({}^{j}\mathrm{E})$ with respect to a chosen isotope ${}^{j}\mathrm{E}$. With the summations taken over all isotopes i only, one can calculate atomic weights from the $R_{i/j}$ values, the quantities actually measured:

$$A_\mathrm{r}(\mathrm{E}) = \Sigma\,[A_\mathrm{r}({}^{i}\mathrm{E})\cdot R_{i/j}({}^{i}\mathrm{E})]\,/\,\Sigma\,R_{i/j}({}^{i}\mathrm{E}). \tag{8}$$

This equation is readily proved by multiplying every right-hand term by $x({}^{j}\mathrm{E})$, thereby changing the denominator into $\Sigma\,x({}^{i}\mathrm{E}) = 1$ and the numerator into the right-hand side of eq. 2.

"Absolute" isotope abundances yield "absolute" atomic weights

Isotope-abundance values that are free from all known sources of bias within stated uncertainties are referred to as "absolute" isotope abundances, and they can be determined by "calibrating" the mass spectrometer by means of gravimetrically measured, synthetic mixtures of materials in which an isotope is enriched (or depleted) by a known or measurable factor. The isotope-abundances ratios in the original materials and in the synthetic mixture are used to eliminate biases and thus to convert the "observed" isotope ratios into "absolute" isotope ratios and hence into "absolute" isotope abundances. It is CAWIA custom to estimate the uncertainties in the calibrated isotope-abundance values so as to engender great reliability to these values. Such uncertainties are called expanded uncertainties [38].

In its simplest form, an isotope-abundance ratio mass spectrometer is an instrument that provides for the ionization of the atoms of a sample, the mass-dependent dispersion, the ion collection, and the measurement of the isotopes as ion currents. One might assume that the isotope-abundance ratios of an element in a sample would be identical to the corresponding ion-current ratios. Unfortunately, this is not always true at the level of uncertainty desired. A variety of physical and chemical mechanisms conspire to alter the ion beams within the mass spectrometer so that the observed isotope ratios, R_obs, are not identical to the "true" ratios, R_true. The most typical, and often unrecognized error that must be corrected is mass-dependent isotope fractionation. Indeed, many chemical and physical processes involved in the isotope-abundance measurement procedures are mass dependent (e.g., mass law in chemical reactions, mass effects in gas inlet flows, Raleigh distillation, mass dependence of some collectors, etc.). Hence, $R_\mathrm{true} = K_\mathrm{i}R_\mathrm{obs}$, where K_i is an instrumental mass bias correction factor that is often a multivariate function comprised of some or all of the following:

- biases introduced when loading the sample into the ion source,
- biases introduced by the physical and chemical processes involved in ion production,
- biases introduced during the transmission of the ion beam from the ion source to the collector (for example, wall adsorption and desorption), and
- biases introduced in the collector systems and in ion-current measurement.

The first attempt to "calibrate" a mass spectrometer to enable measurements of "absolute" isotope abundances was undertaken for the noble gas Ar, using synthetic mixtures of enriched ^{36}Ar and ^{40}Ar to correct for mass discrimination effects in a gas-source mass spectrometer [65]. This procedure permitted the calculation of the atomic weight of Ar together with nine other elements in the same mass spectrometer, assuming that the mass discrimination for all these elements could be corrected by using the same "calibration" factor as had been determined for Ar [65,66].

In 1954, NBS commenced a mass spectrometry-based program at the request of the U.S. Atomic Energy Commission and the USGS to produce certified isotopic reference materials [67]. Metrology, the science and practice of precise and reliable measurements, generally involves the quantification and certification of a quantity (property) in a divisible or transportable reference material, the constancy and homogeneity of that quantification in that material having been appropriately tested at or near the highest attainable precision. The important role of reference materials in metrology is to check, verify, disseminate, and calibrate measurement procedures and instrumentation [68]. Such reference materials in atomic-weight and isotopic-composition measurements have become very important and are sure to become more and more indispensable in the future. CAWIA conservatively estimates the uncertainty of their certified values [37].

Initially, the aim of the NBS (now renamed the National Institute of Standards and Technology, NIST) program was to assure in-sample and between-sample homogeneity for these isotopic reference materials. NBS progressively introduced isotopic reference materials with certified values based on "calibrated" isotope measurements. These "absolute" isotope abundances, together with the corresponding atomic masses, yielded atomic weights of a specific element in a specific sample. The European Commission's (EC) CBNM, in Geel (Belgium), later renamed the Institute for Reference Materials and Measurements (IRMM), joined the effort, the results of which are listed in Table 2.

Table 2 Atomic weights of the elements in specified reference materials as determined by NBS/NIST and CBNM/IRMM by "calibrated" mass spectrometry.

Element	Atomic weight A_r(E) and uncertainty $U[A_r(E)]^a$		Year of publication	Relative uncertainty^a $\times 10^6$
Chlorine	35.452 73	±0.000 97	1962	27.4
Silver	107.8682	±0.001 0	1962	9.3
Bromine	79.903 63	±0.000 92	1964	11.5
Copper	63.5455	±0.001 0	1964	15.7
Chromium	51.996 12	±0.000 33	1966	6.3
Magnesium	24.304 97	±0.000 44	1966	18.1
Lead	207.2152	±0.000 15	1968	0.72
Boron	10.811 756	±0.000 20	1969	18.4
Rubidium	85.467 76	±0.000 26	1969	3.0
Boron	10.811 756	±0.000 053	1970	4.8
Rhenium	186.206 79	±0.000 31	1973	1.7
Potassium	39.098 304	±0.000 058	1975	1.5
Silicon	28.085 5258	±0.000 0555	1975	2.0
Thallium	204.383 33	±0.000 18	1980	0.9
Silver	107.868 15	±0.000 11	1982	1.0
Strontium	87.616 814	±0.000 117	1982	1.3
Lithium	6.940 69	±0.000 29	1983	41.8
Gallium	69.723 07	±0.000 13	1986	1.9
Nickel	58.693 353	±0.000 147	1989	2.5

(*continues on next page*)

Table 2 (*Continued*).

Element	Atomic weight A_r(E) and uncertainty $U[A_r(E)]^a$		Year of publication	Relative uncertainty^a $\times 10^6$
Iron	55.845 14	±0.000 48	1992	8.6
Silicon	28.085 382	±0.000 023	1992	0.82
Lithium	6.940 05	±0.000 24	1997	34.6
Silicon	28.085 3842	±0.000 003 5	1997	0.12
Xenon	131.292 77	±0.000 36	1998	2.7
Sulfur	32.065 333	±0.000 080	1999	2.5
Uranium	238.028 906	±0.000 27	1999	1.13

[a] As given by the authors.

Powell and Murphy [69] have described the calibration procedures developed at NBS/NIST to determine the "absolute" isotopic compositions of elements. The NBS initiative has prompted other laboratories to make "absolute" determinations of isotopic composition. De Laeter et al. [36] have described a similar but alternative approach used at IRMM. In such cases, the reference material should comprise a large lot of high-purity material, which can then be distributed to the science community. A comprehensive mass-spectrometric study to identify and control sources of measurement bias using this material is then undertaken. By these methods, high-precision measurements of the isotopic composition of Si have been made at IRMM as part of an international effort to redetermine the Avogadro constant and the molar volume of Si in crystals of high perfection and purity [70,71]. At the present time, the best-calibrated measurements for eight elements listed in Rosman and Taylor [72] have been carried out in laboratories other than NBS/NIST and CBNM/IRMM. The work of T.-L. Chang and his associates at the University of Beijing is particularly noteworthy.

Variations in isotope abundances yield variations in atomic weights

Although the calibration systems outlined above can produce accurate values for the isotope abundances and hence for the atomic weights of specific samples, it must be recognized that the uncertainty associated with the standard atomic weights as listed in TSAW for a given element may be limited by variations in its isotopic composition amongst readily available "normal" terrestrial materials. Substantial variations in the isotopic compositions of many elements result from radioactive decay and from isotope fractionation processes, both natural and man-made. Comprehensive compilations of published papers on isotope abundances have been maintained at CBNM (now IRMM) since 1965, and this database has been used extensively by the Commission on Atomic Weights (now CAWIA) in preparing its reports since at least 1976 [7,73].

For some elements, including many with low atomic numbers, the real isotope-abundance variations are much larger than the uncertainties of "absolute" isotope-abundance measurements. In such cases, the uncertainties in the standard atomic weights cannot be reduced by improved measurements. It is actually more likely that future studies will cause the ranges of some standard atomic weights to be enlarged as new occurrences of varying isotopic composition are revealed. For some elements, real variations have only been observed by high-precision differential isotope-abundance measurements, but those variations are smaller than the overall uncertainties of the "absolute" isotope-abundance measurements. In such cases, future work may either expand or reduce the uncertainties in the standard atomic weights. In this review, and in the decisions of CAWIA generally, variations in the atomic weights caused by deliberate actions designed to produce isotopically fractionated materials are excluded from consideration. However, it must be recognized that such materials have become distributed in the environment, and may be encountered unexpectedly in the laboratory.

Radioactive decay

A given isotope may be radioactive (subject to radioactive decay), radiogenic (a product of radioactive decay), or both. Radioactive isotopes decrease in abundance according to the radioactive decay equation:

$$N/N_0 = \mathrm{e}^{-\lambda t} \tag{9}$$

where N_0 and N are the initial and measured (after time t) numbers of atoms of a radioactive isotope, respectively, and λ is the decay constant, in units of t^{-1} (for long-lived isotopes usually in reciprocal years). In the absence of other isotope fractionation mechanisms, radioactive decay alone can alter the isotope abundance of the parent element over time, but it may not necessarily lead to variations among different samples at a given time (such as the present) because all occurrences of the element have decayed at the same rate. For example, the radioactive decay of ^{87}Rb ($\lambda = 2.1 \times 10^{-11}$ a^{-1}) is calculated to have caused the $n(^{87}\mathrm{Rb})/n(^{85}\mathrm{Rb})$ ratio to change by about 6 % in the 4.56×10^9 a since the formation of the earth, but all occurrences of Rb of terrestrial origin sampled within historic times have essentially the same value of $n(^{87}\mathrm{Rb})/n(^{85}\mathrm{Rb})$, hence the same atomic weight.

Radioactive decay also can alter substantially the isotopic composition of the element that includes the product isotope. Stable radiogenic isotopes increase in abundance as the products of radioactive decay:

$$N_p = N_0\,[1 - \mathrm{e}^{-\lambda t}] \tag{10}$$

where N_p is the number of atoms of the product (radiogenic) isotope after time t. Substantial variations in isotope abundances occur for some elements whose isotopes include products of radioactive decay. The degree of variation largely depends on the age of the sample and the relative abundances of the parent and product element in a sample, which can vary widely owing to geochemical processes. For example, the decay of ^{87}Rb to ^{87}Sr can cause a substantial increase in the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ ratio of a material with a large $n(\mathrm{Rb})/n(\mathrm{Sr})$ ratio, but will have relatively little effect on the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ ratio of a material with a small $n(\mathrm{Rb})/n(\mathrm{Sr})$ ratio. Furthermore, the magnitude of the change in the Sr isotope-abundance ratio of any substance caused by the decay of Rb will depend on the period of time the substance has had its present form, and the extent to which it has approximated a closed system. Because certain rock formations and specific mineral grains typically crystallize with very different $n(\mathrm{Rb})/n(\mathrm{Sr})$ ratios and commonly are closed with respect to Rb and Sr exchange with the external environment, it is possible to have variations in the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ ratio in individual samples. The most extreme variations in the isotope-abundance ratios of Sr and other elements with radiogenic isotopes are likely to be found at relatively small scales of observation, such as in individual mineral grains. This is especially evident for some of the noble gases, which may be almost entirely radiogenic in some occurrences. Reported variations in the isotope abundances of many elements are increasing as a result of the use of microprobe techniques in mass spectrometry. The selection of uncertainties for the standard atomic weights is especially difficult for elements with radiogenic isotopes.

Isotopes that are both radioactive and radiogenic can either increase or decrease in relative abundance depending on the decay constants for production and decay, and on the geochemical processes that may separate different elements in a decay series. Some types of nuclear transformations other than radioactive decay also can cause variations in the abundances of certain isotopes in natural terrestrial materials. For example, the interaction of energetic cosmic-ray particles with the atmosphere and with the earth's surface results in the production of a large number of isotopes by nuclear reactions such as spallation (a nuclear reaction with more than one product nucleon) and neutron capture. Some well-known cosmogenic isotopes (e.g., ^{14}C and ^{36}Cl) are radioactive and are used in geochronology [74]. However, the abundances of isotopes such as these are generally many orders of magnitude too small to have a measurable effect on the atomic weights of these elements in materials in which they are normally found.

Isotope fractionation from natural processes

Isotopes of some elements may be fractionated substantially by physical, chemical, or biological processes, the rates or equilibrium states of which are mass dependent. Processes that differentiate on mass, and that commonly yield measurable changes in isotopic composition, include changes of physical state (e.g., evaporation, condensation, crystallization, melting, and sublimation), ion exchange, sorption and desorption, diffusion, ultra-filtration, and a variety of biological processes including photosynthesis, assimilation, respiration, and dissimilatory oxidation-reduction reactions. These changes are commonly larger and more readily detected in the case of "light" elements. For example, as early as 1939, it was shown that the $n(^{13}\mathrm{C})/n(^{12}\mathrm{C})$ ratios in various samples of C varied by up to 5 % of that ratio [75]. The atomic weight of C is therefore dependent on the source of the material used in the analysis, and on the extent of C isotope fractionation in nature.

Equilibrium isotope fractionation results when the forward and backward reaction rates are the same between multiple coexisting phases or species with a common element. The equilibrium isotope fractionation factor (α) is given by:

$$\alpha_{\mathrm{a/b}} = R_{\mathrm{a}} / R_{\mathrm{b}} \tag{11}$$

where a and b are two chemical species in isotopic equilibrium and R is the abundance ratio of two isotopes of an element [$R = n(^{i}\mathrm{E})/n(^{j}\mathrm{E})$, where $^{i}\mathrm{E}$ and $^{j}\mathrm{E}$ typically are the heavier and lighter isotopes of an element, respectively]. The factor α is related to the thermodynamic equilibrium constant for the isotope exchange reaction between two isotopes of the element E.

Kinetic isotope fractionation results from differences in the dissociation energies of isotopically different molecules of a given chemical species undergoing an irreversible transformation. The kinetic isotope fractionation factor commonly is designated either in the same way as the equilibrium fractionation factor ($\alpha_{\mathrm{a/b}}$, where a is the product species and b is the reactant species), or as its reciprocal ($\beta = 1/\alpha$). Kinetic fractionation can also be expressed as the ratio of the reaction rates of the two isotopically different molecules (or substrates) undergoing the reaction: $\alpha_{\mathrm{kin}} = k_i / k_j$ where k_i and k_j refer to the reaction rates of molecules containing the heavier and lighter isotopes of the element in question.

The magnitudes of equilibrium isotope fractionations depend in part on state variables, temperature being the most important, whereas the magnitudes of kinetic fractionations commonly vary with the overall reaction rate and mechanism. Equilibrium isotope fractionation commonly results in heavier isotopes being concentrated in more oxidized compounds and in more condensed phases, whereas kinetic isotope fractionation generally results in lighter isotopes being concentrated in the products of the reaction and heavier isotopes concentrated in the residual (unreacted) molecules ($k_j > k_i$; $\alpha_{\mathrm{kin}} < 1$). Measurements of mass-dependent fractionations of the stable isotopes of H, Li, B, C, N, O, S, and Cl have been used in a wide variety of studies in the earth sciences [76–81]. As is the case with the radiogenic isotopes, some of the largest variations in isotope-abundance ratios caused by fractionation processes are commonly observed at relatively small scales, or in substances with low concentrations of an element. Thus, it is likely that the ranges in atomic weights reported for environmental occurrences of these elements will continue to increase as analytical methods improve to permit smaller quantities and a wider range of samples to be analyzed with increasing precision.

Because natural variations in the isotopic compositions of the elements commonly are small and because the differences commonly are more useful than the actual values [33,36,37], several different expressions have been used to amplify the differences and to obviate the need for "absolute" measurements for reporting purposes. Isotopic measurements of elements exhibiting isotope fractionation commonly are given with respect to a δ (delta) scale defined by:

$$\delta(^{i}\mathrm{E})_{\mathrm{S}} = [R_{\mathrm{S}} / R_{\mathrm{RM}}] - 1 \tag{12}$$

where R_{S} and R_{RM}, refer to the isotope-abundance ratios $n(^{i}\mathrm{E})/n(^{j}\mathrm{E})$ in a sample, S, and a reference material, RM, respectively [9,16,17].

Delta values commonly are reported in parts per thousand, or per mill ($\delta \times 1000$ ‰), and measured by comparing the apparent isotope-abundance ratio in a sample with that of a reference material measured under precisely the same conditions, without any attempt to determine the "absolute" isotope-abundance ratios of either material. For light elements such as H, C, N, O, and S, many of these types of analyses have been made on dual-inlet mass spectrometers by comparing the mass detector signals from a sample gas and a reference gas that are admitted alternately in several cycles to the ion source while flowing steadily from a large reservoir [82]. A static gas-source mass spectrometer was introduced subsequently for isotopic analyses of rare gases [83]. Recently, large numbers of relative isotope-abundance ratio measurements have been made on continuous-flow-inlet machines by integrating the detector signals for whole pulses of sample or reference gas admitted to the ion source in a He-carrier stream [84]. Relative isotope-abundance ratio measurements by TIMS and ICPMS have revealed subtle isotope fractionations in some of the heavier elements such as Ca, Fe, and Cu, among others [85].

Delta scales of differential isotope-ratio measurements have been used extensively in the earth sciences since the 1950s, and most of the documented variations in the atomic weights of common light elements were determined by these methods. It is possible to calculate atomic weights from δ measurements if the isotope abundances of the reference material (values of R_{RM}) are known independently, but this may be a source of substantial uncertainty in some cases. Other quantities have been defined for reporting subtle variations in the isotopic compositions of some of the heavier elements in the earth sciences. For example, to emphasize processes related to planetary evolution, an ε scale has been defined for elements such as Nd, Hf, and Sr in rocks and minerals as the deviation, at the time of crystallization of the sample, from the isotopic composition in a hypothetical chondritic meteorite or bulk earth reservoir.

Documented variations in isotope-abundance ratios and corresponding atomic-weight variations in normal materials have been studied by the Commission since 1979 [9]. A preliminary report on the statistical evaluation of isotope abundances was prepared by the Commission in 1991 [15]. The relation between delta scales, isotope abundances, and atomic-weight values is illustrated by the large variations observed in H (Fig. 1). Relative measurements of variations in $n(^{2}\mathrm{H})/n(^{1}\mathrm{H})$ are made by comparison to the isotopic reference material Vienna standard mean ocean water (VSMOW). A positive sign for $\delta(^{2}\mathrm{H})$ indicates that the sample is enriched in the isotope of higher mass compared to VSMOW. Isotope fractionation in H occurs largely because of vapor-pressure differences between $^{1}\mathrm{H}_2{}^{16}\mathrm{O}$ and $^{1}\mathrm{H}^{2}\mathrm{H}^{16}\mathrm{O}$, and occurs when evaporation or condensation takes place, the magnitude depending on the temperature. As a result, the $^{2}\mathrm{H}$ content in $\mathrm{H_2O}$ on earth ranges from about 0.0082 to 0.025 % [85]. Polar ice contains approximately two-thirds as much $^{2}\mathrm{H}$ as ocean water. The altitude at which precipitation occurs also affects the isotopic composition. Including all natural sources of H, the extreme values of the atomic weight are 1.007 851 to 1.008 010 [85]. Measured variations in $\delta(^{2}\mathrm{H})$ have provided useful information about natural processes in hydrology, meteorology, paleoclimatology, oceanography, and cosmochemistry.

A classic example of natural isotopic variations in commercially available materials is that of B. As early as 1948, Thode et al. [86] showed that variations from 4.222 to 4.270 existed in the $n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$ ratios in samples from different geological sources. The isotope fractionation in aqueous B solutions is caused by differences in inter-atomic vibrational energy and symmetry between the trigonal species $\mathrm{B(OH)_3}$ and the tetragonal anion $\mathrm{B(OH)_4^-}$. McMullen et al. [87] reported calibrated B isotope measurements in brines and minerals from Searle's Lake, which enabled the standard atomic weight to be set at 10.811(3), giving a range that covered all major mineral sources of B known at that time.

For elements with more than two isotopes, the conversion of relative isotope abundance-ratio measurements to atomic weights may involve an assumption about the mass dependence of the isotope fractionation processes. For example, most variations in the isotope abundance of $^{17}\mathrm{O}$ may be calculated from those of $^{18}\mathrm{O}$ and $^{16}\mathrm{O}$: $\{[n(^{17}\mathrm{O})/n(^{16}\mathrm{O})]_{\mathrm{a}}/[n(^{17}\mathrm{O})/n(^{16}\mathrm{O})]_{\mathrm{b}}\} = \{[n(^{18}\mathrm{O})/n(^{16}\mathrm{O})]_{\mathrm{a}}/[n(^{18}\mathrm{O})/n(^{16}\mathrm{O})]_{\mathrm{b}}\}^{z}$, where z is approximately equal to the ratio of the relative mass differences, i.e., $z \approx [m(^{17}O) - m(^{16}O)]/[m(^{18}O) - m(^{16}O)] \approx 1/2$, though it may differ slightly for different materials. In tabulating atomic-weight variations caused by isotope fractionation for elements with more than two isotopes, CAWIA generally has applied this approximation of the mass-dependent relation to the variations in reported δ values, using the "absolute" isotopic composition of a reference material as a basis. This relation clearly cannot be applied to elements whose isotopic variations are caused by radioactive decay, which is not a mass-dependent fractionation process. In addition, it is now recognized that photochemical reactions among atmospheric compounds can cause isotope fractionation that cannot be approximated by the mass-dependent fractionation equation. For example, several minor atmospheric O-bearing compounds commonly exhibit variations in the relative abundances of ^{16}O, ^{17}O, and ^{18}O in which the exponent z is significantly larger than 1/2 [88].

Examples of exceptional natural variability in atomic weights for some elements occur at the Oklo mine site in the Gabon, southwest Africa. Fission reactions occurred spontaneously approximately 1.8×10^9 a ago in high-grade U ore, which at that time had a ^{235}U abundance in excess of 3 %, as compared to the present-day abundance of 0.72 %. As a result of this event, elements enriched in isotopes that are the stable end members of fission chains are found within the ore body and the surrounding sedimentary materials [89]. In addition, some isotopes with large neutron-capture cross-sections are depleted, and the products of these reactions correspondingly enriched [90]. Such exceptional geological occurrences are excluded by CAWIA in recommending standard atomic weights, but an annotation "g" is included for the affected elements in TSAW to indicate that such abnormal variations are known.

The standard atomic weight of H and its uncertainty include most, but not all, of the variations observed. Analytical uncertainties normally are of the order of 1 ‰ on the δ scale.

As TSAW is intended to be used largely by the chemical community, the values listed have been derived from both natural occurrences and bench chemicals ("off-the-shelf" reagents). Cameron and Wichers [22] stated that the standard atomic weights apply to elements as they exist in Nature, without artificial alteration of isotopic composition, and to mixtures that do not include isotopes of radiogenic origin. De Bièvre and Peiser [91] argued that, with minor exceptions to be covered by footnotes and annotations, the implied range of the standard atomic weights is intended to apply to all samples from natural terrestrial occurrences as well as to samples found in laboratories involved in chemical investigations, technological applications, and to materials of commerce. Thus, according to current practice, an essential task in determining the standard atomic weight of an element is to conduct a survey of naturally occurring materials and commercially available reagents to ensure that the uncertainty limits associated with each standard atomic weight include the observed range of isotope abundances. A Subcommittee on Natural Isotopic Fractionation of CAWIA recently has prepared a report that examines the extent of isotope fractionation for certain key elements in order to give a better understanding of the limitations imposed on standard atomic weights by the variations in the isotope abundances of natural materials [85]. Unfortunately, complete surveys have not, as yet, been undertaken for a number of elements.

In recommending standard atomic weights, CAWIA generally has not attempted to estimate the average or composite isotopic composition of the earth or of any subset of terrestrial materials. This is partly because many of these quantities are poorly known and because the numbers of analyses in the literature commonly are biased toward specific substances or unusual geochemical situations that have been the subject of ongoing research. Instead, CAWIA has attempted to find a single value and symmetrical uncertainty that would include almost all substances likely to be encountered, especially in the laboratory and in commerce.

Isotopic anomalies also occur in meteoritic and lunar materials. They have provided insights into the nuclear and chemical processes involved in the formation and evolution of the solar system [92]. It is even possible to identify some of this anomalous material with sites where nucleosynthetic processes

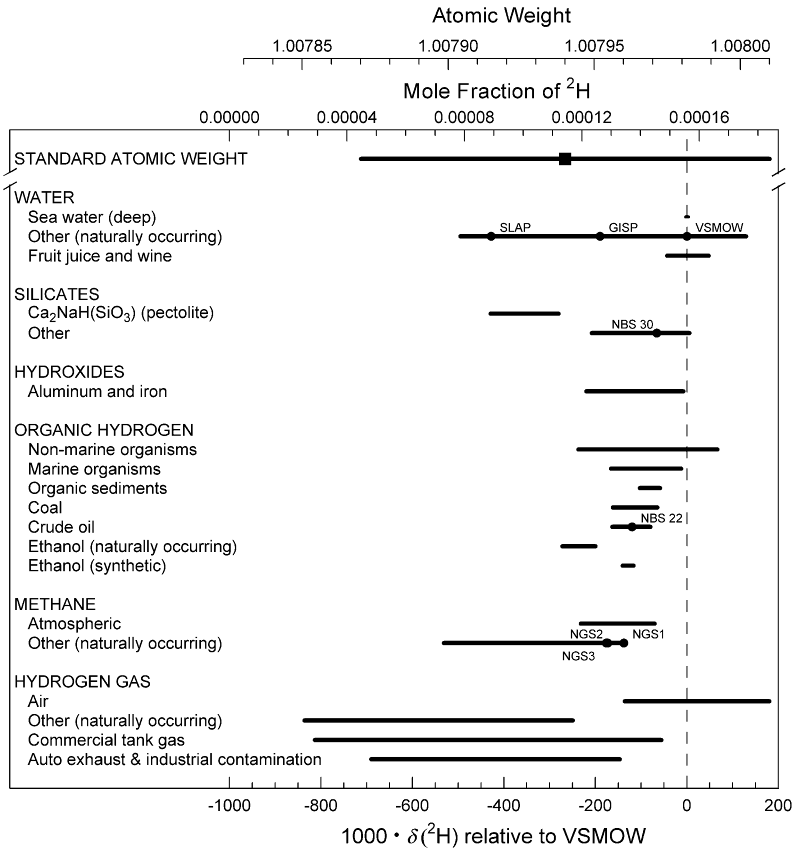

Fig. 1 Summary of variations in the atomic weight of H in terrestrial materials [from 85]. Horizontal axes indicate:

- variations in measured relative isotope-abundance ratios $\delta(^2H)$ expressed as deviations from the $n(^2H)/n(^1H)$ ratio of VSMOW (in ‰),
- corresponding variations in the mole fractions of ^{2}H, calculated from the $\delta(^2H)$ values by using the calibrated isotope measurements of VSMOW and SLAP isotopic reference materials, and
- corresponding atomic weights calculated from the mole fractions and atomic masses.

have taken place. Because of their importance to cosmochemistry, CAWIA, through a Subcommittee on Non-Terrestrial Isotope Abundance Data, maintains an ongoing survey of reported isotope abundances in non-terrestrial materials and the processes responsible for their differences from terrestrial values. Non-terrestrial materials are not included in CAWIA's definition of a "normal" material and, therefore, do not affect TSAW, but selective reviews of non-terrestrial isotopic compositions and processes have been included regularly in CAWIA documents [9–18].

Artificial isotopic variations

Apart from natural processes causing variations in the isotopic compositions of the elements, there are several technological effects that need to be recognized. Some isotopically altered elements may be produced by distillation, electrolysis, or crystallization, as well as from nuclear bomb tests, nuclear reactors, and nuclear fuel-processing plants. Some of the isotopes released into the environment from these sources have been used as "environmental tracers" in hydrology, oceanography, biology, and geology. For example, a large quantity of radioactive tritium, ^{3}H, which has a relatively low natural cosmogenic abundance in the atmosphere, was released to the troposphere and stratosphere by thermonuclear bomb tests in the 1950s and 1960s. The resulting long-lived pulse of high concentrations in atmospheric water vapor of ^{3}H, with a half-life of 12.3 a, has been exploited as a tracer of subsurface water movement in oceans, lakes, aquifers, and ice fields. Many isotopes, including ^{3}H, that were released inadvertently to the environment by human activities are widely distributed, but their concentrations are usually too small to have a significant effect on the atomic weights.

In contrast, there are a number of materials used for experimental or industrial purposes that have deliberately altered isotopic compositions. Isotope separation has been used to produce enriched isotopes for the past 50 years, ^{235}U enrichment being a well-known example of this technology. De Bièvre [93] drew attention to the variability in the isotopic composition of Li. The minor isotope ^{6}Li is valuable as a nuclear source material for tritium production and as a neutron absorber in nuclear fusion. As a result, Li distributed commercially for use in laboratories may be depleted in ^{6}Li by as much as 80 % relative to its normal abundance, with a range in A_r(Li) from 6.94 to >6.99 [94,95]. This range is much larger than that implied by the standard atomic weight for Li, 6.941(2), for which reason CAWIA introduced a specific annotation to alert users of TSAW [16]. It should also be noted that the best value obtained on a material referred to in Table 5 is associated with a still much smaller uncertainty of ±0.000 24 than the implied range of ±0.002 for the standard atomic weight, A_r(Li).

Nitrogen enriched in ^{15}N has been widely used as an experimental tracer for studies of nutrient cycles in agriculture. Many other similar uses have been made of isotopically altered H, O, C, N, S, and other elements. Synthetic isotope mixtures and pure isotopic compounds are produced for use in calibration of measurements of isotope-abundance ratios, and of concentration measurements by isotope dilution mass spectrometry (IDMS). Substances with deliberately altered isotopic compositions can have atomic weights that are far outside the uncertainties given in TSAW, but they tend to be more localized in occurrence. Those substances should be appropriately labeled, but such markings may be viewed to have only limited reliability.

Although artificial enrichment of isotopes such as ^{2}H and ^{235}U gained substantial technological importance and success during the last 60 years, separation methods based on thermal diffusion, centrifugation, electrophoresis, evaporation, neutron irradiation, or crystallization have so far failed economically to supply the small quantities of many stable isotopes that would find beneficial use in IDMS for analytical and other applications. Selective laser excitement, followed by chemical separation, may conceivably provide the future method of choice for the numerous small quantities of isotopic materials that are needed.

Atomic weights of the monoisotopic elements

An element is considered to be monoisotopic by CAWIA if it has one and only one isotope that is either stable or has a half-life greater than 1×10^{10} a. At various times, the term “mononuclidic” has been used synonymously with “monoisotopic”; similarly, radioactive isotopes have been referred to as “radionuclides” or “radioisotopes”. Thus, CAWIA considers Th to be monoisotopic because ^{232}Th has a half-life of 1.4×10^{10} a, and the half-lives of the other isotopes of Th are all less than 1×10^{10} a. In contrast, Pa is not classified as a monoisotopic element because the half-life of the most abundant isotope ^{231}Pa is only $3.25(1) \times 10^{4}$ a. All isotopes of elements of atomic number greater than 83 have half-lives less than 10^{10} a, except for ^{232}Th. The following 21 elements are considered to be monoisotopic in the evaluation of the atomic weights: Be, F, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au, Bi, and Th.

With the exception of Be, all monoisotopic elements have odd numbers of protons, even numbers of neutrons, and, therefore, odd atomic numbers. The mass formula in nuclear physics has a pairing term such that nuclei with even numbers of protons or neutrons tend to be more stable than those with single unpaired particles. This pairing explains why the great majority of monoisotopic elements have odd masses and atomic numbers and, incidentally, why elements with even atomic numbers have relatively large numbers of isotopes. Naturally occurring radioisotopes of some of the monoisotopic elements (e.g., ^{10}Be, ^{129}I) are generated by cosmic-ray reactions with other elements. Although trace amounts of these cosmogenic isotopes may occur in isolation from the major isotopes of the corresponding elements, such anomalous occurrences in minute quantities are, for the time being, considered to be insignificant in the evaluation of the atomic weights. Some radioisotopes were more abundant early in earth's history (e.g., ^{26}Al, ^{129}I) and have decayed to very low concentrations over geologic time, so they also have no significant effect on the atomic weights of the corresponding elements.

The atomic (nuclidic) masses are known with small uncertainties, and the standard atomic weights of monoisotopic elements are at first sight identical to their respective atomic masses. It is, nevertheless, necessary to examine causes for small differences in the two number sets and their respective uncertainties. Both the atomic-weight values of the monoisotopic elements and their respective atomic-mass values have changed in the past as a result of differing changes in the defining scales. Both sets of values now refer to the common numeric scale based on the atomic mass of the ^{12}C isotope.

The Table of Atomic Masses published by Audi and Wapstra [51], which is recognized by IUPAP, is the basis for the atomic weights of the monoisotopic elements in recent editions of the TSAW [17–19]. When adopting these values, CAWIA has had to consider how uncertainties assigned to the atomic weights in TSAW should compare with the standard uncertainties given in the Table of Atomic Masses. Examination of the history of published atomic masses of the monoisotopic elements reveals changes that are large compared with the earlier-stated uncertainties. It has been shown [96,97] that the standard deviations of least-squares adjusted data, such as the atomic-mass values, can be subject to small discrepancies between different portions of the set of values, as well as between subsequent evaluations. To minimize the frequency of changes in the recommended atomic weights of the monoisotopic elements, CAWIA currently assigns expanded uncertainties to the atomic-weight values in TSAW that are a factor of six times the standard deviations given in the Table of Atomic Masses. From 1961 to 1969, CAWIA abbreviated the atomic-mass values to five or six significant figures and equated them numerically to atomic weights with the justification that chemists were not interested in additional significant figures. That argument was rejected by CAWIA in 1969 when it decided to disseminate the most precise A_r(E) values consistent with all reasonably reliable published information, and to round off the last digit of A_r(E) if it was uncertain by more than ±1. This restriction has subsequently been relaxed.

Until recently, CAWIA also considered increasing the uncertainties of the standard atomic weights of monoisotopic elements to account for the remote possibility of undetected isotopes or isomers with long half-lives. CAWIA now discounts this possibility for several reasons:

- Many searches for specific isotopes with sensitive mass spectrometers have been unsuccessful.
- Since the discovery of ^{180}Ta over 40 years ago, no naturally occurring radioisotope of a monoisotopic element has been found.
- The likelihood of finding undiscovered isotopes that could affect the standard atomic weights of monoisotopic elements is further restricted by the fact that the island of β stability for isotopes is very narrow. One would expect to find any naturally occurring odd atomic-number isotope only within one or two mass units of the stable isotopes.

At the time of the 1984 CAWIA review [24], it was still customary to calculate the maximum possible concentrations of undiscovered isotopes as derived from failures to discern them by sensitive mass-spectrometric measurements. These maxima are referred to subsequently in some cases in this report, even though, on the one hand, they are so low that they would hardly affect the atomic weights at the current levels of precision, while on the other hand, they probably overestimate the likely abundances of hypothetical isotopes. The end result is that in TSAW of recent years, the standard atomic-weight values of the monoisotopic elements are numerically equal to the respective atomic masses, but with larger uncertainties arising from IUPAC's preference for expanded uncertainties and in recognition of the effects of minor revisions to the atomic-mass tables.

Atomic weights for fundamental constants

The responsibility for examining experimental and theoretical work on fundamental constants, and providing a self-consistent set of values for the fundamental constants and associated conversion factors on a regular basis, is held by CODATA. This data set is derived from a least-squares adjustment involving a large number of measurements including the atomic-mass compilation [51,52]. Some fundamental constants are directly dependent on atomic mass and atomic-weight data, and these in turn affect the values of other fundamental constants (as shown in Fig. 2).

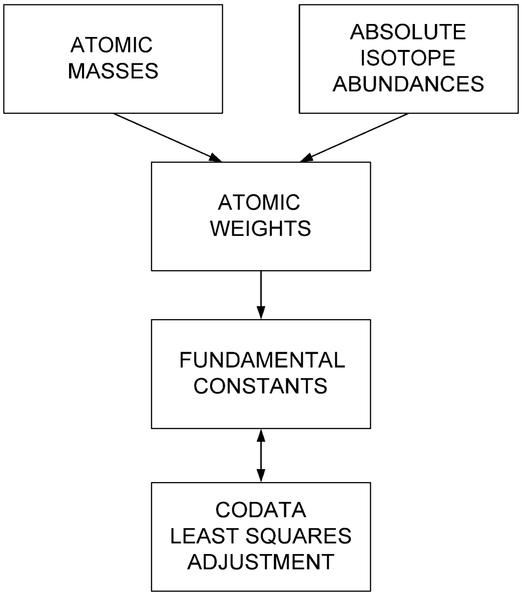

Fig. 2 Role of atomic weights in influencing the magnitude and uncertainty of fundamental constants such as N_A, F and R.

The traditional method of determining the universal gas constant, R, is based on measurements of the molar volume of O and N, but such measurements have been hampered by sorption of gas on the walls of the vessel. An alternative procedure is to measure the speed of sound C_o in Ar at the triple point temperature of water using an acoustic interferometer because this avoids the necessity of an "absolute" volume determination. Thus, R can be determined from the equation

$$R = M(\mathrm{Ar})\, C_o^2 / (\gamma T_i) \tag{13}$$

where M(Ar) is the molar mass of Ar, γ is the heat-capacity ratio c_p/c_v for an ideal monatomic gas, and T_i is the temperature of the triple point of water [98]. A new value of $R = 8.314\,472$ J mol^{-1} K^{-1}, with a relative uncertainty of 1.7×10^{-6}, has been determined by measuring the speed of sound in Ar in a spherical acoustical resonator [98]. This uncertainty is approximately five times smaller than the uncertainty in the 1986 CODATA value [99]. The 1998 CODATA value [52] gives the relative uncertainty in R as 1.7×10^{-6}, in agreement with the experimental value [98]. The work of Nier [65] is still accepted as the best measurement of the isotope abundances of Ar [72], which in turn determines the atomic weight of Ar through which R is derived. Improvements in mass-spectrometric techniques, together with careful control of synthetic isotope mixtures, might permit the uncertainty of the current value of M(Ar) to be reduced, especially if the isotope abundances of the actual sample of Ar used in the acoustical-resonator experiment are measured.

Improvement in the value of R was and remains important because it would yield a reduction in the uncertainties of all the 1986 CODATA recommended values that are derived from R [99]. These include the Stefan–Boltzmann constant, σ, and the Boltzmann constant, k. When the value of R derived by Moldover et al. [98] is used to evaluate σ, the resulting value of $5.670\,400(40) \times 10^{-8}$ W m^{-2} K^{-4} has a relative uncertainty of 6.9×10^{-6}, some five times smaller than the previous value [100]. Similarly, the value of k is $1.380\,6503(24) \times 10^{-23}$ J K^{-1}, with an uncertainty of 1.7×10^{-6}, approximately five times smaller than the previous relative uncertainty of 8.5×10^{-6}. The CODATA values were adjusted to reflect these improvements in 1998 [52].

The Faraday constant F is the molar elementary charge and can be calculated from fundamental constants such as N_A, the electronic charge, the proton magnetogyric ratio, the magnetic moment of the proton in nuclear magnetons, and the ampere. In 1973, a serious discrepancy was reported between the electrochemically determined value of F and the CODATA value derived from the least-squares adjustment technique [100]. It was decided to exclude the existing electrochemical values from the CODATA recommended value, which was therefore based purely on calculations from other fundamental constants. The 1973 CODATA value of F was 96 484.55 C mol^{-1}, whereas the electrochemical values ranged from 96 486.2 to 96 487.2 C mol^{-1}. In an attempt to resolve the discrepancy, a new experimental determination was performed on the mass equivalence of the unit quantity of electricity involved in the electrochemical deposition or dissolution of Ag (E_{Ag}). Using the IUPAC value for the atomic weight of Ag, 107.8682(10), and the equation $F = M(\mathrm{Ag})/E_{Ag}$, a new value of F = 96 486.33 C mol^{-1} was obtained [101]. The relative uncertainty of 2.5×10^{-6} in this value represented an approximate threefold improvement over the previous best determination of F. More importantly, it was consistent with the earlier electrochemically based determinations. Since the largest source of uncertainty in the calculation of F was $A_r(\mathrm{Ag})$, a new value of 107.868 15(11) was obtained for $A_r(\mathrm{Ag})$ [102]. This reduced the uncertainty in F by almost a factor of 10 and yielded $F = 96\,486.18(13)$ C mol^{-1}. As a result of these new determinations, the 1986 CODATA value was adjusted to $F = 96\,485.309$ C mol^{-1}, with a relative uncertainty of 0.30×10^{-6} [99]. The 1998 CODATA recommended value, with greater influence from the least-squares adjusted values of other fundamental constants, is now $F = 96\,485.3415(39)$ C mol^{-1} with a relative standard uncertainty of 4.0×10^{-8} [52].

The Avogadro constant N_A is defined as "the number of atoms per mole contained in 0.012 kg of the ground-state carbon isotope, ^{12}C, at rest". An accurate determination of the value of N_A is important because it relates the macroscopic masses of chemically equivalent substances to those of the corresponding atomic-scale entities. Thus, it has the potential to provide a more reliable and consistent international system of measurement units through a least-squares adjustment of fundamental constants. For example, a determination of N_A to a relative uncertainty of 10^{-7} would yield a more accurate value of the volt on the basis of the Josephson effect. Further improvements in the determination of N_A would permit the SI unit of mass, the kilogram, to be defined by a fixed number of specified atomic-scale entities. The kilogram is the only one remaining of the seven base SI units that is still defined by means of an artifact. The International Prototype Kilogram, a platinum-iridium cylinder, is maintained at the BIPM in France. However, the mass of this standard changes with time owing to surface effects and cleaning. This variability of the Prototype Kilogram necessarily introduces a relative uncertainty contribution of about 5×10^{-8} not only into the value of N_A, but also into any mass measurements made on the unified atomic-mass scale of u, but expressed in terms of the kilogram of the SI.

Various methods have been used to measure N_A: gas kinetics, Brownian motion, gravitational and electrical field effects acting on oil drops, and X-ray diffraction analysis by using the equation: $N_A = M(\mathrm{E})/\rho\, V_c$ applicable to atoms of mean molar mass, M(E), occupying a crystal of macroscopic density, ρ, with a primitive unit-cell volume, V_c [103,104]. Deslattes et al. [105] reported measurements of the cell dimensions, density, and atomic weight of nearly perfect Si crystals. These measurements give a value of N_A of $6.022\,0943 \times 10^{23}$ mol^{-1}, with an uncertainty of $1.05 \times 10^{-6} \times N_A$. This appeared to represent a 30-fold reduction in the uncertainty from previous direct measurements [99], but, owing to an unsuspected error in measurement, had to be corrected later by more than the originally estimated uncertainty [52,106].

At the 36th General Assembly of IUPAC in 1991, CAWIA endorsed an “absolute” determination of the atomic weight of Si in a single sample of 28.085 382(23), which, when combined with new determinations of density and interatomic spacing, gave a value of $N_A = 6.022\ 1363 \times 10^{23}$ mol^{-1} with an uncertainty of 1.1×10^{-6} [106]. The new value was in excellent agreement with the 1987 CODATA value of N_A ($6.022\ 1367 \times 10^{23}$ mol^{-1}), which has a relative uncertainty of 0.59×10^{-6}. The demands of the semiconductor industry have resulted in the production of Si crystals of great purity and physical perfection. This development has permitted a new set of measurements, which have been carried out by scientists from the Physikalisch-Technische Bundesanstalt (PTB), in Braunschweig, Germany, IRMM, and NIST. Improvements in the mass spectrometry of Si have yielded a more accurate value for its atomic weight, and the notion of the molar volume of Si as being a “natural constant” is now well confirmed [71,107]. Based on a worldwide collaboration of IRMM in Geel, the PTB, National Research Laboratory for Metrology (NRLM) in Tsukuba, the Istituto di Metrologie “Gustavo Colonnetti” (IMGC) in Torino, NIST, and the National Measurement Laboratory (NML) in Sydney, a value of $6.022\ 137\ 7(12) \times 10^{23}$ mol^{-1} may now be held to be more reliable than the value resulting from electromagnetic measurements because it is based exclusively on independent measurements with no assumptions made for any other fundamental constant(s). Moreover, scanning tunneling microscopy, capable of detecting small surface imperfections, and new methods for detecting and measuring micro-voids should lead to a reduction of the uncertainty of measurement of the dimensions of the molar volume of Si in ideal crystal form. The 1998 CODATA value 6.022 141 99(47) mol^{-1} with a relative uncertainty of 7.9×10^{-8} [52] may be modified in the next CODATA reassessment based on the best current knowledge of the fundamental constants.

Atomic weights and metrology in chemistry

The end of the 20th century set the scene in which measurements of amount of substance (and of chemical measurements in general) could adopt the concepts of metrology and metrological requirements, generating a renewed interest in the link between amounts of substance and mass. On the one hand, chemistry and chemical reactions are most conveniently described in terms of numbers of well-defined entities, wherefore the adoption of “amount of substance” as an SI base quantity has strong appeal. Amount-of-substance measurements are essentially a process of counting numbers or, rather, measuring ratios of large numbers [108]. On the other hand, we usually work with mass, which is not based on well-identified entities, but simply on mass ratios. It is well suited for “bulk” material measurements, as we have a convenient tool available to measure mass ratios: the balance. It is important, however, to recognize that mass does not offer a unique way for quantification of materials—as many chemists implicitly think and use mass—both types of measurements relate to important, useful, and differing base quantities. For pure substances of known composition, there is the possibility of converting the one into the other by use of the factor of the atomic weight. As the isotopic composition of the substances we handle deviate from a “constant” because of natural and anthropogenic reasons, it is important to realize that we have an apparently “variable” conversion factor (atomic weight or atomic-weight sum) between mass and amount of substance [109].

At some time in the future when the A_r(Si) and, through it or by other means, the value of N_A, will have a relative uncertainty of less than 5×10^{-8} (the current uncertainty related to the artifact “prototype kilogram”, the SI primary standard of mass), it will become convenient to “define” N_A in an equivalent way as the speed of light has now been “defined” as an invariant, exactly known constant. Just as the speed of light now links the more precisely defined unit of frequency exactly to that of length, so N_A would then link the unit of mass exactly to that more perfectly defined unit for amount of substance. That opens the possibility for making all mass measurements of precisely defined chemical substances in terms of the number of specified chemical entities.

Tables of standard atomic weights

The IUPAC-recommended atomic weights of the elements and their uncertainties are listed in the Table of Standard Atomic Weights, TSAW [19] (Table 3). TSAW and its predecessor tables represent, with minor exceptions covered by footnotes and annotations, the values that are intended to apply to virtually all samples from terrestrial sources as well as those found in laboratories involved in chemical investigations, for technological applications, and in materials of commerce. TSAW lists a single atomic weight for each element (with at least one stable isotope) associated with an estimated symmetrical uncertainty that would include the majority of substances likely to be encountered in elemental or chemically bound form. These uncertainties have always been estimated by CAWIA (and its predecessor Commissions) by consideration and evaluation of all the relevant published literature such that any user of the atomic-weight data would with high probability find the atomic weight of any element in any normal sample to be in the range indicated by the uncertainty for the currently recommended TSAW atomic weight. These values thus correspond to expanded uncertainties as now defined by ISO [38], and they also are found to be generally consistent with those calculated by orthodox statistical procedures from column 9 in Table 5. Since 1979, the atomic weights in TSAW [9] have been called the "standard atomic weights". Excluded from consideration in these atomic weights are most materials with deliberately altered isotopic compositions, extraterrestrial materials, and materials affected by nuclear reactions as at the Oklo natural nuclear reactor.

CAWIA has adopted the practice of adding annotations to the standard atomic weights that now form an integral part of the TSAW (Table 3). The exceptional situation with respect to Li has been addressed by including a special footnote referring to the large variations of A_r(Li) in commercial products. Other annotations used repetitively in TSAW are as follows:

g: Geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic weight of the element in such specimens and that given in the Table may exceed the stated uncertainty.

m: Modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotope fractionation. Substantial deviations in the atomic weight of the element from that given in the Table can occur.

r: Range in isotopic composition of normal terrestrial material prevents a more precise A_r(E) being given; the tabulated A_r(E) value should be applicable to any normal material.

Roth [110] has discussed the rationale behind these annotations, and the more fundamental question of how an atomic weight should be defined for a polyisotopic element, in light of the knowledge that its value depends on the population of atoms on which the measurement is made. Nature does not provide uniform samples of polyisotopic elements, the atomic weights of which can be measured with ever increasing precision. It is, therefore, necessary to select an adequately homogeneous sample that is available in sufficient quantity, and distributed with prescribed safeguards, so that it can be used for the purpose of specifying it as a carrier of an atomic-weight reference value.

The current TSAW (Table 3) reflects the best experimental values of atomic weights, taking account of the natural variabilities and experimental errors outlined above. Although the majority of users of atomic weights tend not to follow detailed discussions on reliability and applicability of data, these details are provided in the CAWIA report for the year in which the last change in the relevant atomic weight was made. Since the 1971 report [5], Commission reports have provided graphical displays of the widely differing uncertainties of the recommended atomic weights (see Fig. 3).

Table 3 Table of Standard Atomic Weights (TSAW) 2001. [Scaled to $A_r(^{12}\mathrm{C}) = 12$, where $^{12}\mathrm{C}$ is a neutral atom in its nuclear and electronic ground state. From ref. 19, with the addition of four changes to the atomic weights recommended by CAWIA at the General Assembly in 2001.]

Atomic number	Name	Symbol	Atomic weight	Footnotes
1	Hydrogen	H	1.007 94(7)	g m r
2	Helium	He	4.002 602(2)	g r
3	Lithium	Li	[6.941(2)]†	g m r
4	Beryllium	Be	9.012 182(3)	
5	Boron	B	10.811(7)	g m r
6	Carbon	C	12.0107(8)	g r
7	Nitrogen	N	14.0067(2)	g r
8	Oxygen	O	15.9994(3)	g r
9	Fluorine	F	18.998 4032(5)	
10	Neon	Ne	20.1797(6)	g m
11	Sodium (Natrium)	Na	22.989 770(2)	
12	Magnesium	Mg	24.3050(6)	
13	Aluminium (Aluminum)	Al	26.981 538(2)	
14	Silicon	Si	28.0855(3)	r
15	Phosphorus	P	30.973 761(2)	
16	Sulfur	S	32.065(5)	g r
17	Chlorine	Cl	35.453(2)	g m r
18	Argon	Ar	39.948(1)	g r
19	Potassium (Kalium)	K	39.0983(1)	
20	Calcium	Ca	40.078(4)	g
21	Scandium	Sc	44.955 910(8)	
22	Titanium	Ti	47.867(1)	
23	Vanadium	V	50.9415(1)	
24	Chromium	Cr	51.9961(6)	
25	Manganese	Mn	54.938 049(9)	
26	Iron (Ferrum)	Fe	55.845(2)	
27	Cobalt	Co	58.933 200(9)	
28	Nickel	Ni	58.6934(2)	
29	Copper (Cuprum)	Cu	63.546(3)	r
30	Zinc	Zn	65.409(4)	
31	Gallium	Ga	69.723(1)	
32	Germanium	Ge	72.64(1)	
33	Arsenic	As	74.921 60(2)	
34	Selenium	Se	78.96(3)	r
35	Bromine	Br	79.904(1)	
36	Krypton	Kr	83.798(2)	g m
37	Rubidium	Rb	85.4678(3)	g
38	Strontium	Sr	87.62(1)	g r
39	Yttrium	Y	88.905 85(2)	
40	Zirconium	Zr	91.224(2)	g
41	Niobium	Nb	92.906 38(2)	
42	Molybdenum	Mo	95.94(2)	g

(*continues on next page*)

Table 3 (*Continued*).

Atomic number	Name	Symbol	Atomic weight	Footnotes		
43	Technetium*	Tc				
44	Ruthenium	Ru	101.07(2)	g		
45	Rhodium	Rh	102.905 50(2)			
46	Palladium	Pd	106.42(1)	g		
47	Silver (Argentum)	Ag	107.8682(2)	g		
48	Cadmium	Cd	112.411(8)	g		
49	Indium	In	114.818(3)			
50	Tin (Stannum)	Sn	118.710(7)	g		
51	Antimony (Stibium)	Sb	121.760(1)	g		
52	Tellurium	Te	127.60(3)	g		
53	Iodine	I	126.904 47(3)			
54	Xenon	Xe	131.293(6)	g	m	
55	Caesium (Cesium)	Cs	132.905 45(2)			
56	Barium	Ba	137.327(7)			
57	Lanthanum	La	138.9055(2)	g		
58	Cerium	Ce	140.116(1)	g		
59	Praseodymium	Pr	140.907 65(2)			
60	Neodymium	Nd	144.24(3)	g		
61	Promethium*	Pm				
62	Samarium	Sm	150.36(3)	g		
63	Europium	Eu	151.964(1)	g		
64	Gadolinium	Gd	157.25(3)	g		
65	Terbium	Tb	158.925 34(2)			
66	Dysprosium	Dy	162.500(1)	g		
67	Holmium	Ho	164.930 32(2)			
68	Erbium	Er	167.259(3)	g		
69	Thulium	Tm	168.934 21(2)			
70	Ytterbium	Yb	173.04(3)	g		
71	Lutetium	Lu	174.967(1)	g		
72	Hafnium	Hf	178.49(2)			
73	Tantalum	Ta	180.9479(1)			
74	Tungsten (Wolfram)	W	183.84(1)			
75	Rhenium	Re	186.207(1)			
76	Osmium	Os	190.23(3)	g		
77	Iridium	Ir	192.217(3)			
78	Platinum	Pt	195.078(2)			
79	Gold (Aurum)	Au	196.966 55(2)			
80	Mercury (Hydrargyrum)	Hg	200.59(2)			
81	Thallium	Tl	204.3833(2)			
82	Lead (Plumbum)	Pb	207.2(1)	g		r
83	Bismuth	Bi	208.980 38(2)			
84	Polonium*	Po				
85	Astatine*	At				
86	Radon*	Rn				
87	Francium*	Fr				
88	Radium*	Ra				
89	Actinium*	Ac				
90	Thorium*	Th	232.0381(1)	g		
91	Protactinium*	Pa	231.035 88(2)			

(*continues on next page*)

Table 3 (*Continued*).

Atomic number	Name	Symbol	Atomic weight	Footnotes
92	Uranium*	U	238.028 91(3)	g m
93	Neptunium*	Np		
94	Plutonium*	Pu		
95	Americium*	Am		
96	Curium*	Cm		
97	Berkelium*	Bk		
98	Californium*	Cf		
99	Einsteinium*	Es		
100	Fermium*	Fm		
101	Mendelevium*	Md		
102	Nobelium*	No		
103	Lawrencium*	Lr		
104	Rutherfordium*	Rf		
105	Dubnium*	Db		
106	Seaborgium*	Sg		
107	Bohrium*	Bh		
108	Hassium*	Hs		
109	Meitnerium*	Mt		
110	Ununnilium*	Uun		
111	Unununium*	Uuu		
112	Ununbium*	Uub		
114	Ununquadium*	Uuq		
116	Ununhexium*	Uuh		

*Element has no stable isotopes. However, three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

†Commercially available Li materials have atomic weights that range between 6.939 and 6.996; if a more accurate value is required, it must be determined for the specific material.

g	Geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic weight of the element in such specimens and that given in the Table may exceed the stated uncertainty.
m	Modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotopic fractionation. Substantial deviations in atomic weight of the element from that given in the Table can occur.
r	Range in isotopic composition of normal terrestrial material prevents a more precise A_r(E) being given; the tabulated A_r(E) value should be applicable to any normal material.

At the time of the 1961 review [22], only a limited number of elements were assigned an uncertainty. The first year in which CAWIA included the uncertainty for each element was in 1969 [4]. The uncertainties, $U[A_r(\mathrm{E})]$ were constrained to be either ±1 or ±3 in the last digit, except for the monoisotopic elements, for which ±1 alone was used. At that time, the approximate "uncertainty" estimates did not seem to justify a more precise statement. In 1985, CAWIA adopted a procedure that allowed single-digit uncertainties from 1 to 9 [12].

For the 21 monoisotopic elements, the atomic weights depend only on the atomic masses, and therefore are now known to a relative uncertainty of at most 1×10^{-7} (see above, "Atomic weights of the monoisotopic elements"). Consequently, their atomic weights can be considered for most purposes as constants of nature, as all atomic weights were once believed to be. Peiser et al. [24] compared the atomic weights determined by the Harvard method with the currently accepted physically determined values for the monoisotopic elements. With the exception of Sc, the values were the same to within a factor of 4×10^{-4}, demonstrating the high level of precision of the Harvard method. For the polyiso-

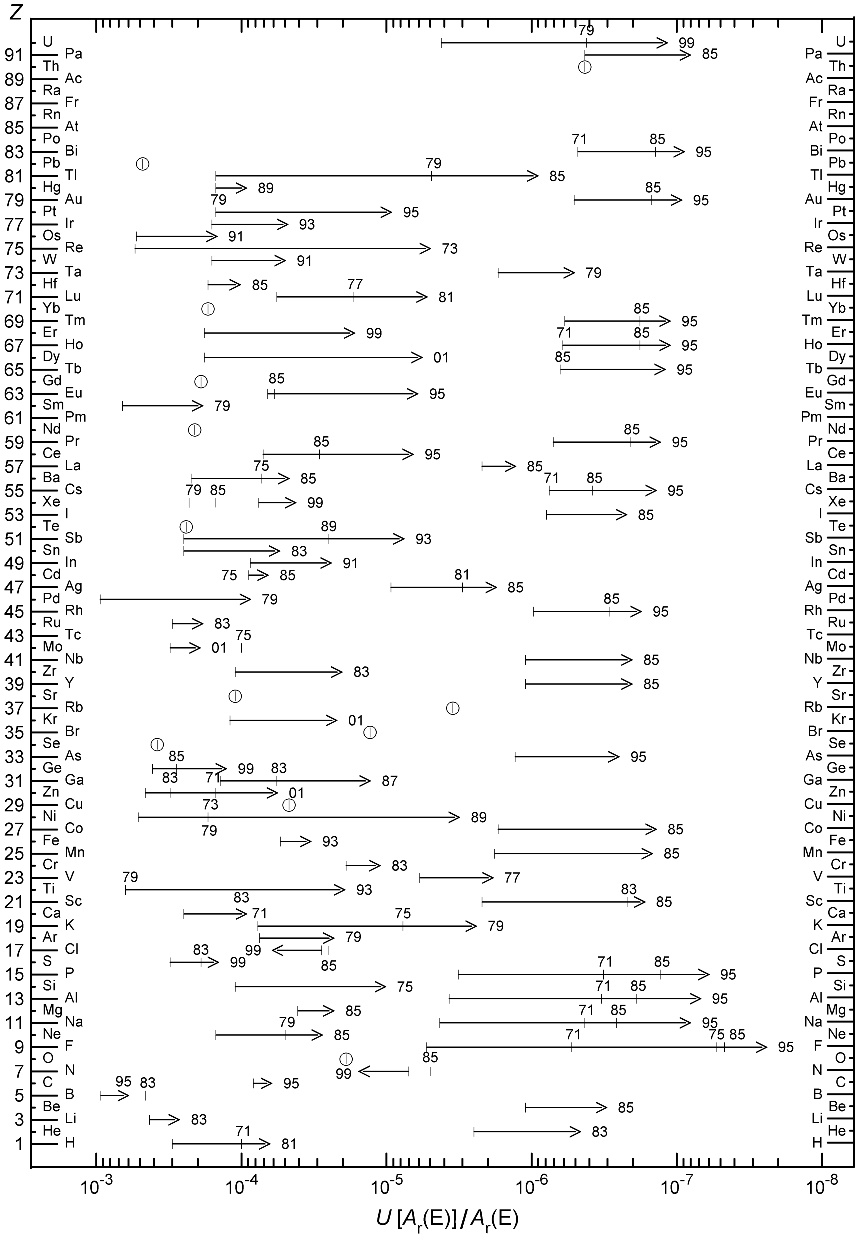

Fig. 3 Changes in the relative uncertainties of the IUPAC recommended (standard) atomic weights from 1969 to 2001. Plotted along the ordinate are the elements, E, in order of ascending atomic number, Z. The relative uncertainties of the recommended atomic weights, $U[A_r(E)]/A_r(E)$, are displayed along the exponential abscissa, decreasing to the right. For each element, the tip of the arrow indicates the current (2001) value, and the two-digit year indicates when that value was last changed. The foot of the arrow indicates the 1969 value, which is not labeled. For K, Ti, Cd, Cs, Ho, Pt, and Bi, the label at the foot of the arrow indicates a year when the atomic weight was changed by an amount that left the relative uncertainty unchanged at the scale of this illustration. Whenever an uncertainty was changed in intervening years of biennial IUPAC reviews, the change is indicated by a small vertical stroke with the two-digit year of change, even when that stroke falls outside the arrow line. Small circles indicate situations in which no change in relative uncertainty occurred between 1969 and 2001. For all elements except N and Cl, the relative uncertainties in 2001 were less than or equal to the relative uncertainties in 1969.

topic elements, important improvements in our knowledge of atomic weights since the review by Cameron and Wichers [22] have been due almost entirely to new mass-spectrometric measurements of isotope abundances, or to reassessments of uncertainties of mass-spectrometric data underlying earlier values.

Relative differences between the isotopic compositions of different samples commonly can be measured with greater precision than the "absolute" isotopic compositions. For this reason, there are essentially four different categories of elements with contrasting constraints on their atomic weights:

1. monoisotopic,
2. polyisotopic with no reliable current evidence for natural variation,
3. polyisotopic with credible evidence of variation within the uncertainties of the best "absolute" measurement, and
4. polyisotopic with considerable variation extending beyond the range implied by the uncertainties of the best "absolute" measurement.

The annotation "r", referring to atomic weights whose uncertainties reflect variation, applies only to elements of category 4. Atomic-weight values of elements in category 3 may enter category 4 as more precise "absolute" determinations are made, or as materials with wider variability are discovered. Similarly, elements in category 2 can change to higher categories as measurements improve.

An example of an element with large isotope-abundance variability in common materials is H (Fig. 1 and [85]). Accurate "absolute" isotope-abundance measurements have been made on two water samples, VSMOW and standard light Antarctic precipitation (SLAP), which also form the basis for normalizing the δ scale in most laboratories. Delta measurements on other natural substances and artificial reagents range widely, illustrating the difficulty of assigning a single value to the standard atomic weight for H. In 1997, CAWIA selected a standard atomic weight and uncertainty that include the values of essentially all types of materials likely to be encountered in laboratories [18]. The atomic weight of H in tap water is included within the range of the uncertainty, but its value may be expected to differ among laboratories and it is likely to be somewhat higher in most cases than the standard atomic weight. Similarly for O, the standard atomic weight and uncertainty were assigned in 1997 to include those of all common materials, even though it is substantially different than that in normal tap water. Other elements for which analogous decisions have been made include He, Li, B, C, N, Si, S, Cl, Si, Cu, Se, Sr, and Pb, as described in Part 2 of this review.

For some elements, and for some purposes (e.g., geochronology), it may be necessary to determine the atomic weight of an element in a given material used in an experiment rather than relying on the standard atomic weight. In analytical laboratories receiving a variety of samples, it may be necessary either to measure the isotopic compositions of all samples, or to accept the uncertainty of the atomic weight as a component of analytical uncertainty associated with chemical calibration. Compiled data (e.g., Fig. 1; see also [85]) may be compared with the requirements of a proposed investigation to indicate whether the standard atomic weight is sufficiently precise or if an isotope analysis is needed for a particular material under study.

Table 4 gives the comparison of the atomic weights in 1900 (at the beginning of the 20th century) and as they were at the conclusion of the 20th century [19]. The changes that have occurred to the atomic weights as a function of time are graphically represented in Fig. 3, and described in detail by Coplen and Peiser [111]. At the 2001 IUPAC General Assembly, CAWIA recommended four changes to the 1999 TSAW, namely: $A_r(\mathrm{Zn}) = 65.409(4)$, $A_r(\mathrm{Kr}) = 83.798(2)$, $A_r(\mathrm{Mo}) = 95.94(2)$, and $A_r(\mathrm{Dy}) = 162.500(1)$. These 2001 changes are incorporated in Tables 3 and 4 and in Fig. 3.

In the reports for 1981, 1989, and 1993 [10,14,16], CAWIA published atomic-weight tables abridged to five significant figures because the full TSAW "exceeds the needs of many users," and the abridged table would increase "the length of time during which a given table has full validity, a desirable attribute for textbooks and numerical tables." These expectations were not fully realized because every set of TSAW revisions so far has necessitated at least one change in the abridged table.

Tables of the isotopic compositions of the elements

Although Tables of Atomic Weights have been published since before the turn of the 20th century, the Table of the Isotopic Compositions of the Elements (TICE) is a much more recent innovation. Nier [21] carried out an evaluation of relative isotope-abundance measurements for the Atomic Weights Committee in 1954, but comprehensive compilations of TICE were not prepared by CAWIA until 1975 [7], 1977 [8], and 1979 [9], when they were contained in the CAWIA biennial reports. Subsequent versions of TICE were published by CAWIA separately from the biennial reports [72,112–114].

The production of TICE was initiated by CBNM from 1965 and was institutionalized in SAIC (1975–1984) leading up to the previous element-by-element review [24]. It is now managed by SIAM, which reviews all the mass-spectrometric determinations of isotope abundances that have been published since the last TICE has been published. This involves a critical evaluation of the published literature to reach a consensus on which is the "best" measurement from a single terrestrial source, together with a determination as to whether or not the "best" measurement on a single source is representative of other occurrences of the same element.

The "best" measurement is most useful if made on a homogeneous material available in bulk so that samples of it can be used as a reference material, but this is not the case for all reference materials currently in use. If the best measurement was made on a reference material, the identity of the material is given in TICE. The isotope abundances of the "best" measurement are reproduced from the original literature after due CAWIA evaluation. The uncertainties on the last digits are given in parentheses as reported in the original publication, and TICE indicates the type of uncertainty listed. Where data are published as isotope-abundance ratios, the ratios and their uncertainties are converted to abundances using orthodox procedures [115]. The symbol "C" is appended to the "best" measurement when calibrated mixtures have been used to correct the mass spectrometer for bias, giving an "absolute" result to within the uncertainties stated in the original publication. "F" is appended when calibrated mixtures have been used to correct the mass spectrometer for isotope fractionation, but the measurement fails to fulfill all the requirements of a fully calibrated measurement. "L" is appended when the linearity of the mass spectrometer has been established for the relevant abundance ratios by using synthetic mixtures of isotopes or certified materials produced by a standards laboratory. "N" is appended when none of the above requirements have been met. TICE includes values for normal terrestrial samples, but does not include values published for meteoritic or other extraterrestrial materials.

In the most recent published version of TICE [72], an attempt is made to list the range in natural variations derived from the publications whose measurements have been accepted by SIAM. No data are given unless a range in isotope abundances has been reliably established. The limits do not include certain exceptional geological samples that carry the annotation "g".

Table 4 Comparison of the Table of Atomic Weights in 1900 [20] and 2001.

The 2001 data are from Table 3. The 1900 values are scaled to $A_r(\mathrm{O}) = 16$; those for 2001 to $A_r(^{12}\mathrm{C}) = 12$. Since on the latter scale $A_r(\mathrm{O}) = 15.9994(3)$ the two data sets can be fairly compared within the accuracy of the set for 1900.

Element name	1900	2001[a]	Element name	1900	2001[a]
Aluminium	27.1	26.981 538(2)	Molybdenum	96.0	95.94(2)
Antimony	120.4	121.760(1)	Neodymium	143.6	144.24(3)
Argon	Not measured	39.948(1)	Neon	Not measured	20.1797(6)
Arsenic	75.0	74.921 60(2)	Nickel	58.7	58.6934(2)
Barium	137.40	137.327(7)	Niobium	93.7	92.906 38(2)
Beryllium	9.1	9.012 182(3)	Nitrogen	14.0	14.0067(2)
Bismuth	208.1	208.980 38(2)	Osmium	191.0	190.23(3)
Boron	11.0	10.811(7)	Oxygen	16.000	15.9994(3)
Bromine	79.95	79.904(1)	Palladium	107.0	106.42(1)
Cadmium	112.4	112.411(8)	Phosphorus	31.0	30.973 761(2)
Calcium	40.1	40.078(4)	Platinum	194.9	195.078(2)
Carbon	12.0	12.0107(8)	Potassium	39.11	39.0983(1)
Cerium	139	140.116(1)	Praseodymium	140.5	140.907 65(2)
Caesium	132.9	132.905 45(2)	Protactinium	Not known	231.035 88(2)
Chlorine	35.45	35.453(2)	Rhenium	Not known	186.207(1)
Chromium	52.1	51.9961(6)	Rhodium	103.0	102.905 50(2)
Cobalt	58.93	58.933 200(9)	Rubidium	85.4	85.4678(3)
Copper	63.6	63.546(3)	Ruthenium	101.7	101.07(2)
Dysprosium	Not known	162.500(1)	Samarium	150.3	150.36(3)
Erbium	166.0	167.259(3)	Scandium	44.1	44.955 910(8)
Europium	Not known	151.964(1)	Selenium	79.2	78.96(3)
Fluorine	19.05	18.998 4032(5)	Silicon	28.4	28.0855(3)
Gadolinium	157.0	157.25(3)	Silver	107.92	107.8682(2)
Gallium	70.0	69.723(1)	Sodium	23.05	22.989 770(2)
Germanium	72.5	72.64(1)	Strontium	87.6	87.62(1)
Gold	197.2	196.966 55(2)	Sulfur	32.07	32.065(5)
Hafnium	Not known	178.49(2)	Tantalum	182.8	180.9479(1)
Helium	Not measured	4.002 602(2)	Tellurium	127.5	127.60(3)
Holmium	Not known	164.930 32(2)	Terbium	160	158.925 34(2)
Hydrogen	1.008	1.007 94(7)	Thallium	204.15	204.3833(2)
Indium	114	114.818(3)	Thorium	232.6	232.0381(1)
Iodine	126.85	126.904 47(3)	Thulium	170.7	168.934 21(2)
Iridium	193.1	192.217(3)	Tin	119.0	118.710(7)
Iron	56.0	55.845(2)	Titanium	48.15	47.867(1)
Krypton	Not measured	83.798(2)	Tungsten	184.0	183.84(1)
Lanthanum	138.6	138.9055(2)	Uranium	239.6	238.028 91(3)
Lead	206.92	207.2(1)	Vanadium	51.4	50.9415(1)
Lithium	7.03	6.941(2)	Xenon	Not measured	131.293(6)
Lutetium	Not known	174.967(1)	Ytterbium	173.2	173.04(3)
Magnesium	24.3	24.3050(6)	Yttrium	89.0	88.905 85(2)
Manganese	55.0	54.938 049(9)	Zinc	65.4	65.409(4)
Mercury	200.0	200.59(2)	Zirconium	90.4	91.224(2)

[a] Figures in parenthesis indicating uncertainties in the preceding digit.

TICE also lists "representative" isotopic compositions, which, in the opinion of CAWIA, represent the isotopic compositions of substances that may be encountered in the laboratory. The uncertainties listed in parentheses cover the range of probable variations of chemicals and natural materials as well as estimates for experimental errors. Annotations applied to these values are “m”, which refers to modified isotopic compositions found in commercially available materials and “r”, indicating that the range in isotopic compositions existing in normal terrestrial material limits the precision of the isotope abundances. The atomic weights calculated from the representative isotopic compositions in TICE generally are consistent with the A_r(E) values listed in TSAW, but with minor discrepancies in some cases resulting from: (1) rounding errors may be caused by the single-digit rule for $U[A\mathrm{r}(\mathrm{E})]$; (2) the representative isotopic compositions of the noble gases refer to their occurrences in air; and (3) TSAW is updated and published on a biennial basis whereas TICE is published less frequently. Table 5 presents the current version of TICE, including modifications from the 2001 meeting of CAWIA and from the compilation of Coplen et al. [85].

Table 5 Table of the Isotopic Compositions of the Elements (TICE), 2001.

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials[a]	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
1	H	1	0.999 816–0.999 974	m,r	0.999 844 26(5) 2s C	[116]	VSMOW*	0.999 885(70)
		2	0.000 026–0.000 184		0.000 155 74(5)		CEA	0.000 115(70)[b]
							IAEA	
							NIST	
2	He	3	4.6×10^{-10}–0.000 041	g,r	0.000 001 343(13) 1s C	[117]	Air*	0.000 001 34(3)
		4	0.999 959–1		0.999 998 657(13)			0.999 998 66(3)
								(in air)
3	Li	6	0.077 14–0.072 25	m,r	0.075 89(24) 2s C	[118]	IRMM-016*	[0.0759(4)][c]
		7	0.922 75–0.927 86		0.924 11(24)			[0.9241(4)]
							IAEA	
							NIST	
4	Be	9			1.0000	[119]		1.0000
5	B	10	0.189 29–0.203 86	m,r	0.1982(2) 2s C	[120]	IRMM-011*	0.199(7)
		11	0.796 14–0.810 71		0.8018(2)			0.801(7)
							NIST	
6	C	12	0.988 53–0.990 37	r	0.988 922(28) P C	[121]	NBS19*	0.9893(8)
		13	0.009 63–0.011 47		0.011 078(28)		IAEA	0.0107(8)
							NIST	
7	N	14	0.995 79–0.996 54	r	0.996 337(4) P C	[122]	Air*	0.996 36(20)[d]
		15	0.003 46–0.004 21		0.003 663(4)		IAEA	0.003 64(20)
							NIST	
8	O	16	0.997 38–0.997 76	r	0.997 6206(5) 1s N	[123]	VSMOW*	0.997 57(16)
		17	0.000 37–0.000 40		0.000 3790(9)[e]	[124]	IAEA	0.000 38(1)
		18	0.001 88–0.002 22		0.002 0004(5)		NIST	0.002 05(14)
9	F	19			1.0000	[125]		1.0000
10	Ne	20	0.8847–0.9051	g,m,r	0.904 838(90) 1s C	[126]	Air*	0.9048(3)
		21	0.0027–0.0171		0.002 696(5)			0.0027(1)
		22	0.0920–0.0996		0.092 465(90)			0.0925(3)
								(in air)

(*continues on next page*)

Table 5 (*Continued*).

Z 1	E 2	M 3	Range of natural variations (mole fraction) 4	Annotation 5	Best measurement from a single terrestrial source (mole fraction) 6	Ref. 7	Available reference materials[a] 8	Representative isotopic composition (mole fraction) 9
11	Na	23			1.0000	[127]		1.0000
12	Mg	24	0.789 58–0.790 17		0.789 92(25) 2s C	[128]	NIST-SRM980*	0.7899(4)
		25	0.099 96–0.100 12		0.100 03(9)			0.1000(1)
		26	0.109 87–0.110 30		0.110 05(19)			0.1101(3)
13	Al	27			1.0000			1.0000
14	Si	28	0.922 05–0.92241	r	0.922 2968(44) 2s C	[70]	IAEA	0.922 23(19)
		29	0.046 78–0.046 92		0.046 8316(32)		IRMM	0.046 85(8)
		30	0.030 82–0.031 02		0.030 8716(32)		NIST	0.030 92(11)
15	P	31			1.0000	[119]		1.0000
16	S	32	0.944 54–0.952 81	r	0.9504074(88) 2s C	[129]	IAEA-S1*	0.9499(26)
		33	0.007 30–0.007 93		0.0074869(60)		CEA	0.0075(2)
		34	0.039 76–0.047 34		0.0419599(66)		IAEA	0.0425(24)
		36	0.000 13–0.000 19		0.00014579(89)		NIST	0.0001(1)
17	Cl	35	0.756 44–0.759 23	m,g	0.757 71(45) 2s C	[130]	NIST-SRM975*	0.7576(10)
		37	0.240 77–0.243 56		0.242 29(45)			0.2424(10)
18	Ar	36		g	0.003 365(6) P C	[65]	Air*	0.003 365(30)
		38			0.000 632(1)			0.000 632(5)
		40			0.996 003(6)			0.996 003(30) (in air)
19	K	39			0.932 5811(292) 2s C	[131]	NIST-SRM985*	0.932 581(44)
		40			0.000 116 72(41)			0.000 117(1)
		41			0.067 3022(292)			0.067 302(44)
20	Ca	40	0.969 33–0.969 47	g,r	0.969 41(6) 2s N	[132]	NIST-SRM915*	0.969 41(156)[h]
		42	0.006 46–0.006 48		0.006 47(3)			0.006 47(23)
		43	0.001 35–0.001 35		0.001 35(2)			0.001 35(10)
		44	0.020 82–0.020 92		0.020 86(4)			0.020 86(110)
		46	0.000 04–0.000 04		0.000 04(1)			0.000 04(3)
		48	0.001 86–0.001 88		0.001 87(1)			0.001 87(21)
21	Sc	45			1.0000	[133]		1.0000
22	Ti	46			0.082 49(21) 2s C	[134]		0.0825(3)
		47			0.074 37(14)			0.0744(2)
		48			0.737 20(22)			0.7372(3)
		49			0.054 09(10)			0.0541(2)
		50			0.051 85(13)			0.0518(2)
23	V	50	0.002 487–0.002 502	g	0.002 497(6) 1s F	[135]		0.002 50(4)
		51	0.997 498–0.997 513		0.997 503(6)			0.997 50(4)
24	Cr	50	0.042 94–0.043 45		0.043 452(85) 2s C	[136]	NIST-SRM979*	0.043 45(13)
		52	0.837 62–0.837 90		0.837 895(117)			0.837 89(18)
		53	0.095 01–0.095 53		0.095 006(110)			0.095 01(17)
		54	0.023 65–0.023 91		0.023 647(48)			0.023 65(7)
25	Mn	55			1.0000	[119]		1.0000

(*continues on next page*)

Table 5 (*Continued*).

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials[a]	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
26	Fe	54	0.058 37–0.058 61		0.058 45(23) 2s C	[137]	IRMM-014*	0.058 45(35)
		56	0.917 42–0.917 60		0.917 54(24)			0.917 54(36)
		57	0.021 16–0.021 21		0.021 191(65)			0.021 19(10)
		58	0.002 81–0.002 82		0.002 819(27)			0.002 82(4)
27	Co	59			1.0000	[119]		1.0000
28	Ni	58			0.680 769(59) 2s C	[138]		0.680 769(89)
		60			0.262 231(51)			0.262 231(77)
		61			0.011 399(4)			0.011 399(6)
		62			0.036 345(11)			0.036 345(17)
		64			0.009 256(6)			0.009 256(9)
29	Cu	63	0.689 83–0.693 38	r	0.691 74(20) 2s C	[139]	NIST-SRM976*	0.6915(15)
		65	0.306 62–0.310 17		0.308 26(20)			0.3085(15)
30	Zn	64			0.482 68(214) 2s C	[140]		0.482 68(321)
		66			0.279 75(51)			0.279 75(77)
		67			0.041 02(14)			0.041 02(21)
		68			0.190 24(82)			0.190 24(123)
		70			0.006 31(6)			0.006 31(9)
31	Ga	69		m	0.601 079(62) 2s C	[141]	NIST-SRM994*	0.601 08(9)
		71			0.398 921(62)			0.398 92(9)
32	Ge	70			0.203 75(77) 2s C	[351]		0.2038(18)
		72			0.273 11(103)			0.2731(26)
		73			0.077 56(46)			0.0776(8)
		74			0.367 29(85)			0.3672(15)
		76			0.078 30(43)			0.0783(7)
33	As	75			1.0000	[119]		1.0000
34	Se	74		r	0.008 89(3) 1s N	[142]		0.0089(4)
		76			0.093 66(18)			0.0937(29)
		77			0.076 35(10)			0.0763(16)
		78			0.237 72(20)			0.2377(28)
		80			0.496 07(17)			0.4961(41)
		82			0.087 31(10)			0.0873(22)
35	Br	79			0.506 86(26) 2s C	[143]	NIST-SRM977*	0.5069(7)
		81			0.493 14(26)			0.4931(7)
36	Kr	78		g,m	0.003 5518(32) 2s C	[144]		0.003 55(3)
		80			0.022 8560(96)			0.022 86(10)
		82			0.115 930(62)			0.115 93(31)
		83			0.114 996(58)			0.115 00(19)
		84			0.569 877(58)			0.569 87(15)
		86			0.172 790(32)			0.172 79(41) (in air)
37	Rb	85		g	0.721 654(132) 2s C	[145]	NIST-SRM987*	0.7217(2)
		87			0.278 346(132)			0.2783(2)

(*continues on next page*)

Table 5 (*Continued*).

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials[a]	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
38	Sr	84	0.0055–0.0058	g,r	0.005 574(16) 2s C	[146]	NIST-	0.0056(1)
		86	0.0975–0.0999		0.098 566(34)		SRM987*	0.0986(1)
		87	0.0694–0.0714		0.070 015(26)		NIST	0.0700(1)[h]
		88	0.8229–0.8275		0.825 845(66)			0.8258(1)
39	Y	89			1.0000	[147]		1.0000
40	Zr	90		g	0.514 52(9) 2s N	[148]		0.5145(40)
		91			0.112 23(12)			0.1122(5)
		92			0.171 46(7)			0.1715(8)
		94			0.1738(12)			0.1738(28)
		96			0.027 99(5)			0.0280(9)
41	Nb	93			1.0000	[127]		1.0000
42	Mo	92		g	0.147 69(1) 2s L	[149]		0.1477(31)
		94			0.092 28(1)			0.0923(10)
		95			0.159 022(4)			0.1590(9)
		96			0.166 76(7)			0.1668(1)
		97			0.095 618(7)			0.0956(5)
		98			0.241 959(6)			0.2419(26)
		100			0.096 671(4)			0.0967(20)
43	Tc				—			—
44	Ru	96		g	0.055 420(1) 1s N	[150]		0.0554(14)
		98			0.018 688(2)			0.0187(3)
		99			0.127 579(6)			0.1276(14)
		100			0.125 985(4)			0.1260(7)
		101			0.170 600(10)			0.1706(2)
		102			0.315 519(11)			0.3155(14)
		104			0.186 210(11)			0.1862(27)
45	Rh	103			1.0000	[119]		1.0000
46	Pd	102		g	0.01020(8) 2s C	[151]		0.0102(1)
		104			0.1114(5)			0.1114(8)
		105			0.2233(5)			0.2233(8)
		106			0.2733(2)			0.2733(3)
		108			0.2646(6)			0.2646(9)
		110			0.1172(6)			0.1172(9)
47	Ag	107		g	0.518 392(51) 2s C	[102]	NIST-	0.518 39(8)
		109			0.481 608(51)		SRM978*	0.481 61(8)
48	Cd	106		g	0.0125(2) 2s F	[152]		0.0125(6)
		108			0.0089(1)			0.0089(3)
		110			0.1249(6)			0.1249(18)
		111			0.1280(4)			0.1280(12)
		112			0.2413(7)			0.2413(21)
		113			0.1222(4)			0.1222(12)
		114			0.2873(14)			0.2873(42)
		116			0.0749(6)			0.0749(18)

(*continues on next page*)

Table 5 (*Continued*).

Z 1	E 2	M 3	Range of natural variations (mole fraction) 4	Annotation 5	Best measurement from a single terrestrial source (mole fraction) 6	Ref. 7	Available reference materials[a] 8	Representative isotopic composition (mole fraction) 9
49	In	113		g	0.042 88(5) 2s N	[153]		0.0429(5)
		115			0.957 12(5)			0.9571(5)
50	Sn	112		g	0.009 73(3) 1s C	[154]		0.0097(1)
		114			0.006 59(3)[f]	[155]		0.0066(1)
		115			0.003 39(3)[f]			0.0034(1)
		116			0.145 36(31)			0.1454(9)
		117			0.076 76(22)			0.0768(7)
		118			0.242 23(30)			0.2422(9)
		119			0.085 85(13)			0.0859(4)
		120			0.325 93(20)			0.3258(9)
		122			0.046 29(9)			0.0463(3)
		124			0.057 89(17)			0.0579(5)
51	Sb	121		g	0.572 13(32) 2s C	[156]		0.5721(5)
		123			0.427 87(32)			0.4279(5)
52	Te	120		g	0.000 96(1) 2se N	[157]		0.0009(1)[i]
		122			0.026 03(1)			0.0255(12)
		123			0.009 08(1)			0.0089(3)
		124			0.048 16(2)			0.0474(14)
		125			0.071 39(2)			0.0707(15)
		126			0.189 52(4)			0.1884(25)
		128			0.316 87(4)			0.3174(8)
		130			0.337 99(3)			0.3408(62)
53	I	127			1.0000	[158]		1.0000
54	Xe	124		g,m	0.000 952(3) 3s C	[58]		0.000 952(3)
		126			0.000 890(2)			0.000 890(2)
		128			0.019 102(8)			0.019 102(8)
		129			0.264 006(82)			0.264 006(82)
		130			0.040 710(13)			0.040 710(13)
		131			0.212 324(30)			0.212 324(30)
		132			0.269 086(33)			0.269 086(33)
		134			0.104 357(21)			0.104 357(21)
		136			0.088 573(44)			0.088 573(44) (in air)
55	Cs	133			1.0000	[127]		1.0000
56	Ba	130		g	0.001 058(2) 3se F	[159]		0.001 06(1)
		132			0.001 012(2)			0.001 01(1)
		134			0.024 17(3)			0.024 17(18)
		135			0.065 92(2)			0.065 92(12)
		136			0.078 53(4)			0.078 54(24)
		137			0.112 32(4)			0.112 32(24)
		138			0.716 99(7)			0.716 98(42)
57	La	138		g	0.000 9017(5) 2se N	[160]		0.000 90(1)
		139			0.999 0983(5)			0.999 10(1)

(*continues on next page*)

Table 5 (*Continued*).

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials^a	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
58	Ce	136	0.001 85–0.001 86	g	0.001 86(1) 2s C	[161]		0.001 85(2)
		138	0.002 51–0.002 54		0.002 51(1)			0.002 51(2)^h
		140	0.884 46–0.884 49		0.884 49(34)			0.884 50(51)
		142	0.111 14–0.111 14		0.111 14(34)			0.111 14(51)
59	Pr	141			1.0000	[147]		1.0000
60	Nd	142	0.2680–0.2730	g	0.2716(4) 2se N	[162]		0.272(5)
		143	0.1212–0.1232		0.1218(2)			0.122(2)^h
		144	0.2379–0.2397		0.2383(4)			0.238(3)
		145	0.0823–0.0835		0.0830(2)			0.083(1)
		146	0.1706–0.1735		0.1717(3)			0.172(3)
		148	0.0566–0.0578		0.0574(1)			0.057(1)
		150	0.0553–0.0569		0.0562(1)			0.056(2)
61	Pm				—			—
62	Sm	144		g	0.030 734(9) 2s F	[163]		0.0307(7)
		147			0.149 934(18)			0.1499(18)
		148			0.112 406(15)			0.1124(10)
		149			0.138 189(18)			0.1382(7)
		150			0.073 796(14)			0.0738(1)
		152			0.267 421(66)			0.2675(16)
		154			0.227 520(68)			0.2275(29)
63	Eu	151		g	0.47810(42) 2se C	[164]		0.4781(6)
		153			0.52190(42)			0.5219(6)
64	Gd	152		g	0.002 029(4) 2se N	[165]		0.0020(1)
		154			0.021 809(4)			0.0218(3)
		155			0.147 998(17)			0.1480(12)
		156			0.204 664(6)			0.2047(9)
		157			0.156 518(9)			0.1565(2)
		158			0.248 347(16)			0.2484(7)
		160			0.218 635(7)			0.2186(19)
65	Tb	159			1.0000	[147]		1.0000
66	Dy	156		g	0.000 56(2) 2S C	[166]		0.000 56(3)
		158			0.000 95(2)			0.000 95(3)
		160			0.023 29(12)			0.023 29(18)
		161			0.188 89(28)			0.188 89(42)
		162			0.254 75(24)			0.254 75(36)
		163			0.248 96(28)			0.248 96(42)
		164			0.2826(36)			0.282 60(54)
67	Ho	165			1.0000	[147]		1.0000
68	Er	162		g	0.001 391(30) 2s C	[167]		0.001 39(5)
		164			0.016 006(20)			0.016 01(3)
		166			0.335 014(240)			0.335 03(36)
		167			0.228 724(60)			0.228 69(9)
		168			0.269 852(120)			0.269 78(18)
		170			0.149 013(240)			0.149 10(36)

(*continues on next page*)

Table 5 (*Continued*).

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials^a	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
69	Tm	169			1.0000	[147]		1.0000
70	Yb	168		g	0.001 27(2) 2se N	[162]		0.0013(1)
		170			0.0304(2)			0.0304(15)
		171			0.1428(8)			0.1428(57)
		172			0.2183(10)			0.2183(67)
		173			0.1613(7)			0.1613(27)
		174			0.3183(14)			0.3183(92)
		176			0.1276(5)			0.1276(41)
71	Lu	175		g	0.974 16(5) 2se N	[168]		0.9741(2)
		176			0.025 84(5)			0.0259(2)
72	Hf	174	0.001 619–0.001 621		0.001 620(9) 2se N	[168]		0.0016(1)
		176	0.052 06–0.052 71		0.052 604(56)			0.0526(7)^h
		177	0.185 93–0.186 06		0.185 953(12)			0.1860(9)
		178	0.272 78–0.272 97		0.272 811(22)			0.2728(7)
		179	0.136 19–0.1363		0.136 210(9)			0.1362(2)
		180	0.350 76–0.351		0.350 802(26)			0.3508(16)
73	Ta	180			0.000 123(3) 1se N	[127]		0.000 12(2)
		181			0.999 877(3)			0.999 88(2)
74	W	180			0.001 198(2) 1s N	[169]		0.0012(1)
		182			0.264 985(49)			0.2650(16)
		183			0.143 136(6)			0.1431(4)
		184			0.306 422(13)			0.3064(2)
		186			0.284 259(62)			0.2843(19)
75	Re	185			0.373 98(16) 2s C	[170]	NIST-SRM989*	0.3740(2)
		187			0.626 02(16)			0.6260(2)
76	Os	184		g,r	0.000 197(5) 1s N	[171]		0.0002(1)
		186			0.015 859(44)			0.0159(3)
		187			0.019 644(12)			0.0196(2)^h
		188			0.132 434(19)			0.1324(8)
		189			0.161 466(16)			0.1615(5)
		190			0.262 584(14)			0.2626(2)
		192			0.407 815(22)			0.4078(19)
77	Ir	191			0.372 72(15) 1s N	[172]		0.373(2)
		193			0.627 28(15)			0.627(2)
78	Pt	190			0.000 136 34(68) 1s N	[173]		0.000 14(1)
		192			0.007 826 59(35)			0.007 82(7)
		194			0.329 6700(77)			0.329 67(99)
		195			0.338 315 57(42)			0.338 32(10)
		196			0.252 4166(36)			0.252 42(41)
		198			0.071 6349(42)			0.071 63(55)
79	Au	197			1.0000	[119]		1.0000

(*continues on next page*)

Table 5 (*Continued*).

Z	E	M	Range of natural variations (mole fraction)	Annotation	Best measurement from a single terrestrial source (mole fraction)	Ref.	Available reference materials[a]	Representative isotopic composition (mole fraction)
1	2	3	4	5	6	7	8	9
80	Hg	196			0.001 5344(19) 1s N	[174]		0.0015(1)
		198			0.099 68(13)			0.0997(20)
		199			0.168 73(17)			0.1687(22)
		200			0.230 96(26)			0.2310(19)
		201			0.131 81(13)			0.1318(9)
		202			0.298 63(33)			0.2986(26)
		204			0.068 65(7)			0.0687(15)
81	Tl	203	0.294 94–0.295 28		0.295 24(9) 2s C	[175]	NIST-SRM997*	0.2952(1)
		205	0.704 72–0.705 06		0.704 76(9)			0.7048(1)
82	Pb	204	0.0104–0.0165	g,r	0.014 245(12) 2s C	[176]	NIST-SRM981* NIST	0.014(1)
		206	0.2084–0.2748		0.241 447(57)			0.241(1)[h]
		207	0.1762–0.2365 0.1762		0.220 827(27)			0.221(1)[h]
		208	0.5128–0.5621		0.523 481(86)			0.524(1)[h]
83	Bi	209			1.0000	[119]		1.0000
84	Po							
85	At							
86	Rn							
87	Fr							
88	Ra							
89	Ac							
90	Th	232		g	1.0000	[177]		1.0000
91	Pa	231			1.0000	[178]		1.0000
92	U	234	0.000 050–0.000 059	g,m,r	0.000 054 20(42) 2s C	[179]	IRMM-184* CEA IRMM NBL	[0.000 054(5)]
		235	0.007 198–0.007 207		0.007 200(1)			[0.007 204(6)][c]
		238	0.992 739–0.992 752		0.992 745(10)			[0.992 742(10)]

*Reference material used for the best measurement.

[a] NIST materials were previously labeled NBS. IRMM materials were previously labeled CBNM.

[b] Tank hydrogen has a ^{2}H abundance as low as 0.0032 atom %.

[c] Materials depleted in ^{6}Li and ^{235}U are commercial sources of laboratory shelf reagents. In the case of Li such samples are known to have ^{6}Li abundances in the range 2.007–7.672 %, with natural materials at the higher end of this range. In the case of U, the ^{235}U abundance has been reported to range from 0.21–0.7207 atom percent, far removed from the natural value.

[d] The Commission recommends that the value of 272 be employed for $^{14}N/^{15}N$ of N_2 in air for the calculation of atom percent ^{15}N from measured $\delta^{15}N$ values.

[e] The best measurement reports a calibrated $^{16}O/^{18}O$ ratio on VSMOW.

[f] The original data for Sn has been adjusted to take into account possible errors due to ^{115}In contamination, and an error in the ^{114}Sn abundance.

[h] Evaluated isotopic composition is for most but not all commercial samples.

[i] An electron multiplier was used for these measurements and the measured abundances were adjusted using a "square root of the masses" correction factor.

(*continues on next page*)

Table 5 (*Continued*).

The column contents are as follows:

Column l: The elements are tabulated in order of ascending atomic number (Z).

Column 2: The symbols for the elements (E) are listed using the abbreviations recommended by IUPAC.

Column 3: The mass number (M) for each isotope is listed.

Column 4: Range of natural variations (from [72,85]). No data are given in this column unless a range has been reliably established. The limits given do not include certain exceptional samples; these are noted with a "g" in column 5.

Column 5: Annotations

- g Geologically exceptional specimens are known in which the element has an isotopic composition outside the reported range (refers to column 4).
- m Modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotope fractionation. Substantial deviations from the isotopic compositions given can occur (refers to column 9).
- r Range in isotopic composition proven to exist in normal terrestrial material limits the precision of the isotope abundances (refers to column 9).

Column 6: The best measurement from a single terrestrial source. The values are reproduced from the original literature. The uncertainties on the last digits are given in parenthesis as reported in the original publication. As they are not reported in any uniform manner in the literature, ls, 2s, 3s indicates l, 2, or 3 standard deviations, P indicates some other error as defined by the author, and "se" indicates standard error (standard deviation of the mean). Where data are published as isotope-abundance ratios, the ratios and their uncertainties are converted to mole fractions using orthodox procedures.

"C" is appended when calibrated mixtures have been used to correct the mass spectrometer for bias, giving an "absolute" result within the errors stated in the original publication.

"F" is appended when calibrated mixtures have been used to correct for isotope fractionation but the measurement fails to fulfill all of the requirements of a "C" measurement.

"L" is appended when the linearity of the mass spectrometer has been established for the relevant abundance ratios by using synthetic mixtures of isotopes or certified materials produced by an appropriate Standards laboratory.

"N" is appended when none of the above requirements are met.

The user is cautioned that:

a. Since the data are reproduced from the literature, the sum of the isotope abundances may not equal l exactly.
b. When a range of compositions has been established, the samples used for the best measurement may come from any part of the range.
c. An uncalibrated "best measurement" is not necessarily free of systematic errors.

Column 7: Reference for the best measurement given in Column 6.

Column 8: Reference materials with normal terrestrial isotopic compositions that are known to be available. An asterisk indicates the reference material used for the best measurement. When additional reference materials are available, the distributors are listed in lieu of specific reference materials (see Appendix).

Column 9: Representative isotopic composition. In this column are listed the values that, in the opinion of CAWIA, represent the isotopic composition of chemicals and/or natural materials that may be encountered in the laboratory. For most elements, these values will yield approximately the standard atomic weight, but may not necessarily correspond to the most abundant natural material. The uncertainties listed in parentheses cover the range of probable isotope-abundance variations among different materials as well as experimental errors, which are derived by applying statistical guidelines used by CAWIA for assigning uncertainties to published isotope-abundance measurements.

NOTE: This table has been adapted from the Table of the Isotopic Compositions of the Elements, 1997 [72] with additions from the compilation of Coplen et al. [85,180] and unpublished data prepared by CAWIA at the General Assembly in 2001.

Continuing significance of atomic weights and isotope abundances

During the second half of the 20th century, CAWIA witnessed the increasing importance of isotope-abundance measurements for the determination of atomic weights. Thus, mass-spectrometric methods have replaced older chemical methods for precise atomic-weight measurements, and it is difficult to foresee substantial use of the only known alternative, the X-ray-crystal-cell-density method. With the development of mass-spectrometric methods, it has become widely recognized that variations in the isotopic compositions of many elements can provide useful information about chemical behavior as well as the history and sources of different chemical substances. CAWIA has had and will continue to have an important role in this area of study. In recognition of this shift in focus, CAWIA was renamed by IUPAC in 2001 to become the Commission on Isotopic Abundances and Atomic Weights.

One of the primary future aims of the Commission will be to ensure that every polyisotopic element is represented by a homogeneous bulk reference material that can be divided into precisely similar samples, with a certified atomic weight having an estimated relative uncertainty of less than 1 in 10^5. Precise isotopic compositions and atomic weights for individual samples could be determined by differential mass spectrometry in comparison with those reference materials. Isotopic surveys of natural sources and knowledge of isotope fractionation by natural and artificial processes could provide more precise atomic-weight values for users in chemistry and commerce.

Another important development of the latter part of the 20th century was the proliferation of many types of mass spectrometers for a variety of uses. Inductively coupled plasma/mass spectrometry (ICP/MS), glow-discharge mass spectrometry, accelerator mass spectrometry, secondary-ion mass spectrometry (SIMS) and various types of laser-source mass spectrometers are available on a commercial basis. The continuous-flow gas-source mass spectrometer is a recent instrument, which is being applied with success in many scientific areas [84]. This trend toward diversity of instrumentation should continue into the future, especially by integrating mass spectrometers with other equipment, for instance, those in which ongoing rapid chemical reactions are studied for fractionation effects and equilibria between isotopes. Because of the widespread availability of these various types of instruments, it is increasingly important to provide guidelines for producing accurate isotope-abundance data that are based on a full understanding of the principles of mass spectrometry and mass-fractionation effects. Widely available reference materials will be essential for routine testing of sample preparation and calibration of mass spectrometry. In addition, future experimenters should expect periodic testing regimes for optimum mass-spectrometer performance.

In this review, we have described by examples how physicochemical mechanisms are responsible for variations in isotopic composition that can be explored using mass spectrometers. These observed variations are meaningful and reflect real processes in nature in addition to those arising from instrumental mass fractionation. Such physicochemical mechanisms in future will continue to be exploited much more widely in many fields of science to aid understanding of natural and industrial processes, including extraterrestrial phenomena. Measured isotopic anomalies in meteoritic material, using SIMS, have already been helpful to our understanding of astrophysical mechanisms and even the sites of nucleosynthesis [92]. We can expect element isotopic compositions to be used increasingly for diagnosis of substance histories in geology, cosmology, biology, archeology, and in materials derived from synthesis or those submitted to regulatory authority assessment of fraud, adulteration, or illegal brand-imitation. Precise isotopic signatures could be used widely in chemical process control, accompanied by immediate feedback before a rejectable product has been manufactured.

Isotope-abundance studies have thus played and will continue to play an essential role in the environmental arena. The study of Pb isotopes in ice cores is chosen from the past as just one successful example. It has confirmed that industrial processes and the use of leaded petrol have increased the amount of Pb in the atmosphere by a factor of at least 100 since preindustrial times, and that this atmospheric Pb can be traced over long distances. Because Pb additives to gasoline have a variety of isotopic compositions, owing to variations in the age and constitution of their U and Th parents in respective ore-bodies, details of the origin of Pb pollution can be successfully deciphered [181]. More reliable detail of man's use of lead in history is to be expected from future improved isotope-abundance measurements, on topics such as when lead was first melted or when the Romans started using lead lining in aqueducts.

The world must learn to live with the use and misuse of radioactivity and nuclear reactions. In the management of these opportunities and hazards we see a vital application for isotope analysis. For example, plutonium is a particularly hazardous component of nuclear bombs in which the isotopic composition of the Pu depends on the nature of the nuclear reactions. From measurements of the $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ ratio, Kersting et al. [182] have traced the movement of Pu in groundwater from the underground bomb site in Nevada. Similarly, at the Oklo natural reactor, the element and isotope abundances of a number of elements have been measured in the surrounding geological formations. These measurements indicate that some elements were relatively immobile and remained within the reactor zones, whereas others migrated to the surrounding geological materials and some escaped almost entirely [89]. Such studies of natural geological repositories will become of vital importance in understanding the effectiveness in containing radioactive waste products of the nuclear industry.

A very large number of environmental studies have made use of isotope-abundance measurements of the light elements, especially H, C, N, O, and S, which all exhibit rather pronounced isotope fractionation. Such measurements have been used extensively for tracing sources and movement of water, nutrients, and pollutants in the hydrosphere and biosphere of earth. Already, the published literature in isotopic-composition measurements in the environment is very extensive and will surely multiply in volume and importance.

"Fingerprinting" has been a function first of analytical chemistry, and later also of crystallography through phase identification. Now, isotope-abundance measurements have an analogous function and are likely to play an increasing role. Almost every molecule in every material, living or inanimate, has an isotopic fingerprint, a signature of its past. These isotopic signatures find important application in such areas as detection of fraud; for example, by using C isotope ratios to assess the origins of sugars, wines, and fruit juices or O isotope ratios to assess the origins of fruit juices [183]. As such cases will often be taken to court, isotope-abundance measurements on food and drink will need to be firmly "anchored" in "absolute" or SI-traceable values. IRMM has therefore started to anchor δ scales in such values, by certifying primary isotopic gas standards as an alternative to consensus procedures [59]. Voluntary isotopic standards generally will contribute powerfully to fair trade in the world.

CAWIA [17] has advised manufacturers to provide more detailed information about the atomic weights or isotopic compositions of laboratory chemicals made from elements that exhibit substantial variation. With increasing precision of analytical measurements, it may be expected that this advice will become more widely followed and, possibly in some instances, recognized in law.

De Bièvre et al. [37] have discussed the advantages of using IDMS in elemental concentration (content) measurements. It has already been used extensively in characterising elemental reference materials. Nature has provided more than 300 stable and long-lived isotopes so that IDMS can be an excellent metrological technique for accurate elemental concentration measurements. With the improved capabilities of automated mass spectrometers, and an anticipated wider availability of radioisotopes, their use in IDMS may become more widespread and, in some ways, more convenient than stable isotopes. Only radioisotopes are available for the IDMS assay of the monoisotopic elements, all of which, other than F, have radioisotopes of sufficient half-life. The measurement of minute amounts of Pb in the environment (e.g., ice cores), to demonstrate atmospheric pollution levels, using the radioisotope $^{205}\mathrm{Pb}$ as a tracer, is a good illustration of the established value of high-sensitivity IDMS [184]. Suitable facilities for handling radioactive materials will surely become widespread in chemical laboratories.

It is our hope that the atomic-weights community will remain well represented by the renamed Commission on Isotopic Abundances and Atomic Weights. The Commission should retain and disseminate a good understanding of the importance and use of the instrumentation necessary to produce precise and accurate isotopic-composition data and of isotopic reference materials for sample atomic-weight measurements and calibration of mass spectrometers. The Commission should maintain close contact with laboratories having experience in atomic-weight measurements and the production of credibly certified reference materials as this is a highly specialized and expensive task. Because atomic-weight and isotopic-composition measurements are now recognized as within "la haute métrologie", and amount-of-substance measurements are integrated into the SI, a strong liaison activity among the different groups involved in harmonization of symbols and notations, including IUPAC, will be highly desirable. An internationally agreed set of standard atomic weights will remain useful, even for BIPM, because the atomic weights constitute the link between the quantities mass and amount-of-substance. The Commission will have a continuing role also in summarizing source-specific isotopic-composition data such as given in the recent compilation of Coplen et al. [85], and preparing related materials for teaching in chemistry.

PART 2: ELEMENT-BY-ELEMENT REVIEW OF THE STANDARD ATOMIC WEIGHTS

Introduction

The aim of this part is to provide interested specialists and scholars with a condensed account of the assessment of individual atomic weights and their uncertainties, with emphasis on the developments during the past 40 years, as they have arisen almost exclusively from mass spectrometry. The review does not describe or analyze details of the experimental techniques, and does not raise issues of nomenclature.

A section for an element is included if it occurs naturally on earth with a characteristic isotopic composition, and if it has at least one stable or quasi-stable isotope. The entries are in order of atomic number. Each section begins with a heading comprising the chemical symbol, with its preceding subscript atomic number, and the chemical name or names in English texts. This is followed by the standard atomic-weight value $A_r(E)$, and its expanded uncertainty $U[A_r(E)]$. This uncertainty is numerically the same in the positive and negative directions and is expressed by a single digit in parentheses applicable to the last figure of the decimal in $A_r(E)$. Thus, for example, $A_r(Si) = 28.0855(3)$ indicates that the standard atomic weight of Si is between 28.0852 and 28.0858. This means that the Commission on Atomic Weights and Isotopic Abundances (CAWIA) is confident that the true atomic weight of Si in the great majority of normal samples of natural terrestrial materials and laboratory chemicals will fall within this range. The annotations "g", "m", and "r" may then be listed on the same line as the atomic-weight value depending on whether one or more of those annotations apply to that element. Definitions of these annotations are given in Part 1. The following entry (in square brackets) gives the date when the atomic weight and/or the annotations were last modified by CAWIA.

The tabulation next lists all the stable and quasi-stable isotopes of the element by chemical symbol with preceding mass number in subscript. The following column lists the atomic masses (in unified atomic mass units), with their uncertainties, from Audi and Wapstra [51]. The figures in parentheses represent the uncertainties in the last significant figure of the atomic mass value. The last column records the mole fractions of these isotopes in a representative normal occurrence as evaluated by CAWIA (Table 5, column 9). The representative isotopic compositions generally correspond approximately to the standard atomic weight and are recommended for evaluating average properties of materials of unspecified commercial or natural terrestrial origin. Thus, a given sample may not be represented exactly by the values given if the element exhibits natural variation in its isotopic composition. Figures in parentheses indicate the estimated uncertainties of the isotopic composition that are due to either measurement uncertainty (as evaluated by CAWIA) or documented variability, whichever is larger. For elements with no known variation, the given uncertainties are based on statistical evaluation of experimental errors.

The text for each element begins with a brief description of the origin of the name of each element and its discoverer, followed by a summary of the information and its literature sources as given in the former Element by Element Review [24]. Developments are then followed through the last 16 years of CAWIA analysis of significant literature publications. Relevant concepts and discussions in CAWIA's biennial reports are described. These sections emphasize the current status and mention any additional pertinent comparisons. The text for some elements ends with notes on radioactive properties of some isotopes and their possible effect on the atomic weights. It should be noted that reference materials are available for a number of polyisotopic elements. These reference materials may have been calibrated using synthetic mixtures of enriched isotopes and are provided by a number of internationally recognized agencies. Details of these reference materials are not given in Part 2, but are listed in column 8 of Table 5 in Part 1. Details of the sources of the reference materials are given in Appendix A.

$_1$H Hydrogen A_r(H) = 1.007 94(7) g, m, r [Since 1981]

Isotope	Atomic mass/u	Mole fraction
^{1}H	1.007 825 0319(6)	0.999 885(70)
^{2}H	2.014 101 7779(6)	0.000 115(70)

The name derives from the Greek *hydro* for "water" and *genes* for "forming" because it burned in air to form water. It was discovered by the English physicist Henry Cavendish in 1766.

The major stable isotope ^{1}H is also known as protium. The minor stable isotope ^{2}H is known as deuterium, with symbol D. The low concentration of ^{2}H in normal sources of H may have delayed its discovery until 1931 when H isotope fractionation was demonstrated by distillation, electrolysis, evaporation, and in environmental samples. The atomic weight of H has been based on mass-spectrometric measurements since 1938. In its report for 1961 [22], CAWIA recommended A_r(H) = 1.007 97(1) based on the average and the range of ^{2}H concentrations measured in H extracted from fresh- and saltwaters [185]; however, it was noted that substances other than water could have a wider range of atomic weights. In 1969, CAWIA [4] rounded the atomic-weight value and increased the uncertainty to A_r(H) = 1.0080(3), accounting for variations in the isotopic composition of a wider range of substances. In 1971, CAWIA [5] recommended A_r(H) = 1.0079(1) to reflect more accurately the atomic weights of the most abundant H sources, and yet to incorporate the major known variations. In 1981, CAWIA [10] altered the atomic weight and reduced the uncertainty again to include all but a very small fraction of the known variations and recommended A_r(H) = 1.007 94(7).

The currently accepted "best measurement" of the "absolute" isotopic composition of H from a single natural source was performed on VSMOW (distributed by the IAEA and NIST), the reference material endorsed by CAWIA as the basis of the delta (δ) scale for relative isotope-ratio measurements [16]. According to this measurement [116], VSMOW has a mole fraction of ^{2}H = 0.000 155 74(5), corresponding to $A_r(\mathrm{H_{VSMOW}})$ = 1.007 981 75(5). The uncertainty of that value corresponds to a δ^2H uncertainty of 0.3 ‰, which is equal to or slightly smaller than typical uncertainties of most relative isotope-ratio measurements of H. Variations in the isotopic composition of H in chemicals and natural terrestrial systems are known to exceed 1000 ‰, which is much larger than the uncertainty due to either relative or "absolute" isotope-ratio measurements. Therefore, the accuracy and precision of the standard atomic weight of H are limited almost entirely by real variations, hence the annotation "r".

For water sources, the range of published δ^2H values extends from –495 ‰ (mole fraction of ^{2}H = 0.000 0787; A_r(H) = 1.007 9042) [186], to +129 ‰ (mole fraction of ^{2}H = 0.000 1758; A_r(H) = 1.008 0020) [187]. Seawater, the largest reservoir of water near the earth's surface, has a relatively uniform isotopic composition and atomic weight near that of VSMOW; whereas precipitation, polar ice, lakes, rivers, and groundwaters have atomic weights that range widely, generally decreasing with latitude and elevation and increasing with evaporation. The highest δ^2H value reported for a material of natural terrestrial origin is +180 ‰ for atmospheric H_2 [188]. An unusual anthropogenic occurrence of water from a H_2S well yielded δ^2H values as high as +375 ‰ (mole fraction of ^{2}H = 0.000 0214; A_r(H) = 1.008 0404 [189]). Hydrogen samples with low atomic weights, some of which are outside the range of the standard atomic-weight uncertainties, have been reported from some types of natural and artificial H_2 gases, hence the annotation "g". The naturally occurring H sample with the lowest atomic weight (δ^2H = –836 ‰; mole fraction of ^{2}H = 0.000 0255; A_r(H) = 1.007 8507) is H_2 gas collected from a natural gas well in Kansas, USA [190]. That sample, and other similar ^{2}H-depleted H_2-rich natural gases elsewhere, may have formed by natural chemical reduction of water during low-temperature reactions with ultramafic (Fe-Mg-silicate) rocks. Hydrogen gases produced artificially by electrolysis and as by-products of petrochemical processing commonly are depleted in ^{2}H. Though not natural, those gases are considered to be important because they are used commonly in laboratories. Commercial tank H_2 has been reported to have δ^2H as low as –813 ‰ [mole fraction of ^{2}H = 0.000 0291; A_r(H) = 1.007 8543] [85].

The radioactive isotope ^{3}H, also known as tritium with symbol T, decays by negative beta emission to ^{3}He with a half-life of 12.3 years. Tritium is formed naturally in the atmosphere by cosmic-ray reactions such as ^{14}N (n,t) ^{12}C and artificially in nuclear reactors. Large quantities of ^{3}H were injected into the atmosphere as a by-product of thermonuclear bomb tests, mostly in the 1950s and 1960s. Tritium reacts in the atmosphere to form HTO and other compounds that are distributed with widely varying concentrations in the near-surface environment of the earth. Those variations, and other local anthropogenic ^{3}H anomalies, are used commonly in environmental studies; however, concentrations of ^{3}H in normal sources of H are too low by several orders of magnitude to have a measurable effect on the atomic weight of H.

$_2$He Helium A_r(He) = 4.002 602(2) g, r [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{3}He	3.016 029 3094(12)	0.000 001 34(3)
^{4}He	4.002 603 2497(15)	0.999 998 66(3)

The name derives from the Greek *helios* for "sun". The element was discovered by spectroscopy during a solar eclipse in the sun's chromosphere by the French astronomer Pierre-Jules-Cesar Janssen in 1868. It was independently discovered and named helium by the English astronomer Joseph Norman Lockyer. It was thought to be only a solar constituent until it was later found to be identical to the helium in the uranium ore cleveite by the Scottish chemist William Ramsay in 1895. Ramsay originally called his gas kypton, until it was identified as helium. The Swedish chemists Per Theodore Cleve and Nils Abraham Langet independently found helium in cleveite at about the same time.

In contrast to the other noble gases, which are separated for commercial use almost entirely from air, a large amount of commercial He is derived from natural gas deposits containing relatively high concentrations of radiogenic ^{4}He. In its 1961 report [22], CAWIA recommended A_r(He) = 4.0026 based on the atomic mass of ^{4}He to four decimal places from Everling et al. [23]. The ^{3}He mole fraction in air of 0.000 137 % as determined by Nier [191] had a negligible effect on this atomic weight. This isotope is present in natural sources of He with a smaller abundance than that of any other stable isotope relative to its elemental composition. After an evaluation of the natural variations in the isotopic composition of He, based chiefly on the paper by Mamyrin et al. [192], CAWIA in 1969 [4] recommended A_r(He) = 4.002 60(1), which was identical to the atomic mass of ^{4}He to six significant figures. A subsequent "absolute" determination of the isotopic composition of atmospheric He by Clarke et al. [193] yielded a $n(^3\mathrm{He})/n(^4\mathrm{He})$ ratio of 1.384×10^{-6}, corresponding to A_r(He) = 4.002 6019, confirming CAWIA's recommended value. As a result of this measurement, but also acknowledging evidence for significant variation in the atomic weight of He in materials other than the atmosphere, CAWIA in 1983 [11] recommended A_r(He) = 4.002 602(2). This was the first time the atomic weight of He differed from that of the ^{4}He isotope, but the uncertainty included both the atmospheric value and the value of pure ^{4}H because almost pure ^{4}He can be found in some natural gases and radioactive ores, hence, the annotation "r". The isotope-abundance data of Sano et al. [117] were accepted subsequently as the "best measurement" from a single source (air), but did not result in a change in the standard atomic weight of He. The indicated range for the standard atomic weight of He has a lower limit of 4.002 600, corresponding to a mole fraction of ^{3}He = 3.3 × 10^{-6}. That range includes some natural ^{3}He-enriched sources, but it does not include all He from volcanic rocks or associated geothermal springs and gases, some of which have ^{3}He mole fractions more than 10 times that of atmospheric He, hence the annotation "g." Those types of ^{3}He-enriched sources are considered to represent emissions of primordial He from incompletely degassed regions deep within the earth [194].

Helium, a "noble" gas, is chemically the most unreactive element with the lowest boiling point (4.2 K). Apart from its presence in gaseous or fluid inclusions and interstitial positions in crystals, and in voids in clathrate compounds, He occurs naturally only as a monoatomic gas. Helium is too light to be held in the atmosphere by earth's gravitation over periods comparable with the age of the earth; thus, ^{4}He in the atmosphere has been derived almost entirely from degassing of the solid earth, where it is produced by alpha decay of heavy radioisotopes. The minor isotope ^{3}He is believed to be largely primordial, with minor amounts derived from beta decay of ^{3}H, which is produced by the reaction ^{6}Li (n,α) ^{3}H in the earth, by cosmic-ray reactions in the atmosphere, or by nuclear explosions and industry. Accumulations of ^{3}He produced by radioactive decay of anthropogenic ^{3}H provide a useful tool for determining ages of groundwaters and surface waters, including the ocean. The physical properties of ^{3}He in gas, liquid, and solid phases and of ^{3}He/^{4}He mixtures have been the subjects of many experimental studies that have contributed decisively to our understanding of quantum physics and chemistry [195].

$_3$Li Lithium A_r(Li) = 6.941(2) g, m, r [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{6}Li	6.015 1223(5)	0.0759(4)
^{7}Li	7.016 0041(5)	0.9241(4)

The name derives from the Latin *lithos* for "stone" because lithium was thought to exist only in minerals at that time. It was discovered by the Swedish mineralogist Johan August Arfwedson in 1818 in the mineral petalite $LiAl(Si_2O_5)_2$. Li was isolated in 1855 by the German chemists Robert Wilhelm Bunsen and Augustus Matthiessen.

In its 1961 report [22], CAWIA altered A_r(Li) from 6.940 to 6.939 based on the adjustment of the chemical determinations by Richards and Willard [196] to the A_r(^{12}C) = 12 scale. CAWIA recognized evidence of natural variability of the isotopic composition of Li from mass spectrometry by Cameron [197]. In 1969, CAWIA [4] changed the basis to the "absolute" mass-spectrometric measurement by Svec and Anderson [198] and other mass-spectrometric data, and recommended A_r(Li) = 6.941(3). That value of A_r(Li) has remained unchanged, but is now based on other calibrated mass-spectrometric measurements of superior accuracy by Flesch et al. [199], Callis et al. [200], Michiels and De Bièvre [201], and Qi et al. [94,118], yielding with current atomic masses [51], A_r(Li) = 6.9391(2), 6.940 15(30), 6.940 69(24), and 6.940 05(24), respectively. Although Li occurs in diverse geological associations and although the relative mass difference of the isotopes is large, the variability in most terrestrial sources appears to be smaller than an implied range ±0.002 in the A_r(Li) value. Hence, CAWIA in 1983 felt justified in lowering $U[A_r(\text{Li})]$ to ±0.002, but the annotations "g" and "r" could not be deleted [11]. In the 1995 report of CAWIA [17], it was recommended that δ^7Li values be reported relative to the lithium carbonate reference material LSVEC. The lowest ^{7}Li content reported for a naturally occurring sample is from dissolved Li in groundwater from a coastal aquifer in South Carolina with δ^7Li = –19 ‰ [85]. For this sample, the mole fraction of ^{7}Li = 0.9227 and A_r(Li) = 6.9387. The highest ^{7}Li abundance reported in a naturally occurring sample is from Li in pore water from a marine sediment core with δ^7Li = +56.3 ‰ [202]. For this sample, the mole fraction of ^{7}Li = 0.9278 and A_r(Li) = 6.9438.

The minor isotope ^{6}Li is a potentially valuable nuclear source material for tritium production, an important component in hydrogen bombs, and a neutron absorber for the nuclear-fusion reaction.

Lithium depleted in ^{6}Li may be distributed in commerce, with mole fractions of ^{6}Li as low as 0.02 and atomic weights in excess of 6.99 [93,94]. This is the justification for the "m" annotation. In 1993, CAWIA expressed concern about the availability on the commercial market of such depleted materials and decided to put the atomic-weight value and uncertainty between square brackets and to add a dagger symbol to warn that, if a more accurate value is required, it must be determined on a sample of the material concerned [16].

$_4$Be Beryllium A_r(Be) = 9.012 182(3) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{9}Be	9.012 1822(4)	1.0000

The name derives from the Greek word *beryllos* for "beryl" ($3BeO{\cdot}Al_2O_3{\cdot}6SiO_2$), a gemstone in which it is found. It was discovered by the French chemist and pharmacist Nicholas-Louis Vauquelin in beryl and emerald in 1797. The element was first separated in 1828 by the French chemist Antoine-Alexandre-Brutus Bussy and independently by the German chemist Friedrich Wöhler. Because the salts of beryllium have a sweet taste, the element was also known as glucinium from the Greek *glykys* for "sweet", until IUPAC selected the name beryllium in 1949.

In its 1961 report [22], CAWIA proposed A_r(Be) = 9.0122 based on atomic mass data from Everling et al. [23]. In 1969, CAWIA [4] reassessed the data and added one more significant figure: A_r(Be) = 9.012 18(1). In the 1985 CAWIA report [12], the atomic weight and uncertainty of Be were revised to their current values in light of the atomic mass data of Wapstra and Audi [50]. A search by mass spectrometry for other stable isotopes of Be failed to detect any [119].

^{10}Be is a cosmic-ray spallation product from N, O, Ne, and Ar and decays with a half-life of $1.6(2) \times 10^6$ a. ^{10}Be is pervasive on the earth's surface in equilibrium mole fractions of less than 10^{-11}, which is too small to affect the atomic weight of Be in normal materials. Beryllium is the only monoisotopic element with an even atomic number, but it has an odd mass number like all other monoisotopic elements.

$_5$B Boron A_r(B) = 10.811(7) g, m, r [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{10}B	10.012 9371(3)	0.199(7)
^{11}B	11.009 3055(4)	0.801(7)

The name derives from the Arabic *buraq* for "white". Although its compounds were known for thousands of years, it was not isolated until 1808 by the French chemists Louis-Joseph Gay-Lussac and Louis-Jacques Thenard.

In its 1961 report [22], CAWIA recommended A_r(B) = 10.811(3) based on calibrated mass-spectrometric measurements on brines and minerals from Searles Lake by McMullen et al. [87] and on atomic masses from Everling et al. [23]. The uncertainty was based on variations in natural abundances reported by McMullen et al. [87] and Thode et al. [86]. In 1969, CAWIA [4] reduced the number of significant figures based on new calibrated data showing wider variability of natural abundances of B isotopes by Finley et al. [203] and Schwarcz et al. [204]. New isotope-abundance data of high accuracy further confirmed earlier results [120,205].

In 1981, CAWIA [10] concluded that the range of isotope-abundance variations typical of the most common sources is covered by A_r(B) = 10.811(2). This value includes major commercial sources of B in California and Turkey [206]. However, the existence of normal terrestrial occurrences with sample atomic weights outside these implied limits could not be denied. Under the 1983 policy of a more liberal use of any single-digit uncertainty, CAWIA changed the recommended standard atomic weight to A_r(B) = 10.811(5) to which the annotation "r" clearly applies [11]. In 1985, the "g" annotation was added to reflect the occurrence of materials with anomalous isotopic compositions [12]. Compared with most other standard atomic weights, the tabulated value for B until 1995 was relatively uncertain with $U[A_r(\mathrm{B})]/A_r(\mathrm{B}) = 463 \times 10^{-6}$. That uncertainty increased to 648×10^{-6} in 1995 when CAWIA decided to increase $U[A_r(\mathrm{B})]$ from 0.005 to 0.007 [17] to include the isotopic composition of B in seawater [207]. Natural variations in $n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$ are reported as δ^{11}B values relative to the reference material NIST SRM 951, which has $n(^{11}\mathrm{B})/n(^{10}\mathrm{B}) = 4.0436$ [205]. Reported δ^{11}B values compiled by Coplen et al. [85] range from a low of –34.2 ‰ [mole fraction of ^{11}B = 0.7961; A_r(B) = 10.8062] in a metamorphic mineral sample from Antarctica [208] to a high of +59.2 ‰ [mole fraction of ^{11}B = 0.8107; A_r(B) = 10.8207] in brine from a volcanic crater lake in southeastern Australia [209]. Separated and enriched isotopes of B are commercially available; the atomic weights of such samples can differ from one another by up to almost 10 %. Although CAWIA is unaware of undisclosed commercial sales of such material, an "m" annotation warns users of the possibility of its inadvertent dissemination.

$_6$C Carbon A_r(C) = 12.0107(8) g, r [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{12}C	12 (exactly, by definition)	0.9893(8)
^{13}C	13.003 354 838(5)	0.0107(8)

The name derives from the Latin *carbo* for "charcoal". It was known in prehistoric times in the form of charcoal and soot. In 1797, the English chemist Smithson Tennant proved that diamond is pure carbon.

The ^{12}C isotope has served since 1960 as the scale-determining reference for the definition of the unified atomic mass unit and is the basis of all atomic weights. The zero value for the delta scale used in relative isotope-ratio measurements of C since the 1950s was based on a sample of fossil marine carbonate (Belemnitella Americana, Peedee Formation, Cretaceous Period, South Carolina, also known as PDB). Until 1990, the "best measurement" from a single natural source was attributed to Craig [210] for an evaluation of a measurement by Nier [65] on CO_2 from a Solenhofen limestone sample. For the "absolute" $n(^{13}\mathrm{C})/n(^{12}\mathrm{C})$ ratio in the PDB standard, Craig adopted a value of 0.011 2372(300), corresponding to a ^{13}C mole fraction of 0.01111(3) and an A_r(C) value of 12.011 15(3).

In its 1961 report [22], CAWIA recommended A_r(C) = 12.011 15(5), based on the atomic masses of Everling et al. [23] and the range of natural isotopic variations reported by Craig [211], hence the annotation "r". In its 1969 report [4], CAWIA recommended A_r(C) = 12.011(1). The larger uncertainty was assigned to include all terrestrial sources of C whose isotopic compositions had been measured to that time. After the supply of PDB was exhausted, a modified delta scale was recommended for relative C isotope-ratio measurements (referred to as the Vienna PDB, or VPDB scale) that yields the same zero value as the PDB scale when based on measurements of a new carbonate reference material known as NBS 19 [212]. Chang and Li [121] reported calibrated measurements of the isotopic composition of C in NBS 19, providing an "absolute" basis for the VPDB delta scale, such that a material with a δ^{13}C value of 0 ‰ has $n(^{12}\mathrm{C})/n(^{13}\mathrm{C}) = 89.449$ [mole fraction of ^{13}C = 0.011056; A_r(C) = 12.01109]. Chang and Li's data were adopted subsequently by CAWIA as the "best measurement" of the atomic weight of C from a single source. In 1995, CAWIA recommended A_r(C) = 12.0107(8) as a result of a reevaluation of variations in normal terrestrial materials [17].

Variations in the $n(^{13}\mathrm{C})/n(^{12}\mathrm{C})$ ratio of terrestrial sources of C are caused largely by biogeochemical reactions and physical processes. Some of the largest effects are associated with oxidation-reduction reactions including photosynthesis, such that organic substances and reduced natural gases typically are depleted in ^{13}C relative to carbonate materials and the atmosphere. Differences in the degree of ^{13}C depletion during photosynthesis are characteristic of some groups of plants and may be passed along to plant consumers, such that C isotope studies can be used to identify features of animal diets and paleoclimates. Variations in the relative rates of organic C production, burial, and oxidation through geologic time are recorded in the isotopic compositions of sedimentary rocks. The highest reported δ^{13}C value in the compilation by Coplen et al. [85] [+37.5 ‰; mole fraction of ^{13}C = 0.011 466; A_r(C) = 12.011 50] is from dissolved carbonate in reduced marine sediment pore water [213]. The lowest δ^{13}C value in that compilation [–130.3 ‰; mole fraction of ^{13}C = 0.009 629; A_r(C) = 12.009 66] is from crocetane recovered from the ocean bottom at cold seeps in the northern Pacific Ocean [214]. The annotation "g" indicates that some of the reported analyses are outside the range of the standard atomic-weight uncertainty.

The radioactive ^{14}C isotope has a half-life of 5730 a. It is introduced continuously to the near-surface environment of the earth by cosmic-ray reactions, from cosmic dust, and by nuclear technology. It is of great interest for prehistoric dating as well as archaeological, anthropological, paleotemperature, and zoological studies. Yet, this isotope never occurs in normal C sources in concentrations high enough to affect significantly the A_r(C) value. Before nuclear weapons tests, the abundance of ^{14}C in the atmosphere had an average concentration of only about 10^{-16}. It should be noted that a half-life of 5568 a (the so-called "Libby half-life"), has been adopted by convention for calculations in geochronology [215].

$_7$N **Nitrogen** A_r(N) = 14.0067(2) g, r [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{14}N	14.003 074 0074(18)	0.996 36(20)
^{15}N	15.000 108 973(12)	0.003 64(20)

The name derives from the Latin *nitrum* and Greek *nitron* for "native soda" and *genes* for "forming". It was discovered by the Scottish physician and chemist Daniel Rutherford in 1772.

The primary reference material for the relative abundance measurements of N isotopes is atmospheric N_2 [216], which is homogeneous with respect to analytical uncertainties [217] and is assigned a δ^{15}N value of 0 ‰. Junk and Svec [122] reported calibrated measurements of the "absolute" isotope ratio of N_2 in air with an average $n(^{14}\mathrm{N})/n(^{15}\mathrm{N})$ ratio of 272.0(3). In 1961, CAWIA [22] adopted the calibrated measurements of Junk and Svec [122] as the "best measurement" and recommended A_r(N) = 14.0067. In 1969, CAWIA [4] assigned $U[A_r(\mathrm{N})]$ = 0.0001 in recognition of the predominance of one isotope, ^{14}N. In 1985, CAWIA [12] recommended A_r(N) = 14.006 74 and $U[A_r(\mathrm{N})]$ = 0.000 07 to reflect a change in the procedures for reporting uncertainties. CAWIA subsequently recommended adoption of 272 exactly for the $n(^{14}\mathrm{N})/n(^{15}\mathrm{N})$ ratio corresponding to a δ^{15}N value of 0 ‰ [218]. De Bièvre et al. [219] reported uncalibrated measurements corrected for mass spectrometer inlet fractionation effects that yield a $n(^{14}\mathrm{N})/n(^{15}\mathrm{N})$ ratio for atmospheric N_2 of 271.87(11), in agreement with the earlier measurement [122]. In 1999 [19], CAWIA increased the uncertainty and removed a significant figure from the atomic weight of N after reviewing reported isotope-abundance variations in the literature [85].

Relative isotope-ratio measurements of N commonly have uncertainties of the order of 0.1 ‰, which is significantly smaller than the reported uncertainty of the "absolute" calibrated "best measurement" (±1.1 ‰). Variations in the isotopic composition of N in chemical reagents and natural terrestrial systems are known to exceed 200 ‰, which is much larger than the uncertainty due to either relative or "absolute" isotope-ratio measurements. Therefore, the accuracy and precision of the standard atomic weight of N are limited almost entirely by real variations, hence the annotation "r".

Measurable variations in the isotope abundances (and atomic weights) of N are found in most N compounds. The vast majority of N chemical reagents, manufactured N fertilizers, and environmental samples have δ^{15}N values between about –15 and +20 ‰ [mole fraction of ^{15}N = 0.003 61 to 0.003 74; A_r(N) = 14.006 67 to 14.006 80]. Isotope fractionations are caused by physical, chemical, and biological processes. Some of the largest common effects in the natural environment are caused by microbially mediated oxidation and reduction reactions and by ammonia or nitric acid evaporation. The most ^{15}N-enriched N occurrences reported in nature include dissolved nitrate that had undergone partial microbial reduction (denitrification) in groundwater [e.g., δ^{15}N = +103 ‰; mole fraction of ^{15}N = 0.004 039;

A_r(N) = 14.007 10] [85], and nitrate in Antarctic ice that may have been fractionated by evaporation of HNO_3 [δ^{15}N = 150 ‰; mole fraction of ^{15}N = 0.004 210; A_r(N) = 14.007 27] [220]. The most ^{15}N-depleted substances from natural terrestrial environments include epibenthic algae from a saline pond in the Dry Valleys region of Antarctica [δ^{15}N = –49 ‰; mole fraction of ^{15}N = 0.003 484; A_r(N) = 14.006 55] [221] and nitrous oxide from groundwater undergoing microbial denitrification [δ^{15}N = –55 ‰; mole fraction of ^{15}N = 0.003 462; A_r(N) = 14.006 53] [85]. Still lower values have been reported for NO_x escaping from a nitric acid production facility [δ^{15}N = –150 ‰; mole fraction of ^{15}N = 0.003 115; A_r(N) = 14.006 18] [222], and for a commercially available potassium nitrite reagent [δ^{15}N = –80 ‰; mole fraction of ^{15}N = 0.003 371; A_r(N) = 14.006 43] [85]. The annotation "g" reflects the fact that a number of samples are known to have atomic weights outside the uncertainties of the standard atomic weight of N. Many thousands of isotopic analyses of N have been made since the 1950s; nevertheless, more occurrences of extreme values may be expected as work expands in the fields of contaminant hydrology, biology, and atmospheric chemistry. In addition, the common use of artificially enriched substances in agricultural and environmental research has resulted in substantial numbers of samples with N atomic weights approaching the atomic masses of the ^{15}N and ^{14}N isotopes.

$_8$O **Oxygen** **A_r(O) = 15.9994(3) g, r** **[Since 1969]**

Isotope	Atomic mass/u	Mole fraction
^{16}O	15.994 914 6223(25)	0.997 57(16)
^{17}O	16.999 131 50(22)	0.000 38(1)
^{18}O	17.999 1604(9)	0.002 05(14)

The name derives from the Greek *oxys* for "acid" and *genes* for "forming" because the French chemist Antoine-Laurent Lavoisier originally thought that oxygen was an acid producer because burning phosphorous and sulfur and dissolving them in water produced acids. Oxygen was discovered independently by the Swedish pharmacist and chemist Carl-Wilhelm Scheele in 1771, and the English clergyman and chemist Joseph Priestly in 1774. Scheele's *Chemical Treatise on Air and Fire* was delayed in publication until 1777, so Priestly is credited with the discovery because he published first.

In its 1961 report [22], CAWIA adopted A_r(O) = 15.9994(1) based on the mass-spectrometric measurements of Nier [65] on atmospheric O_2 and the atomic masses of Everling et al. [23], though it was recognized that the uncertainty did not cover the range of known natural variations. In its 1969 report [4], CAWIA increased $U[A_r(O)]$ to 0.0003 to include the range of normal terrestrial sources of O. The value has remained unchanged since then.

Two major sources of O are air and water. The best "absolute" measurement of the complete isotopic composition of O in atmospheric O_2 is that of Nier [65], which yielded values of 0.997 587, 0.000 374, and 0.002 039 for the mole fractions of ^{16}O, ^{17}O, and ^{18}O, respectively. Those values correspond to A_r(O) = 15.999 376 when calculated with current atomic masses [50]. Dole et al. [223] and Kroopnick and Craig [224] detected no variation in the isotopic composition of atmospheric O_2, but found that ^{18}O could be measurably enriched by low-temperature fractional distillation used to separate O_2 from N_2. The best measurement of the partial isotopic composition of O in water, according to CAWIA, is given by Baertschi [123], who obtained a value of 0.002 005 20(45) for $n(^{18}\text{O})/n(^{16}\text{O})$ in the VSMOW reference material. For several years, the isotopic composition of VSMOW was obtained by combining Baertschi's [123] $n(^{18}\text{O})/n(^{16}\text{O})$ ratio with a value of 0.000 372(4) for $n(^{17}\text{O})/n(^{16}\text{O})$, which was derived from Nier's earlier data [65] by assuming that the relative fractionation of the isotopes is governed by the relative mass differences, such that $[n(^{17}\text{O})/n(^{16}\text{O})]_s/[n(^{17}\text{O})/n(^{16}\text{O})]_{RM} = \{[n(^{18}\text{O})/n(^{16}\text{O})]_s/[n(^{18}\text{O})/n(^{16}\text{O})]_{RM}\}^{0.5}$ [210], where s and RM refer to the sample and reference material, respectively. More recently, Baertschi's [123] $n(^{18}\text{O})/n(^{16}\text{O})$ ratio has been combined with a new value of 0.000 3799(8) for $n(^{17}\text{O})/n(^{16}\text{O})$, recommended by Li et al. [124] on the basis of new measurements, to obtain the “best measurement” of the total isotopic composition of O in a water sample (VSMOW).

Relative isotope-ratio measurements of O in water and many other substances commonly are expressed relative to VSMOW, in which case the δ^{18}O value of VSMOW is 0 ‰ by definition. However, two other scales have been used commonly: (1) in studies of atmospheric gases and related topics, atmospheric O_2 may be assigned a δ^{18}O value of 0 ‰; (2) in studies of marine carbonate deposits and related topics, a specimen of marine carbonate (PDB, Peedee belemnite) may be assigned a δ^{18}O value of 0 ‰. The carbonate scale has been retained since the supply of PDB was exhausted by assigning a value of –2.2 ‰ for the δ^{18}O value of NBS 19 carbonate, yielding the VPDB (Vienna PDB) δ^{18}O scale [212].

Relating atomic weights to relative isotope-ratio measurements may be complicated in principle by the observation that the exponent in the mass-dependent fractionation equation may deviate significantly from one half, and by the fact that relative isotope-ratio measurements generally do not include ^{17}O. Nevertheless, though the value of the exponent may be as high as 0.52 [225] or 0.53 [226] in common substances, the atomic-weight errors caused by these differences are small compared to the uncertainty of the “absolute” measurement of atomic weight. Larger deviations from mass-dependent fractionation of ^{18}O, ^{17}O, and ^{16}O have been observed in minor atmospheric gases such as O_3, CO_2, N_2O, and CO, apparently as a result of non-mass-dependent photochemical reactions [88]. Similar features have been observed in sulfate and nitrate in atmospheric deposition and some types of soils [227,228], and it is likely that the number and variety of samples reported to exhibit non-mass-dependent O isotope fractionation will increase rapidly in the future.

Variations in the atomic weight of O in surface water on the earth commonly are correlated with those of H, as the isotopes of both elements are fractionated by evaporation and condensation [229]. Whereas ocean water has almost constant values of H and O atomic weight worldwide (near that of VSMOW), precipitation varies widely with the lowest values being at high latitudes. Natural variations in the isotopic composition of O have been exploited since the 1950s in studies of the hydrological cycle, biogeochemistry, and paleoclimates. The highest natural terrestrial δ^{18}O value in the compilation of Coplen et al. [85] [+109 ‰; mole fraction of ^{18}O = 0.002 218; A_r(O) = 15.999 76] is from marine N_2O [230]. The lowest natural δ^{18}O value in the compilation [–63 ‰; mole fraction of ^{18}O = 0.001 875; A_r(O) = 15.999 04] is from Antarctic precipitation [231]. Given the relatively small uncertainties in the best “absolute” measurements (±0.25 ‰) and in typical relative measurements (±0.1 ‰ or less), it is evident that the uncertainty of the standard atomic weight of O (corresponding to ±70 ‰) is dominated by real natural variations, hence the annotation “r”. The annotation “g” is given because some natural terrestrial materials have atomic weights that are outside the range of the standard atomic weight uncertainty, at both the high and low ends. For example, a commercial tank CO gas was reported to have δ^{18}O = –229 ‰ [mole fraction of ^{18}O = 0.001543; A_r(O) = 15.998 34] [85].

$_9$F Fluorine A_r(F) = 18.998 4032(5) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{19}F	18.998 403 20(7)	1.0000

The name derives from the Latin *fluere* for “flow” or “flux” because fluorite (CaF_2) was used as a flux in metallurgy owing to its low melting point. It was discovered in hydrofluoric acid by the Swedish pharmacist and chemist Carl-Wilhelm Scheele in 1771, but it was not isolated until 1886 by the French pharmacist and chemist Ferdinand-Frederic-Henri Moisson.

The CAWIA report in 1961 [22] proposed A_r(F) = 18.9984 based on atomic mass data by Everling et al. [23]. The revision of these data by Wapstra and Gove [48] led to a refinement of A_r(F) to 18.998 40 in the CAWIA report of 1971 [5] and to 18.998 403 in 1975 [7]. The atomic weight and uncertainty of F were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51]. Radioisotopes of F are not suitable for IDMS because of their short half-lives.

$_{10}$Ne Neon A_r(Ne) = 20.1797(6) g, m [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{20}Ne	19.992 440 176(3)	0.9048(3)
^{21}Ne	20.993 846 74(4)	0.0027(1)
^{22}Ne	21.991 385 50(25)	0.0925(3)

The name derives from the Greek *neos* for "new". It was discovered from its bright orange spectral lines by the Scottish chemist William Ramsay and the English chemist Morris William Travers in 1898 from a liquefied air sample.

In its 1961 report [22], CAWIA recommended A_r(Ne) = 20.183 based on gas-density measurements by Baxter and Starkweather [232] and Baxter [233], recalculated to the $A_r(^{12}C) = 12$ scale. At that time, the only reported measurements by mass spectrometry were uncalibrated and were not considered to be reliable enough to serve as the basis for the atomic weight. In 1967, CAWIA evaluated the results of two new calibrated measurements [3]. Measurements by Eberhardt et al. [234] and by Walton and Cameron [235] were in excellent agreement, and CAWIA recommended A_r(Ne) = 20.179(3). Both groups compared their calibrated samples with various commercial sources of Ne and reported that no variations were found. The assignment of $U[A_r(\text{Ne})] = 0.003$ was caused by the concern of CAWIA that because almost all commercial Ne was liquefied for purification from air, laboratory samples might be enriched in the heavy isotope relative to natural atmospheric Ne. After a review of the published data in 1979, CAWIA reduced its assessment of this potential fractionation effect and recommended $U[A_r(\text{Ne})] = 0.001$ [9]. In 1985, CAWIA [12] reduced $U[A_r(\text{Ne})]$ further and recommended A_r(Ne) = 20.1797(6) by combining the earlier results with new calibrated measurements reported by Bottomley et al. [126]. The atomic weight and its uncertainty refer to atmospheric Ne. The annotation "g" refers to occurrences of Ne with diverse and anomalous isotopic compositions in some minerals and natural gases, derived in part from earth's mantle and from various nuclear reactions such as ^{18}O (α,n) ^{21}Ne and ^{25}Mg (n,α) ^{22}Ne [236–238].

$_{11}$Na Sodium (Natrium) A_r(Na) = 22.989 770(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{23}Na	22.989 769 66(26)	1.0000

The name derives from the English soda and Latin *sodanum* for "headache remedy". The chemical symbol Na derives from the Latin *natrium* for "natron" (soda in English). It was discovered in 1807 by the English chemist Humphry Davy from electrolysis of caustic soda (NaOH).

The 1961 CAWIA report [22] proposed the atomic weight for Na to be A_r(Na) = 22.9898 based on atomic mass data by Everling et al. [23], and also quoted experimental evidence from the literature concerning upper limits for the hypothetical presence of ^{21}Na and ^{22}Na, which were determined as 10^{-8} and 3×10^{-8}, respectively [127]. These stable isotopes—if they exist at all—cannot cause a change in the eighth significant figure in A_r(Na).

The revision of the atomic mass data by Wapstra and Gove [48] led to a refinement of A_r(Na) to 22.989 77(1) in the 1971 CAWIA report [5]. The atomic weight and uncertainty of Na were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{12}$Mg Magnesium A_r(Mg) = 24.3050(6) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{24}Mg	23.985 041 87(26)	0.7899(4)
^{25}Mg	24.985 837 00(26)	0.1000(1)
^{26}Mg	25.982 593 00(26)	0.1101(3)

The name derives from Magnesia, a district in the northeastern region of Greece called Thessalia. The Scottish chemist Joseph Black recognized it as a separate element in 1755. In 1808, the English chemist Humphry Davy obtained the impure metal, and in 1831 the French pharmacist and chemist Antoine-Alexandre Brutus Bussy isolated the metal in the pure state.

In the 1961 CAWIA report [22], the atomic weight of Mg was based on the isotopic composition reported by White and Cameron [128] and the atomic masses from the 1960 compilation of Everling et al. [23]. In its 1967 report [3], CAWIA adopted A_r(Mg) = 24.305 based on the "absolute" isotopic measurements of Catanzaro et al. [239] and the mineral survey of Catanzaro and Murphy [240], who reported no detectable variations in 60 samples of natural Mg from various geological sources. In 1969, CAWIA assigned the uncertainty $U[A_r(\mathrm{Mg})] = 0.001$ to this value [4]. The value and uncertainty were slightly modified by CAWIA in 1985 to 24.3050(6), to be consistent with its own Technical Guidelines [12].

The annotation "g" was added to Mg by CAWIA in its 1971 report [5], based on a published abstract report of a partial mineral survey by Lepin et al. [241] who documented considerable natural variability in sources from the former Soviet Union. Since there were no comparable findings in other publications on Mg such as that by Catanzaro and Murphy [240], CAWIA concluded that the specimens studied by Lepin et al. [241] must have been very exceptional, thereby justifying the annotation "g" in preference to reducing the precision of the tabulated value. A later credible study by Schramm et al. [242] found no anomalies in atomic-weight values greater than experimental error. Although cosmochemical-induced anomalies in ^{26}Mg can be produced, they will not affect the atomic weight of Mg of natural terrestrial origin. CAWIA, therefore, decided to make a study of the actual data obtained by Lepin et al. [241]. As a result, CAWIA concluded that experimental uncertainties and not atomic weight variability probably caused a considerable range of values to be reported, and therefore removed the annotation "g" from the Mg standard atomic weight. Recently, precise measurements by ICPMS have indicated variations of $n(^{26}\mathrm{Mg})/n(^{24}\mathrm{Mg})$ that can be reported as δ^{26}Mg values relative to the SRM-980 reference material [85]. Chang et al. [243] report a range of δ^{26}Mg values from a low of –1.95 ‰ (mole fraction of ^{26}Mg = 0.1099; A_r(Mg) = 24.3046) in marine calcareous shell material (foraminifera) to a high of +2.55 ± 0.12 ‰ (mole fraction of ^{26}Mg = 0.1103; A_r(Mg) = 24.3055) in seawater.

$_{13}$Al Aluminium (Aluminum) A_r(Al) = 26.981 538(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{27}Al	26.981 538 41 (24)	1.0000

The name derives from the Latin, *alum* and *alumen* for "stringent" because the early Romans called any substance with a stringent taste alum. The element was known in prehistoric times. In 1825, the Danish physicist, Hans Christian Oersted, isolated impure aluminum. The pure metal was first isolated by the German chemist Friedrich Wöhler in 1827.

The CAWIA report in 1961 [22] proposed the atomic weight of Al to be A_r(Al) = 26.9815, based on atomic mass data by Everling et al. [23], and experimental evidence from the literature concerning upper limits for the hypothetical presence of ^{25}Al, ^{26}Al, ^{28}Al, ^{29}Al, and ^{30}Al [127]. This evidence shows that these isotopes could at most affect A_r(Al) by one digit in the seventh significant figure. The revision of the atomic mass data by Wapstra and Gove [48] led to a refinement of A_r(Al) to 26.981 54(1) in the 1971 CAWIA report [5]. The atomic weight and uncertainty of Al were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

^{26}Al is radioactive with a half-life of 7.05(24) × 10^5 a, too short for survival of a detectable amount of primordial isotope. However, ^{26}Al is recognized as a spallation product of Ar from cosmic rays. In addition, secondary cosmic rays including muons interact with Si-bearing rocks to produce ^{26}Al in measurable amounts, but far below levels that would affect the atomic-weight value in normal materials [244]. ^{27}Al is the most abundant isotope in the earth's crustal rocks with an uneven atomic number.

$_{14}$Si Silicon A_r(Si) = 28.0855(3) r [Since 1975]

Isotope	Atomic mass/u	Mole fraction
^{28}Si	27.976 926 49(22)	0.922 23(19)
^{29}Si	28.976 494 68(22)	0.046 85(8)
^{30}Si	29.973 770 18(22)	0.030 92(11)

The name derives from the Latin *silex* and *silicis* for "flint". Amorphous silicon was discovered by the Swedish chemist Jöns Jacob Berzelius in 1824. Crystalline silicon was first prepared by the French chemist Henri Sainte-Claire Deville in 1854.

In its 1961 report [22], CAWIA recommended A_r(Si) = 28.086(1) based on the average value of seven reported mass-spectrometric determinations, with atomic masses by Everling et al. [23]. In 1969, CAWIA [4] noted that the range of these seven values was greater than ±0.001 and recommended A_r(Si) = 28.086(3). In 1975, CAWIA [7] recommended the current value, A_r(Si) = 28.0855(3), based on superior "absolute" mass-spectrometric measurements by Barnes et al. [245] and atomic masses by Wapstra and Gove [48]. CAWIA at that time already had judged some of the reported variability of the isotopic composition of Si to be excessive. This is borne out by an investigation by Douthitt [246] who studied Si in terrestrial materials and comprehensively reviewed the literature. He found that the variability in igneous rocks is much smaller than the range indicated above, but it is real and is related to O isotope fractionation. The Si isotope fractionation in some clays, marine sediments and opals is larger, but still within the range implied by the $U[A_r(\mathrm{Si})]$ value of 0.0003. Therefore, in 1983 [11] CAWIA added the annotation "r" because a more precisely stated standard atomic weight with a single-digit uncertainty would conflict with the actual sample atomic weights of possible sources of Si. In 1991 and 1994, CAWIA noted that, while new values with considerably smaller uncertainties (uncertainty 0.000 12 on an atomic-weight value of 28.085 65) had been determined on Si isotopic reference materials [247,248], the range in isotopic composition of normal terrestrial materials prevent a more precise standard atomic weight being given. δ^{30}Si measurements are expressed relative to NBS 28 SiO_2 as distributed by IAEA and NIST. The lowest δ^{30}Si value found in the literature (–3.7 ‰) is from biogenic sponge spicules [246]. For this sample, the mole fraction of ^{30}Si = 0.030 816 and A_r(Si) = 28.085 22. The highest δ^{30}Si found in the literature (+3.4 ‰) is from silicified algal matter [249] in sediments. For this sample, the mole fraction of ^{30}Si = 0.031 023 and A_r(Si) = 28.085 78.

In recent history, A_r(Si) determinations have been directly related to attempts to quantify as accurately as possible the relationship between atomic scale and macroscopic physical quantities as represented by determinations of Avogadro's constant [70,71,105,106,250,251]. In the course of this work, it was clearly demonstrated that careful crystallization of Si is accompanied by isotope fractionation. Detailed atomic-scale theories of the growing crystal–liquid interface are being developed such as are needed to predict the isotopic composition changes as a function of the parameters controlling crystallization. The preparation of synthetic mixtures of Si isotopes in order to "calibrate" measurements of the Si atomic weight is described in [252].

Radioactive ^{32}Si is a cosmogenic isotope, and it is potentially available from the nuclear industry in sufficient quantities to make it of value in IDMS measurements, given its relatively long half-life.

$_{15}$P **Phosphorus** $A_r(P) = 30.973\ 761(2)$ [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{31}P	30.973 761 49(27)	1.0000

The name derives from the Greek *phosphoros* for "bringing light" because it has the property of glowing in the dark. This was also the ancient name for the planet Venus, when it appears before sunrise. Phosphorus was discovered by the German merchant Hennig Brand in 1669.

The CAWIA report in 1961 [22] recommended the atomic weight $A_r(P) = 30.9738$, based on atomic mass data from Everling et al. [23], and quoted experimental evidence from the literature concerning upper limits for the hypothetical presence of ^{28}P, ^{29}P, ^{30}P, ^{32}P, ^{33}P, and ^{34}P. This evidence, however, does not rule out an effect on $A_r(P)$ in the seventh significant figure. The revision of the atomic mass data by Wapstra and Gove [48] led to a refinement of $A_r(P)$ to 30.973 76(1) in the 1971 CAWIA report [5]. The atomic weight and uncertainty of P were changed to their current values in the 1995 report of CAWIA [17] based on the atomic mass data of Audi and Wapstra [51]. ^{32}P and ^{33}P are cosmogenic and also can be produced by the nuclear industry, but their concentrations in normal materials are too small to affect $A_r(P)$. They have differing half-lives and offer the potential for self-calibration of IDMS measurements.

$_{16}$S **Sulfur** $A_r(S) = 32.065(5)$ g, r [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{32}S	31.972 070 73(15)	0.9499(26)
^{33}S	32.971 458 54(15)	0.0075(2)
^{34}S	33.967 866 87(14)	0.0425(24)
^{36}S	35.967 080 88(25)	0.0001(1)

The name derives from the Latin *sulphurium* and the Sanskrit *sulveri*. Sulfur was known as brenne stone for "combustible stone" from which brim-stone is derived. It was known from prehistoric times and thought to contain hydrogen and oxygen. In 1809, the French chemists Louis-Joseph Gay-Lussac and Louis-Jacques Thenard proved the elemental nature of sulfur.

In its 1961 report [22], CAWIA recommended $A_r(S) = 32.064(3)$ based on the abundances of S isotopes in virgin Texas sulfur reported by Bradt et al. [253] and in meteoritic S reported by MacNamara and Thode [254], with atomic masses from Everling et al. [23]. CAWIA observed that this value was in good agreement with the results of chemical determinations and that the uncertainty was assigned largely on the basis of natural variability, as documented by Rankama [255] and Duckworth [256]. In 1969, CAWIA [4] recommended a change in the value of $A_r(S)$ from 32.064(3) to 32.06(1). The reduction in the number of significant figures was motivated by the reported range of natural variability and by new guidelines for the assignment of uncertainties to the standard atomic weights. A reevaluation of the literature in 1983 led CAWIA to recommend [11] $A_r(S) = 32.066(6)$, which included essentially all reported values at that time. Then, as a result of new "absolute" measurements of the isotopic compositions of several reference materials [59,257], CAWIA in 1999 [19] recommended $A_r(S) = 32.065(5)$. More recent publications confirmed this decision [129,258]. The annotation "g" was added in 1993 [16] and remains currently to account for minor occurrences of S with $A_r(S)$ outside the range covered by the atomic-weight uncertainty [85].

For many years, the "best measurement" of the "absolute" isotope abundances of S according to CAWIA was a calibrated mass-spectrometric measurement by MacNamara and Thode [254] on meteoritic sulfide, with an uncertainty of around ±1 ‰. Relative isotope-ratio measurements of S generally involve only the isotopes ^{34}S and ^{32}S. The δ scale until recently was based on a value of 0 ‰ for Canyon Diablo troilite (CDT), a meteoritic sulfide sample, for which the ratio $n(^{32}S)/n(^{34}S)$ measured by gas source mass spectrometry was assumed to be 22.22 [259], despite the fact that this was not the same as the ratio derived from the calibrated measurement [254]. Recently, a substitute δ scale for relative isotope-ratio measurements (referred to as the Vienna CDT, or VCDT scale) was devised to yield the same zero value as the CDT scale when based on measurements of a new sulfide reference material known as IAEA-S-1, which was assigned a δ^{34}S value of –0.3 ‰ [260,261]. This was done in part because of documented heterogeneity of the original CDT material [262]. Ding et al. [257] reported calibrated measurements of the isotopic composition of S in IAEA-S-1 with an uncertainty of ±0.3 ‰, providing an "absolute" basis for the VCDT δ scale, such that a material with a δ^{34}S value of 0 ‰ has $n(^{32}\mathrm{S})/n(^{34}\mathrm{S}) = 22.6436$. Relative isotope-ratio measurements are commonly made with uncertainties of ±0.2 ‰ or less. Because of natural variations, the uncertainty in the standard atomic weight corresponds to a range of about ±60 ‰, which is more than two orders of magnitude larger than the analytical uncertainties, hence the annotation "r".

Isotopes of S are fractionated by various chemical, physical, and biological processes. The major variations in the atomic weight of S on earth are caused by kinetic isotope fractionations accompanying microbial oxidation-reduction reactions such as bacterial reduction of aqueous sulfate, in which the residual unreacted substrate is gradually depleted in the lighter isotopes, which react more rapidly. Over geologic time, processes such as these have resulted in major reservoirs of terrestrial S with different atomic weights: oxidized forms such as marine sulfate commonly being heavy in comparison with the bulk earth and the majority of reduced forms such as organic S and sulfide. Primordial S held in the deep earth and released in some volcanic emissions has a δ^{34}S value close to 0 ‰ [$A_\mathrm{r}(\mathrm{S}) = 32.0639$]. Seawater sulfate currently has a uniform δ^{34}S value of +21.1 ‰; [$A_\mathrm{r}(\mathrm{S}) = 32.0657$], though it has been different in the geological past. The highest value of the atomic weight of S found in the literature [263] is from sulfate in reduced-sediment pore water undergoing sulfate reduction that had $\delta^{34}\mathrm{S} = +135$ ‰ [mole fraction of $^{34}\mathrm{S} = 0.0473$; $A_\mathrm{r}(\mathrm{S}) = 32.075$]. The lowest value of the atomic weight of S found in the literature [85] is from sulfide in an ice-covered sewage treatment lagoon that had $\delta^{34}\mathrm{S} = -55$ ‰ [mole fraction of $^{34}\mathrm{S} = 0.0398$; $A_\mathrm{r}(\mathrm{S}) = 32.059$].

The radioactive isotope ^{35}S is produced by cosmic-ray interactions with ^{40}Ar in the atmosphere and decays to ^{35}Cl with a half-life of 87 days. ^{35}S is useful as an environmental tracer in hydrologic studies, both at natural and artificially enriched levels, but its abundance is several orders of magnitude too small to affect $A_\mathrm{r}(\mathrm{S})$.

$_{17}$Cl **Chlorine** $A_\mathrm{r}(\mathrm{Cl}) = 35.453(2)$ g, m, r [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{35}Cl	34.968 852 71(4)	0.7576(10)
^{37}Cl	36.965 902 60(5)	0.2424(10)

The name derives from the Greek *chloros* for "pale green or greenish yellow color" of the element. It was discovered by the Swedish pharmacist and chemist Carl-Wilhelm Scheele in 1774. In 1810, the English chemist Humphry Davy proved it was an element.

In its 1961 report [22], CAWIA recommended $A_\mathrm{r}(\mathrm{Cl}) = 35.453(1)$, based on the atomic weight of Ag and on Ag-silver chloride weight ratios determined chemically by many well-known authorities. CAWIA also observed that this value was in excellent agreement with the value determined by calibrated mass spectrometry $A_\mathrm{r}(\mathrm{Cl}) = 35.4527(7)$, reported by Shields et al. [130], who reported no evidence for natural variability. In an extensive discussion of the atomic weights of Ag, Br, and Cl in its 1967 report [3], CAWIA retained the 1961 atomic-weight value, but stated that it was based on the physical measurement by Shields et al. [130] combined with the atomic mass data from Mattauch et al. [264]. Following its 1967 discussion of Ag, Cl, and Br, which were important in the chemical determination of atomic weights of several other elements, CAWIA did not assign any new atomic-weight values defined purely on the basis of chemical measurements. In 1985, CAWIA altered the atomic weight of Cl to 35.4527(9) to conform to the Technical Guidelines on atomic-weight uncertainties [12]. Since

1985, relative isotope-ratio mass spectrometry has yielded abundant evidence for variability in the atomic weight of Cl in both natural and artificial substances [85], which resulted in the 1999 decision of CAWIA to increase the uncertainty and remove a significant figure from the atomic weight of Cl, and to add the annotation "r" [19].

The "best measurement" of the isotopic composition of Cl from a single source was performed on a reference material (NIST SRM 975) that is no longer available. A replacement material (NIST SRM 975a) is in preparation. The best measurement [130] yielded a mole fraction of ^{37}Cl = 0.242 29(45), corresponding to A_r(Cl) = 35.4527(9). The basis of the delta scale for relative Cl isotope-ratio measurements currently is standard mean ocean chloride (SMOC), with δ^{37}Cl = 0 ‰, despite reported evidence for variability in $n(^{37}\text{Cl})/n(^{35}\text{Cl})$ of seawater chloride [85]. SMOC is reported to have a δ^{37}Cl value 0.52 ‰ less than that of NIST SRM 975 [265], implying that SMOC has a mole fraction of ^{37}Cl = 0.242 19 and A_r(Cl) = 35.4525, within the uncertainty of the best "absolute" measurement on SRM 975. Other measurements indicate that SMOC has a δ^{37}Cl value 0.43 ‰ less than that of NIST SRM 975 [266], also within the uncertainty of the best "absolute" measurement.

Chlorine isotopes in the chloride ion may be fractionated in nature and the laboratory by diffusion, ion filtration, and halide mineral precipitation. The lighter isotope ^{35}Cl diffuses more rapidly in aqueous solutions, whereas the concentration of the heavier isotope ^{37}Cl is higher in halide minerals than in coexisting solutions. Chlorine isotopes also have been fractionated photochemically in the laboratory [267]. Environmental chloride samples are reported to have δ^{37}Cl values ranging from about –7.7 ‰ [268] to +7.5 ‰ [269], corresponding to mole fractions of ^{37}Cl = 0.2408 to 0.2436 and A_r(Cl) = 35.450 to 35.455 [85]. Chlorinated organic solvents from different commercial sources commonly have different Cl isotopic compositions. The Cl isotopes of those compounds may also be fractionated by biochemical degradation reactions. Chlorinated solvents are reported to have δ^{37}Cl values ranging from at least –6.0 ‰ to +4.4 ‰ [85], corresponding to mole fractions of ^{37}Cl = 0.2411 to 0.2430 and A_r(Cl) = 35.450 to 35.454. The range of Cl atomic weights in nature and in laboratory reagents is larger than the range indicated by the standard atomic-weight uncertainty value, hence the annotation "g". Larger ranges of variation may be found as measurements are made on a wider range of environments and of Cl-bearing species.

The radioactive isotope ^{36}Cl decays to ^{36}Ar with a half-life of 301(2) × 10^3 a. It is produced both naturally and artificially by slow-neutron reactions with ^{35}Cl. Large quantities of ^{36}Cl were injected into the atmosphere as a by-product of nuclear bomb tests in the oceans. Both natural cosmogenic ^{36}Cl and bomb-produced ^{36}Cl from the atmosphere have been useful as environmental tracers in hydrologic studies [270]; however, the concentrations normally encountered are too low by several orders of magnitude to have a measurable effect on the atomic weight of Cl.

$_{18}$Ar Argon A_r(Ar) = 39.948(1) g, r [Since 1979]

Isotope	Atomic mass/u	Mole fraction
^{36}Ar	35.967 546 26(27)	0.003 365(30)
^{38}Ar	37.962 7322(5)	0.000 632(5)
^{40}Ar	39.962 383 124(5)	0.996 003(30)

The name derives from the Greek *argos* for "lazy" or "inactive" because it does not combine with other elements. It was discovered in 1894 by the Scottish chemist William Ramsay and the English physicist Robert John Strutt (Lord Rayleigh) in liquefied air. Rayleigh's initial interest derived from a problem posed by the English physicist Henry Cavendish in 1785, i.e., when oxygen and nitrogen were removed from air, there was an unknown residual gas remaining.

The atomic weight of Ar is based on analyses of Ar separated from air. In 1961, CAWIA [22] changed the recommended value of A_r(Ar) from 39.944, based on gas-density measurements, to 39.948, based on the calibrated mass-spectrometric measurements reported by Nier [65], which have been accepted since then as the "best measurement" from a single source. In 1969, CAWIA [4] recommended A_r(Ar) = 39.948(3) after a general evaluation of uncertainties. However, at its meeting in 1979, CAWIA examined the available literature and recommended a smaller uncertainty, so that A_r(Ar) = 39.948(1) [9]. This value of A_r(Ar) was one of the critical parameters used by Moldover et al. [98] to determine the value of the universal gas constant *R* by acoustic methods.

Argon isotope abundances commonly are reported as ratios with respect to ^{36}Ar, for example, $n(^{40}\text{Ar})/n(^{36}\text{Ar})$. The calibrated "absolute" isotope-ratio measurement of Nier [65] corresponds to a $n(^{40}\text{Ar})/n(^{36}\text{Ar})$ ratio of 296.0, with uncertainty of ±0.5 in the ratio or ±1.8 ‰ in δ^{40}Ar. Relative isotope-ratio measurements of Ar commonly have uncertainties of similar magnitude, whereas, the isotopic composition of Ar in gases from common sources is known to vary from the atmospheric ratio to almost pure ^{40}Ar [237]. The atomic weight uncertainty assigned to Ar by CAWIA in 1979 is an order of magnitude larger than the uncertainty of the "absolute" isotope-abundance measurement owing to natural variability, hence the annotation "r" [9].

Radiogenic ^{40}Ar is produced (along with ^{40}Ca) by decay of a minor isotope of K (^{40}K), which has a total half-life of $1.26(1) \times 10^9$ a. This radioactivity results in many geological samples having anomalous amounts of ^{40}Ar and is the basis of the K-Ar and Ar-Ar dating methods used in geochronology. It should be noted that a value of 295.5 for the atmospheric $n(^{40}\text{Ar})/n(^{36}\text{Ar})$ ratio has been adopted by convention for calculations in geochronology [271]; this value was derived from the isotope abundances given by Nier [65], but it is not equal to the ratio given by Nier in the same paper. Samples containing only minor components of noble gases from nonradiogenic sources may have A_r(Ar) values approaching the atomic mass of ^{40}Ar. Owing to the wide distribution of K, even major sources of Ar such as some natural gas deposits and geothermal reservoirs can have sufficiently high ^{40}Ar concentrations to be outside the atomic weight uncertainty, hence the annotation "g". In contrast, it is much less common for natural samples to have $n(^{40}\text{Ar})/n(^{36}\text{Ar})$ ratios significantly less than that of air. Radiogenic ^{36}Ar can accumulate by decay of ^{36}Cl (half-life = $3.01(2) \times 10^5$ a), which in turn is produced from ^{35}Cl by neutron capture associated with cosmic-ray interactions in the atmosphere and with U and Th decay in the solid earth. Similarly, ^{38}Ar may accumulate as a result of reactions such as ^{37}Cl (n,γ) ^{38}Cl or ^{35}Cl (α,p) ^{38}Cl. Some samples of Ar extracted from microscopic Cl-bearing inclusions in minerals have been reported to have anomalously high concentrations of ^{36}Ar and ^{38}Ar that may be attributable to nucleogenesis [272].

Radioactive ^{37}Ar and ^{39}Ar are formed continuously in the atmosphere as products of cosmic-ray reactions, and they are components of cosmic dust entering the earth's atmosphere. Both isotopes also are formed by nuclear reactions on and beneath the earth's surface. At the present time, most of the new ^{39}Ar introduced to the atmosphere each year is from nuclear reactors. ^{39}Ar decays to ^{39}K with a half-life of 269 a; while ^{37}Ar decays to ^{37}Cl with a half-life of 35 days. The amounts of ^{37}Ar and ^{39}Ar in normal samples are variable and may be useful in environmental studies, but they are several orders of magnitude too small to affect the standard atomic weight of Ar at its current level of reported uncertainty.

$_{19}$K Potassium (Kalium) A_r(K) = 39.0983(1) [Since 1979]

Isotope	Atomic mass/u	Mole fraction
^{39}K	38.963 7069(3)	0.932 581(44)
^{40}K	39.963 998 67(29)	0.000 117(1)
^{41}K	40.961 825 97(28)	0.067 302(44)

The name derives from the English "potash" or "pot ashes" because it is found in caustic potash (KOH). The chemical symbol K derives from the Latin kalium via the Arabic qali for alkali. It was first isolated by the British chemist Humphry Davy in 1807 from electrolysis of potash (KOH).

The value of A_r(K) = 39.102 for the atomic weight of K was adopted by CAWIA in its 1961 report [22], based on the mass-spectrometric measurements of Nier [65] and atomic masses by Everling et al. [23]. This value was near the upper range of the best chemical determinations. In the 1969 report [4], CAWIA assigned an uncertainty $U[A_r(\mathrm{K})] = 0.003$ to this value. A new analysis by Marinenko [273] of older chemical data by Bates and Wichers [274] led CAWIA in 1971 [5] to assign more credence to the chemical evidence for a lower value, and A_r(K) = 39.098(3) was recommended based on the mean value of chemical and mass-spectrometric determinations. In the 1975 report [7], CAWIA recommended A_r(K) = 39.0983(3), based on the "absolute" mass-spectrometric measurements of Garner et al. [131], who also reported the results of a mineralogical study of possible isotopic variations. The uncertainty was reduced to $U[A_r(\mathrm{K})] = 0.0001$ in the 1979 CAWIA report [9], based on an evaluation of possible variations of the isotope abundances and the effects of small errors in the abundance measurements. CAWIA added the annotation "g" in 1991 [15] because the results of Hinton et al. [275] indicated values outside the atomic-weight uncertainty. The annotation "g" was removed in 1995 [17] after the work of Humayun and Clayton [276] did not support the results of Hinton et al.

The minor isotope, ^{40}K, is radioactive with a total half-life of $1.26(1) \times 10^9$ a [277], and decays to both ^{40}Ar and ^{40}Ca. As a result of decay, A_r(K) will decrease by approximately 1.5×10^{-4} % in one half-life. The K/Ar and K/Ca decay systems are used extensively in geochronology [77].

$_{20}$Ca Calcium A_r(Ca) = 40.078(4) g [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{40}Ca	39.962 5912(3)	0.969 41(156)
^{42}Ca	41.958 6183(4)	0.006 47(23)
^{43}Ca	42.958 7668(5)	0.001 35(10)
^{44}Ca	43.955 4811(9)	0.020 86(110)
^{46}Ca	45.953 6927(25)	0.000 04(3)
^{48}Ca	47.952 533(4)	0.001 87(21)

The name derives from the Latin *calx* for "lime (CaO)" or "limestone ($CaCO_3$)" in which it was found. It was first isolated by British chemist Humphry Davy in 1808 with help from the Swedish chemist Jöns Jacob Berzelius and the Swedish court physician M. M. af Pontin.

In its 1961 report [22], CAWIA recommended A_r(Ca) = 40.08(1), based on the chemical measurements of Hönigschmid and Kempter [278] and isotope-abundance measurements by Nier [279]. A recalculation of the chemical ratio using current values of the atomic weights of the other elements involved [11] gives the following results from the listed comparisons:

$CaCl_2$/2Ag	0.514 451	A_r(Ca) = 40.080	
$CaCl_2$/AgCl	0.387 200	A_r(Ca) = 40.082	[278]

The best mass-spectrometric measurements, as chosen by CAWIA, are those by Moore and Machlan [132], yielding A_r(Ca) = 40.078. Because these measurements were not calibrated for bias, some weight is still given to the chemical determinations. Further evidence is provided by the X-ray density method [280] which, on recalculation with the current atomic weights of the other elements involved, yields A_r(Ca) = 40.079(2). In 1983, CAWIA [11] with its liberalized policy on uncertainties, was able to recommend as standard atomic weight A_r(Ca) = 40.078(4) weighted toward the mass-spectrometric measurement [132]. It would take a large error even to come close to the limit of the indicated uncertainty since Ca has a predominant isotope. Moreover, the stated uncertainty includes all chemical, X-ray, and mass-spectrometric measurements believed to be significant by CAWIA, as enumerated in its 1983 report [11].

There is evidence for minor isotope fractionation of Ca in Nature [281], causing variability of A_r(Ca) in normal sources that is within the uncertainty of the standard atomic weight. Variations in

$n(^{44}Ca)/n(^{40}Ca)$ can be reported as $\delta^{44}Ca$ values relative to the calcium carbonate reference material NIST-SRM 915a [85]. A recent compilation [85] yielded a range of published $\delta^{44}Ca$ values in natural samples from a low of –2.17 ‰ in a cougar bone [mole fraction of ^{44}Ca = 0.02082; $A_r(Ca)$ = 40.0778] [282] to a high of +2.76 ‰ in egg white [mole fraction of ^{44}Ca = 0.02092; $A_r(Ca)$ = 40.0784] [282]. Elemental Ca with $\delta^{44}Ca$ = –6.0 ‰ [mole fraction of ^{44}Ca = 0.02074; $A_r(Ca)$ = 40.0773] also has been reported [281]. De La Roche and DePaolo [283] have shown that variations in the isotopic composition of marine Ca have occurred over the last 80 Ma. In addition, there are many reports of anomalous isotopic composition of some minor samples of Ca, some of which may have arisen from the decay of ^{40}K to ^{40}Ca. The annotation "g" is therefore maintained for this element. ^{41}Ca is an extinct radioisotope (with a half-life of 0.1 Ma), which can be used to date the early history of the solar system through its decay to ^{41}K.

$_{21}$Sc Scandium $A_r(Sc)$ = 44.955 910(8) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{45}Sc	44.955 9102(12)	1.0000

The name derives from the Latin *scandia* for Scandinavia, where the mineral was found. It was discovered by the Swedish chemist Lars-Fredrik Nilson in 1879 in an ytterbium sample. In the same year, the Swedish chemist Per Theodore Cleve proved that scandium was Mendeleev's hypothetical element "eka-boron".

CAWIA in 1961 [22] recommended the atomic weight $A_r(Sc)$ = 44.956, although the atomic mass of its only stable isotope was known with superior precision. At that time, CAWIA considered the possibility of the discovery of other naturally occurring, long-lived, or stable isotopes or isomers of Sc, and cited an experimental limit of 0.00002 for the mole fraction of ^{46}Sc [127], which could affect the atomic weight by up to 2 in the seventh significant figure. In 1969, CAWIA [4] considered the sixth significant figure to be established and recommended $A_r(Sc)$ = 44.9559(1) because, on the basis of theory and experience, the likelihood of the existence of a significant long-lived undiscovered isotope of Sc was remote.

In the atomic mass table published by Wapstra and Gove in 1971 [48], the mass of ^{45}Sc is given as 44.955 9174(22). This uncertainty was calculated from a least-squares adjustment and is largely a measure of the consistency of mass values for isotopes with similar mass and atomic numbers. For conversion of atomic masses to atomic weights of monoisotopic elements, CAWIA's procedure was to round the values to fewer digits so that the uncertainty in the atomic mass value multiplied by six was equal to or less than one in the last digit of the atomic-weight value. By this rule, no change in the atomic-weight value was needed. When the atomic mass table was revised in 1977 by Wapstra and Bos [49], ^{45}Sc was given a mass of 44.955 9136(15), which by the above rule should yield $A_r(Sc)$ = 44.955 91(1). CAWIA, however, did not act at that time because of its hesitation to recommend rounding-off changes in the atomic weights of the monoisotopic elements, which are tabulated to higher precision than is required for the great majority of applications in chemistry.

In a review of that decision in 1983, it was pointed out that in the case of Sc the additional digit represented reliable accuracy. The mass of ^{45}Sc was closely tied to that of Ti [284], which itself is closely tied to ^{12}C, the isotope that defines the atomic-weight scale. Under these circumstances, CAWIA felt justified in refining the standard atomic weight of Sc to $A_r(Sc)$ = 44.955 91(1) in its 1983 report [11]. The atomic weight and uncertainty of Sc were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{22}$Ti **Titanium** A_r(Ti) = 47.867(1) [Since 1993]

Isotope	Atomic mass/u	Mole fraction
^{46}Ti	45.952 6295(12)	0.0825(3)
^{47}Ti	46.951 7637(10)	0.0744(2)
^{48}Ti	47.947 9470(10)	0.7372(3)
^{49}Ti	48.947 8707(10)	0.0541(2)
^{50}Ti	49.944 7920(11)	0.0518(2)

The name derives from the Latin *titans*, who were the mythological "first sons of the earth". It was originally discovered by the English clergyman William Gregor in the mineral ilmenite ($FeTiO_3$) in 1791. He called this iron titanite menachanite and the element menachin, for the Menachan parish where it was found. It was rediscovered in 1795 by the German chemist Martin Heinrich Klaproth, who called it titanium because it had no characteristic properties to use as a name. Titanium metal was first isolated by the Swedish chemists Sven Otto Pettersson and Lars Fredrik Nilson.

In its 1961 report [22], CAWIA recalculated the chemical ratios of Baxter and Butler [285,286] upon which A_r(Ti) had been based since 1927. It recommended A_r(Ti) = 47.90 be retained. In 1969, CAWIA [4] gave the same value with an uncertainty of 0.03 based on the chemical work [285,286] coupled with consideration of the isotope-abundance measurements by Nier [279], Hibbs [287], Mattraw and Pachucki [288], Hogg [289], Darwin [290], and Belsheim [291], which yielded values of A_r(Ti) ranging from 47.87 to 47.89. Hogg [289] and Belsheim [291] searched for but discovered no terrestrial variability in A_r(Ti).

Recalculation of the chemical ratios [285,286] based on current values of the other atomic weights involved [51] yields the following results for the listed comparisons:

$TiCl_4/4Ag = 0.439\,680$	A_r(Ti) = 47.878 [285,286]
$TiBr_4/4Ag = 0.851\,788$	A_r(Ti) = 47.907 [285,286]

In 1979, CAWIA [9] reexamined the chemical and mass-spectrometric determinations and recommended A_r(Ti) = 47.88(3), which includes consideration of all the above values but is weighted toward the calibrated mass-spectrometric measurements of Belsheim [291]. Recalculated with the more recent atomic masses by Wapstra and Bos [49], they yield A_r(Ti) = 47.87(1). Since then, two papers have been published by Heydegger et al. [292] and Niederer et al. [293], reporting isotope-abundance measurements for Ti. Although neither is a calibrated measurement, they are both of high precision. When these are normalized to the $n(^{46}\text{Ti})/n(^{48}\text{Ti})$ ratio of Belsheim [291], the new values confirm the work of Belsheim. However, if Belsheim's ratios are in error, it would be carried as a systematic error to the more recent work. For that reason, CAWIA has retained the high uncertainty of $U[A_r(\text{Ti})] = 0.03$, and continues to be especially concerned in its search for new evidence that might lead to an improvement of A_r(Ti) or $U[A_r(\text{Ti})]$. Titanium is an abundant, widely distributed element, yet it was the element with the most uncertain atomic weight with $U[A_r(\text{Ti})]/A_r(\text{Ti}) = 626 \times 10^{-6}$. This situation changed in 1993 [16] when CAWIA acknowledged the work of Shima and Torigoye [134] by accepting their "calibrated" measurement value of 47.867(1). Titanium has undergone (since 1979), the largest relative change in standard atomic-weight value recommended by CAWIA during the past 25 years.

$_{23}$V **Vanadium** A_r(V) = 50.9415(1) [Since 1977]

Isotope	Atomic mass/u	Mole fraction
^{50}V	49.947 1627(14)	0.002 50(4)
^{51}V	50.943 9635(14)	0.997 50(4)

The name derives from the Scandinavian goddess of love and beauty, Freyja Vanadis, because of its many beautiful multicolored compounds. It was discovered by the Swedish physician and chemist Nils-

Gabriel Sefström in 1830. It had originally been discovered by the Spanish mineralogist Andres Manuel del Rio y Fernandez in 1801, who named it erythronium, after the plant of that name whose flowers have many beautiful colors. Del Rio later decided that it was really chromium in his lead sample. Vanadium metal was first isolated by the English chemist Henry Enfield Roscoe in 1869.

In its 1961 report [22], CAWIA accepted $A_r(\mathrm{V}) = 50.942$ based on mass-spectrometric data by Hess and Inghram [294], Leland [295], and White et al. [127]. CAWIA recommended a more precise $A_r(\mathrm{V}) = 50.9414(3)$ in 1969 because it is an element with a predominant isotope [4]. A number of determinations of the isotopic composition of V, for instance [296] and [297], have since been considered. As a result, CAWIA in the 1977 report [8], refined $A_r(\mathrm{V})$ to 50.9415(1). Balsiger et al. [296] have also shown that the isotopic composition of five chondritic meteorites were identical within experimental error to the terrestrial diabase W-1 and a laboratory standard.

Two stable isobars, $^{50}\mathrm{Ti}$ and $^{50}\mathrm{Cr}$, are the immediate neighbors in the chart of nuclides, to $^{50}\mathrm{V}$, whose β^+ and β^- decay modes are, therefore, predictable. The nuclear angular momentum of $^{50}\mathrm{V}$, however, is high but consistent with long half-lives, evidently too long to be readily observed. The isobars render the mass-spectrometric determination of the abundance of the isotope $^{50}\mathrm{V}$ subject to careful chemical determination of the trace presence of Ti and Cr.

$_{24}$Cr Chromium $A_r(\mathrm{Cr}) = 51.9961(6)$ [Since 1983]

Isotope	Atomic mass/u	Mole fraction
$^{50}\mathrm{Cr}$	49.946 0495(14)	0.043 45(13)
$^{52}\mathrm{Cr}$	51.940 5115(15)	0.837 89(18)
$^{53}\mathrm{Cr}$	52.940 6534(15)	0.095 01(17)
$^{54}\mathrm{Cr}$	53.938 8846(15)	0.023 65(7)

The name derives from the Greek *chroma* for “color”, from the many colored compounds of chromium. It was discovered in 1797 by the French chemist and pharmacist Nicolas-Louis Vauquelin, who also isolated chromium in 1798.

In its 1961 report [22], CAWIA recommended $A_r(\mathrm{Cr}) = 51.996(1)$ calculated from the isotopic composition reported by Flesch et al. [298] with atomic masses from Everling et al. [23]. The mass-spectrometric measurements were corrected for mass bias by calibration with known mixtures of separated N isotopes. In 1966, Shields et al. [136] redetermined the isotopic composition of Cr calibrating the mass spectrometers with carefully prepared gravimetric standards mixed from separated isotopes of Cr, of very high chemical and isotopic purity. The atomic weight calculated from this work using atomic masses from Mattauch et al. [264] was $A_r(\mathrm{Cr}) = 51.9961(3)$. In its 1967 report [3], CAWIA recommended “retaining the atomic weight of 51.996 but stating it without limit of error”. However, in 1969, CAWIA [4] added uncertainties to all atomic weights and recommended a value of 51.996(1) for Cr. With its liberalized policy on single-digit uncertainties, CAWIA recommended the standard atomic weight to four decimal places in 1983, $A_r(\mathrm{Cr}) = 51.9961(6)$ [11]. Measurements of $n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$ can be expressed as $\delta^{53}\mathrm{Cr}$ values with respect to NIST SRM 979 [85,136]. Ellis et al. [299] report isotope fractionation of Cr during chromate reduction, resulting in $\delta^{53}\mathrm{Cr}$ values in groundwater samples as high as +5.8 ‰ [mole fraction of $^{53}\mathrm{Cr} = 0.09553$; $A_r(\mathrm{Cr}) = 51.9982$], which is outside the current range of uncertainty of the standard atomic weight.

$_{25}$Mn Manganese A_r(Mn) = 54.938 049(9) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{55}Mn	54.938 0493(15)	1.0000

The name derives from the Latin *magnes* for "magnet" since pyrolusite (MnO_2) has magnetic properties. It was discovered by the Swedish pharmacist and chemist Carl-Wilhelm Scheele in 1774. In 1774, the Swedish chemist Johan Gottlieb Gahn first isolated the metal.

The 1961 CAWIA report [22] proposed the atomic weight of Mn to be A_r(Mn) = 54.9380 based on atomic mass data by Everling et al. [23]. Leipziger [119] has confirmed experimentally that at the upper limits for the hypothetical presence of stable or quasi-stable Mn isotopes, the atomic weight of Mn would be affected at most by one unit in the seventh significant figure. The atomic weight and uncertainty of Mn were changed to their current values in the 1995 report of CAWIA [17] based on the atomic mass data of Audi and Wapstra [51].

^{53}Mn is radioactive with a half-life of $3.7(2) \times 10^6$ a, too short for survival of a detectable amount of primordial isotope. However, ^{53}Mn has been identified on earth as a cosmic-ray product and as a constituent of cosmic dust by Imamura et al. [300], who measured about one disintegration per min. per gram of Mn in sediment cores corresponding to a concentration of 3×10^{-13}, much too small to affect the standard atomic weight.

$_{26}$Fe Iron (Ferrum) A_r(Fe) = 55.845(2) [Since 1993]

Isotope	Atomic mass/u	Mole fraction
^{54}Fe	53.939 6147(14)	0.058 45(35)
^{56}Fe	55.934 9418(15)	0.917 54(36)
^{57}Fe	56.935 3983(15)	0.021 19(10)
^{58}Fe	57.933 2801(15)	0.002 82(4)

The name derives from the Anglo-Saxon *iron* of unknown origin. The element has been known from prehistoric times. The chemical symbol Fe is derived from the Latin *ferrum* for "firmness." It is of interest to note that ^{56}Fe has a larger mass defect than any other nuclide. It is, therefore, the ultimate end-product of stellar nuclear fusion.

In its 1961 report [22], CAWIA recommended A_r(Fe) = 55.847(3) based on the average value of two reported mass-spectrometric determinations by Valley and Anderson [301,302], and White and Cameron [128], and on atomic masses by Everling et al. [23]. In 1993, CAWIA [16] changed the recommended value for the standard atomic weight to A_r(Fe) = 55.845(2) based on calibrated measurements carried out on a metallic Fe sample of high purity by Taylor et al. [137,303]. Several recent studies have indicated natural isotope fractionation in Fe-containing materials [304–306]. The magnitude of the uncertainty assigned to the atomic-weight value [16] was based mainly on the variations of Fe isotopic composition reported by Dixon et al. [304]; however, subsequent studies have indicated somewhat different ranges. According to the compilation of Coplen et al. [85], reported δ^{56}Fe values range from –2.9 ‰ [mole fraction of ^{56}Fe = 0.91742; A_r(Fe) = 55.8448] in human blood [307] to +1.36 ‰ [mole fraction of ^{56}Fe = 0.91760; A_r(Fe) = 55.8453] in part of a banded iron formation [308]; where δ^{56}Fe refers to $n(^{56}\text{Fe})/n(^{54}\text{Fe})$ relative to the reference material IRMM-014 [85,137].

$_{27}$Co **Cobalt** $A_r(\text{Co}) = 58.933\ 200(9)$ **[Since 1995]**

Isotope	Atomic mass/u	Mole fraction
^{59}Co	58.933 1999(15)	1.0000

The name derives from the German *Kobold* for “evil spirits or goblins”, who were superstitiously thought to cause trouble for miners because the mineral contained arsenic that injured their health and the metallic ores did not yield metals when treated with the normal methods. It was discovered in 1735 by the Swedish chemist Georg Brandt.

The 1961 CAWIA report [22] proposed the atomic weight of Co to be A_r(Co) = 58.9332, based on the atomic mass data by Everling et al. [23]. The atomic weight and uncertainty of Co were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51]. ^{59}Co is readily transformed to ^{60}Co, which decays to ^{60}Ni with a half-life of 5.272 a. ^{60}Co therefore serves as an extremely reproducible standard for radiation exposure.

$_{28}$Ni **Nickel** $A_{r(}\text{Ni}) = 58.6934(2)$ **[Since 1989]**

Isotope	Atomic mass/u	Mole fraction
^{58}Ni	57.935 3477(16)	0.680 769(89)
^{60}Ni	59.930 7903(15)	0.262 231(77)
^{61}Ni	60.931 0601(15)	0.011 399(6)
^{62}Ni	61.928 3484(15)	0.036 345(17)
^{64}Ni	63.927 9692(16)	0.009 256(9)

The name derives from the German *nickel* for “deceptive little spirit” because miners called mineral niccolite (NiAs) by the name *kupfernickel* (false copper) because it resembled copper ores in appearance, but no copper was found in the ore. It was discovered by the Swedish metallurgist Axel-Frederik Cronstedt in 1751.

The 1961 CAWIA report [22] recommended A_r(Ni) = 58.71. That value was based on the isotope-abundance measurements of White and Cameron [128] and the atomic masses determined by Collins et al. [309]. CAWIA noted in this report that all chemical determinations that had been reported and believed to be significant gave a mean value for the atomic weight of 58.69. In 1969, CAWIA [4] assessed the uncertainties of the above measurements and recommended a value of $U[A_r(\text{Ni})] = 0.03$, but CAWIA retained A_r(Ni) = 58.71. In 1973, CAWIA [6] reexamined both the chemical and mass-spectrometric measurements and recommended a lower value of A_r(Ni) = 58.70(1). At the same time, CAWIA lowered the uncertainty because A. E. Cameron believed he could explain the higher value given in ref. [128] through having overestimated ^{64}Ni by failing to recognize ^{64}Zn or ^{48}Ti ^{16}O traces.

The best chemical determinations appeared in a series of papers by Baxter and associates [310–312]. Recalculation of these determinations based on the current atomic weights of the other elements involved [11] yields the following results from the listed comparisons:

Ni/0 (reduction NiO) = 0.366 87	A_r(Ni) = 58.700	[310]
$NiC1_2/2Ag$ = 0.600 729	A_r(Ni) = 58.693	[311]
$NiC1_2/2AgCl$ = 0.452 133	A_r(Ni) = 58.694	[311]
$NiBr_2/2Ag$ = 1.012 120	A_r(Ni) = 58.694	[312]
$NiBr_2/2AgBr$ = 0.581 818	A_r(Ni) = 58.690	[312]

In 1973, CAWIA [6] included in their assessment two other mass-spectrometric determinations by Inghram and Hess [313] and Mattraw and Pachucki [138], which may have been overlooked in the earlier review. Both these determinations, when recalculated with current atomic masses [51], yield A_r(Ni) = 58.700. Thus, all the chemical and mass-spectrometric measurements agreed to establish a value of A_r(Ni) = 58.70(1) based on what appeared as overwhelming evidence. Nevertheless, that value is a little higher than the average (58.694) of Baxter's excellent determinations, whose credibility is increased by the proof of accuracy of the parallel work on the atomic weight of Co.

Barnes et al. [314] completed a superior, but not "absolute" mass-spectrometric measurement, which gave A_r(Ni) = 58.688, in good agreement with the chemical determinations. Following the 1977 CAWIA meeting, another reexamination was begun, and in 1979 [9] CAWIA recommended the standard atomic-weight value of A_r(Ni) = 58.69(1), weighted toward the chemical determinations of Baxter and associates. At its 1989 meeting [14], CAWIA changed its recommended value for the atomic weight of Ni to A_r(Ni) = 58.6934(2) based on the calibrated mass-spectrometric determination by Gramlich et al. [315]. The excellent agreement between the average of the chemical values and this new determination illustrates the remarkable accuracy of the determinations of Baxter and associates. Gramlich et al. [316], in a second paper, have compared the isotopic composition of Ni in 29 minerals, salts, and metals and found no statistically significant variations. Therefore, no additional allowance to the overall uncertainty was necessary because the isotopic composition of terrestrial Ni is apparently invariant within the measurement uncertainty.

It should be noted that with this change the atomic weight of Ni is now one of the most accurately known for a polyisotopic element, with an uncertainty of $U[A_r(\mathrm{Ni})] = 3 \times 10^{-6}$, whereas the 1979 value had a relative uncertainty of 0.02 %. This represents an improvement in accuracy of almost two orders of magnitude.

$_{29}$Cu Copper (Cuprum) A_r(Cu) = 63.546(3) r [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{63}Cu	62.929 6007(15)	0.6915(15)
^{65}Cu	64.927 7938(19)	0.3085(15)

The name derives from the Latin *Cuprum* for Cyprus, the island where the Romans first obtained copper. The chemical symbol, Cu, also comes from the Latin *cuprum*. The element has been known since prehistoric times.

In its 1961 report [22], CAWIA recommended A_r(Cu) = 63.54 based on the chemical determinations of Hönigschmid and Johannsen [317] and Reur and Bode [318]. In its 1967 report [3], CAWIA recommended a value of 63.546(1) based on the "absolute" abundance ratio measurement by Shields et al. [319], who obtained A_r(Cu) = 63.5455(4). The recommended uncertainty was increased to $U[A_r(\mathrm{Cu})] = 0.003$ in 1969 [4] to include natural variations of up to about 0.15 % in the isotope abundances of Cu reported by Shields et al. [139], and given the annotation "r" to indicate that the precision was limited by natural variability. This variability in Nature is supported by recent work by Gale et al. [320] and Maréchal et al. [321]. CAWIA's recommended range is significantly larger than the ±0.001 suggested by Shields et al. [139], who claimed even this was a liberal range of variation for bulk or processed Cu. Variations in $n(^{65}\mathrm{Cu})/n(^{63}\mathrm{Cu})$ can be expressed as δ^{65}Cu values relative to the reference material NIST SRM 976 [85,319]. In the compilation of Coplen et al. [85], the lowest reported δ^{65}Cu value in a naturally occurring sample is –7.65 ‰ [mole fraction of ^{65}Cu = 0.3066; A_r(Cu) = 63.542] for a specimen of a Cu-chloride mineral (atacamite) from Chile [320]. The highest reported δ^{65}Cu value is +9 ‰ [mole fraction of ^{65}Cu = 0.3102; A_r(Cu) = 63.549] for a Cu-carbonate mineral (aurichalcite) from Globe, Arizona [139]. Some of these values are outside the range of the stated atomic-weight uncertainty and may justify a reevaluation by CAWIA of the atomic-weight uncertainty or annotations [85].

$_{30}$Zn Zinc A_r(Zn) = 65.409(4) [Since 2001]

Isotope	Atomic mass/u	Mole fraction
^{64}Zn	63.929 1461(18)	0.482 68(321)
^{66}Zn	65.926 0364(17)	0.279 75(77)
^{67}Zn	66.927 1305(17)	0.041 02(21)
^{68}Zn	67.924 8473(17)	0.190 24(123)
^{70}Zn	69.925 325(4)	0.006 31(9)

The name derives from the German *zink* of unknown origin. It was first used in prehistoric times, where its compounds were used for healing wounds and sore eyes and for making brass. It was recognized as a metal as early as 1374.

In its 1961 report [22], CAWIA recommended A_r(Zn) = 65.37, based on the earlier chemical data (recalculated on the ^{12}C scale) by Hönigschmid and von Mack [322], Baxter and Grose [323], and Baxter and Hodges [324]. CAWIA was aware of isotopic composition data by Hess et al. [325] and Leland and Nier [326], both of which, with atomic masses by Everling et al. [23], yielded the higher value of A_r(Zn) = 65.387. Recognizing this unresolved discrepancy, CAWIA in 1969 [4] assessed $U[A_r(\mathrm{Zn})] = 0.3$.

Marinenko and Foley in 1971 [327] published a coulometric determination, which also yielded a higher value A_r(Zn) = 65.377(3), whereupon CAWIA in its 1971 report [5] changed the recommended value to A_r(Zn) = 65.38(1). Another mass-spectrometric value was published in 1972 when Rosman [328] used a gravimetrically prepared mixture of enriched Zn isotopes to give an "absolute" isotopic composition, which yielded A_r(Zn) = 65.396(5). Faced with this ongoing discrepancy between chemical and physical values, CAWIA in 1983 [11] recommended that A_r(Zn) = 65.39 and increased $U[A_r(\mathrm{Zn})]$ to 0.02, explaining that the value was now weighted toward the mass-spectrometric measurement of Rosman [328], but the uncertainty included the coulometric measurement of Marinenko and Foley [327]. The atomic weight and uncertainty of Zn were changed to their current values in 2001 as a result of the calibrated measurement of Chang et al. [140]. Maréchal et al. [321] report variations in the isotopic composition of Zn in natural samples that are within the uncertainty of the standard atomic weight.

$_{31}$Ga Gallium A_r(Ga) = 69.723(1) [Since 1987]

Isotope	Atomic mass/u	Mole fraction
^{69}Ga	68.925 581(3)	0.601 08(9)
^{71}Ga	70.924 7073(20)	0.398 92(9)

The name derives from the Latin *gallia* for France or perhaps from the Latin *gallus* for "le coq or cock" because it was discovered in zinc blende by the French chemist Paul-Emile Lecoq de Boisbaudan in 1875. It was first isolated in 1878 by Le coq de Boisbaudan and the French chemist Émile-Clément Jungflesch.

In its 1961 report, CAWIA [22] recommended A_r(Ga) = 69.72, based on the chemical ratio determinations by Richards and Craig [329] and Lundell and Hoffman [330] as well as the isotope-abundance determinations by Inghram et al. [331,332]. In 1969, CAWIA assigned the uncertainty $U[A_r(\mathrm{Ga})] = 0.01$ [4]. Recalculating the chemical ratios based on current values of the other atomic weights involved [11] yields A_r(Ga) = 69.735, while the mass-spectrometric value [332] with current atomic masses gives A_r(Ga) = 69.72. CAWIA discounted Marinenko's [333] highly precise coulometric assay of Ga and As. Based on plausible confidence in the stoichiometry of a GaAs sample, he calculated A_r(Ga) = 69.737 [333]. In the meantime, de Laeter and Rosman [334] published a mass-spectrometric measurement that confirmed the earlier mass-spectrometric measurements, yielding A_r(Ga) = 69.724(2). CAWIA therefore recommended an atomic weight of A_r(Ga) = 69.723(4) in 1983 [11].

In 1987, CAWIA [13] reviewed the calibrated mass-spectrometric data of Machlan et al. [141], who reported A_r(Ga) = 69.723 07(13). This value is in excellent agreement with the previous mass-spectrometric measurement of de Laeter and Rosman [334], allowing the previous uncertainty to be decreased to $U[A_r(\mathrm{Ga})] = 0.001$. Although no isotopic variations from six meteorites has been observed by de Laeter [335], Nief and Roth [336] found that the ^{69}Ga isotope was progressively enriched toward the anode and ^{71}Ga enriched toward the cathode when an electric current passes through a liquid Ga column just above its melting point. Furthermore, Gramlich and Machlan [316] showed that significant variations occurred in the $n(^{69}\mathrm{Ga})/n(^{71}\mathrm{Ga})$ ratio of commercially high-purity Ga from different lots of material and different manufacturers, some exhibiting ratios 0.19 % higher and 0.12 % lower than the laboratory reference material. The higher ratio represents a shift of 0.0009 in the atomic weight, which does not exceed $U[A_r(\mathrm{Ga})] = 0.001$. Purification of Ga by successive recrystallizations is accompanied by small variations in isotopic composition, which measurably affect the triple-point temperature [337]. Based on this information, CAWIA in 1987 [13] recommended A_r(Ga) = 69.723(1), which has remained unchanged since that time.

$_{32}$Ge **Germanium** A_r**(Ge) = 72.64(1)** **[Since 1999]**

Isotope	Atomic mass/u	Mole fraction
^{70}Ge	69.924 2500(19)	0.2038(18)
^{72}Ge	71.922 0763(16)	0.2731(26)
^{73}Ge	72.923 4595(16)	0.0776(8)
^{74}Ge	73.921 1784(16)	0.3672(15)
^{76}Ge	75.921 4029(16)	0.0783(7)

The name derives from the Latin *germania* for Germany. It was discovered and isolated by the German chemist, Clemens-Alexander Winkler in 1886 in the mineral argyrodite ($GeS_2 \cdot 4Ag_2S$).

In its 1961 report [22], CAWIA recommended A_r(Ge) = 72.59, based on chemical ratio determinations by Baxter and Cooper [338,339] and Hönigschmid et al. [340]. CAWIA noted that five mass-spectrometric measurements averaged to A_r(Ge) = 72.628, which conflicted with the accepted chemical values. In 1969, CAWIA assigned $U[A_r(\mathrm{Ge})] = 0.03$ [4].

Recalculation of the chemical determinations based on values of the atomic weights in 1983 [11] yielded the following results from the listed comparisons:

$GeCI_4/4Ag = 0.496\,928$	A_r(Ge) = 72.589	[338]
$GeCl_4/4AgCl = 0.374\,010$	A_r(Ge) = 72.602	[338]
$GeBr_4/4Ag = 0.909\,016$	A_r(Ge) = 72.600	[339]
$GeBr_4/4AgBr = 0.522\,195$	A_r(Ge) = 72.599	[339]
$GeBr_4/4Ag = 0.909\,000$	A_r(Ge) = 72.593	[340]
$GeBr_4/4AgBr = 0.522\,175$	A_r(Ge) = 72.584	[340]
$GeCl_4/4Ag = 0.496\,893$	A_r(Ge) = 72.584	[341]
$GeCI_4/4AgCl = 0.373\,977$	A_r(Ge) = 72.583	[341]

Assigning equal weight to these determinations yielded an A_r(Ge) of 72.592.

Early mass-spectrometric determinations [342–346] with atomic mass data [49] gave A_r(Ge) values ranging from 72.602 to 72.638. Ge is a difficult element to analyze by solid-source mass spectrometry. Reynolds [345] and Artakuni et al. [347] avoided the problem by the introduction of volatile GeF_4, from $BaGeF_6$, into the spectrometer, but their measurements experienced other difficulties.

Equating the density of the structural crystal cell of elemental Ge with the macroscopic density gives A_r(Ge) = 72.63 [348], in accord with the mass-spectrometric value. Graham et al. [344] compared six different terrestrial sources of Ge. They found only slight variations in atomic weight of one of these and showed that normal preparative procedures caused no isotope fractionation. Shima [346] also showed that eight meteoritic samples had an indistinguishable isotopic composition from that of a laboratory reference standard. Because there was a large range in the measured isotope abundances and there were no calibrated measurements available, CAWIA had no cogent reason for increasing the standard atomic-weight value of Ge.

In 1985, following a new measurement of the isotopic composition by Green et al. [349], CAWIA reexamined the value for the atomic weight [12]. Although this was not a calibrated measurement, the instrument used was checked for linearity using U isotopic reference materials. The new value confirmed earlier mass-spectrometric work after allowance for known sources of isotopic discrimination. CAWIA then decided that a higher value of A_r(Ge) = 72.61(2) contained the most probable value and recommended this value. It noted that there was still concern over the discrepancy between the chemical value and that determined by mass spectrometry, but while not wishing to discard the chemical work favored the mass-spectrometric value. Green et al. [349], using a double spike, also compared the isotope abundances of Ge in 12 materials including Ge minerals, various reagents and transistor Ge, but found no variations outside of the experimental errors of about 1 ‰ per mass unit corresponding to a change of 0.003 in the atomic weight.

In 1999, two new measurements of the isotopic composition of Ge by Kipphardt et al. [350] and Chang et al. [351] yielded values of 72.6276(32) and 72.639(7), respectively, for the atomic weight. Both measurements were calibrated, but did not agree within their uncertainties. However, at its meeting in 1999, CAWIA chose the higher value of A_r(Ge) = 72.64 and reduced the uncertainty to $U[A_r$(Ge)] = 0.01 [19]. The work of Chang et al. [351] included measurements on five natural terrestrial samples, which showed no evidence of isotope fractionation. However, measurements of Ge in iron meteorites by multicollector inductively coupled plasma mass spectrometry indicate that isotope fractionation of this magnitude may occur in some meteorites [352].

$_{33}$As Arsenic A_r(As) = 74.921 60(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{75}As	74.921 5966(18)	1.0000

The name derives from the Latin *arsenicium* and the Greek *arsenikos* for "masculine or male" because the ancients thought that metals were different sexes. It was known in prehistoric times for its poisonous sulfides. The German scientist and philosopher, Albert von Bollstadt (Albert the Great/Albertus Magnus) is thought to have obtained the metal around 1250.

The 1961 CAWIA report [22] proposed the atomic weight to be A_r(As) = 74.9216 based on atomic mass data by Everling et al. [23]. The atomic weight and uncertainty of As were changed to their current values in the 1995 report of CAWIA [17] based on the atomic mass data of Audi and Wapstra [51].

$_{34}$Se **Selenium** A_r(Se) = 78.96(3) r [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{74}Se	73.922 4767(16)	0.0089(4)
^{76}Se	75.919 2143(16)	0.0937(29)
^{77}Se	76.919 9148(16)	0.0763(16)
^{78}Se	77.917 3097(16)	0.2377(28)
^{80}Se	79.916 5221(20)	0.4961(41)
^{82}Se	81.916 7003(22)	0.0873(22)

The name derives from the Greek *Selene*, who was the Greek goddess of the Moon because the element is chemically found with tellurium (*Tellus*—the Roman goddess of the earth). It was discovered by the Swedish chemist Jöns Jacob Berzelius in 1817, while trying to isolate tellurium in an impure sample.

In its 1961 report, CAWIA [22] recommended A_r(Se) = 78.96 based on the chemical determinations by Hönigschmid and collaborators [142,353]. Two measurements of the isotopic composition of Se were reported by White and Cameron [128] and Hibbs [354], giving A_r(Se) equal to 78.99 and 78.97, respectively. In 1969, CAWIA recommended $U[A_r(\text{Se})] = 0.03$ [4]. Both the atomic weight and the uncertainty values have since remained unchanged, but the underlying considerations deserve to be described here.

Hönigschmid and Kapfenberger [353] criticized all previous atomic-weight determinations because the methods used involved the preparation of elemental Se and the weighing of SeO_2, which operations were subject to unresolved difficulties. In CAWIA's view, the Hönigschmid method was indeed superior. Recalculations of his chemical determinations using current values of the other atomic weights involved [11] yields the following results from the listed comparisons:

2Ag/Ag2Se = 0.732 081	A_r(Se) = 78.953	[353]
SeOCI$_2$/2Ag = 0.768 794	A_r(Se) = 78.951	[142]
SeOC1$_2$/2AgCI = 0.578 624	A_r(Se) = 78.953	[142]

This excellent consistency of the results from three different chemical methods, coupled with the established reliability of Hönigschmid's measurements, must be balanced against adverse factors. Inherent limitations apply to classical chemical methods such that they are uncertain by about 1×10^{-5}. Selenium chemistry also is subject to particular difficulties. Thirdly, the results all come from only one laboratory, which is undesirable. CAWIA had these considerations in mind when it conceded that the above agreement could be fortuitous and chose a standard value displaced a little toward the mass-spectrometric values. A new ionization method for Se was published by Wachsmann and Heumann [355]. The calculated atomic weight from their noncorrected data yields 78.9594(8), which is in good agreement with the existing value. Variations in the isotope abundances of Se in terrestrial samples have been established by Krouse and Thode [356] using high-precision differential methods of measurements. The annotation "r" was added by CAWIA in 1999 [19], based on a reevaluation of the data of Krouse and Thode [356].

^{82}Se is radioactive with the enormously long half-life of about 10^{20} a. For the purposes of this review, therefore, it is considered to be a stable isotope.

$_{35}$Br **Bromine** A_r(Br) = 79.904(1) [Since 1965]

Isotope	Atomic mass/u	Mole fraction
^{79}Br	78.918 3379(20)	0.5069(7)
^{81}Br	80.916 291(3)	0.4931(7)

The name derives from the Greek *bromos* for "bad stench or bad odor". It was first prepared by the German chemist Carl Löwig in 1825, but it was first publicly announced in 1826 by the French chemist and pharmacist Antoine-Jérôme Balard, and so the discovery is, therefore, credited to him.

In its 1961 report [22], CAWIA recommended A_r(Br) = 79.909(2) based on a chemical determination of the mass ratio AgBr/Ag = 1.740 785(6) [357] and an updated evaluation of the atomic weight of Ag, which was then the major source of the uncertainty in A_r(Br). The values of A_r(Br) and A_r(Ag) were especially important at that time because the atomic weights of many other elements were determined by the mass ratios of their bromides to Ag or AgBr. In its 1965 reevaluation, summarized in the 1967 report [3], CAWIA adopted the calibrated mass-spectrometric measurements of Catanzaro et al. [143], which yielded A_r(Br) = 79.904(1) and essentially ended the era of chemical determinations of atomic weights for this element. Catanzaro et al. [143], as Cameron and Lippert [358] had done earlier, reported finding no significant variations in the atomic weight of Br from many different sources.

$_{36}$Kr **Krypton** A_r(Kr) = 83.798(2) g, m [Since 2001]

Isotope	Atomic mass/u	Mole fraction
^{78}Kr	77.920 388(7)	0.003 55(3)
^{80}Kr	79.916 379(4)	0.022 86(10)
^{82}Kr	81.913 4850(28)	0.115 93(31)
^{83}Kr	82.914 137(4)	0.115 00(19)
^{84}Kr	83.911 508(3)	0.569 87(15)
^{86}Kr	85.910 615(5)	0.172 79(41)

The name derives from the Greek *kryptos* for "concealed" or "hidden". It was discovered in liquefied atmospheric air by the Scottish chemist William Ramsay and the English chemist Morris William Travers in 1898. A wavelength in the atomic spectrum of ^{86}Kr is the fundamental standard of length.

The atomic weight of Kr is based on analyses of Kr separated from air. In its 1961 report [22], CAWIA recommended A_r(Kr) = 83.80 based on the isotope-abundance measurements by Nier [66] and the atomic masses given by Everling et al. [23]. In 1969, CAWIA [4] recommended $U[A_r(\mathrm{Kr})] = 0.01$. Walton et al. [359] reported measurements of the isotopic composition of a sample of Kr over a period of four years using two different mass spectrometers with results essentially identical to those of Nier [66]. No evidence was reported in those studies for variations in the isotopic composition of natural Kr. The atomic weight and uncertainty of Kr were changed to their current values in 2001 as a result of the calibrated measurement by Aregbe et al. [144].

Recent reviews have concluded that the vast majority of Kr in and on the earth is indistinguishable isotopically from atmospheric Kr [237,360]. However, minor localized occurrences may be found that have been fractionated isotopically by processes such as diffusion or crystal–liquid partitioning. Also, the isotope abundances of Kr may be altered locally by spontaneous or neutron-induced fission of U, or by neutron capture by Br. The annotation "g" refers mainly to fission product Kr such as is found at the Oklo natural nuclear reactor. The annotation "m" refers to the availability of commercial Kr from which specific isotopes may have been separated.

The radioactive isotopes ^{81}Kr (cosmogenic) and ^{85}Kr (released from nuclear industry) are present in the atmosphere and hydrosphere and are used as environmental tracers in hydrology and oceanography, but their abundances are several orders of magnitude too small to have a measurable effect on the atomic weight of Kr.

$_{37}$Rb Rubidium A_r(Rb) = 85.4678(3) g [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{85}Rb	84.911 7924(27)	0.7217(2)
^{87}Rb	86.909 1858(28)	0.2783(2)

The name derives from the Latin *rubidus* for deepest red because of the two "deep red lines" in its spectra. It was discovered in the mineral lepidolite by the German chemist Robert Wilhelm Bunsen and the German physicist Gustav-Robert Kirchoff in 1861. Bunsen isolated rubidium in 1863.

In its 1961 report [22], CAWIA recommended A_r(Rb) = 85.47 based on the average of A_r(Rb) = 85.473 for the chemical determinations by Archibald et al. [361] and Archibald and Hooley [362] and the mass-spectrometric determination of Nier [66], who reported a mole fraction of ^{85}Rb = 0.7215, corresponding to A_r(Rb) = 85.4678(2). In 1969, CAWIA [4] recommended the current value of A_r(Rb) = 85.4678(3) based on the "absolute" isotope-abundance measurement by Catanzaro et al. [145], who reported a mole fraction of ^{85}Rb = 0.72165(13), plus the work of Shields et al. [363], who found no isotopic variations in terrestrial samples, and the atomic masses of Wapstra and Gove [48].

^{87}Rb is β^- active with a half-life of $4.88(5) \times 10^{10}$ a, which leaves A_r(Rb) unaffected at the currently given precision of about 3×10^{-6} in up to 10^6 a. In contrast, accumulation of the ^{87}Sr product of ^{87}Rb decay causes anomalous atomic-weight values of Sr in many Rb-bearing materials, as noted in the section on Sr.

$_{38}$Sr Strontium A_r(Sr) = 87.62(1) g, r [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{84}Sr	83.913 426(4)	0.0056(1)
^{86}Sr	85.909 2647(25)	0.0986(1)
^{87}Sr	86.908 8816(25)	0.0700(1)
^{88}Sr	87.905 6167(25)	0.8258(1)

The name derives from Strontian, a town in Scotland. The mineral strontianite is found in mines in Strontian. The element was discovered in 1792 by the Scottish chemist and physician Thomas Charles Hope, who observed the brilliant red flame color of strontium. It was first isolated by the English chemist Humphry Davy in 1808.

In its 1961 report [22], CAWIA recommended A_r(Sr) = 87.62 based on the mass-spectrometric determination of Nier [279] and on the atomic masses of Everling et al. [23]. In its 1969 report [4], CAWIA assessed $U[A_r(\mathrm{Sr})] = 0.01$. An "absolute" isotope-abundance determination was published by Moore et al. [146], giving a calculated A_r(Sr) = 87.616 81(12) for a specific sample. Known natural variations in the abundance of ^{87}Sr, the product isotope of radioactive ^{87}Rb decay, prevent the recommendation of a more precise standard atomic-weight value. The $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ ratio is a convenient measure of that variability. In the above sample, it was 0.7103. A value for that ratio as high as 1.200 has been reported by Compston et al. [364]. The annotation "r" indicates that the value of $U[A_r(\mathrm{Sr})] = 0.01$ represents isotopic composition variability more than experimental uncertainty. Anomalous traces of almost pure ^{87}Sr have been reported from Rb ores by Mattauch [365], for which the atomic weight will not be in the tabulated standard atomic weight range. In 1969, CAWIA [4] therefore added the appropriate annotation "g."

The appreciable variability in $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ is the basis for Rb-Sr geochronology, and for analysis of source components in mixtures of water and geologic materials. The variability of the isotopic composition of Sr in nature is discussed by Faure [77].

$_{39}$Y **Yttrium** $A_r(\mathrm{Y}) = 88.905\ 85(2)$ [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{89}Y	88.905 8485(26)	1.0000

The name derives from the Swedish village of Ytterby where the mineral gadolinite was found. In 1794, the Finnish chemist Johan Gadolin discovered yttrium in the mineral ytterbite, which was later renamed gadolinite for Gadolin. Gadolin originally called the element ytterbium after ytterbite. The name was subsequently shortened to yttrium, and later another element was given the name ytterbium. The Swedish surgeon and chemist Carl-Gustav Mosander separated the element in 1843.

The CAWIA report in 1961 [22] proposed the atomic weight of Y to be $A_r(\mathrm{Y}) = 88.905$ based on atomic mass data by Everling et al. [23]. CAWIA also quoted comprehensive experimental data setting the upper limits for other hypothetical stable isotopes of Y with mass numbers 85 to 95 at 5×10^{-6}, corresponding to a possible effect on $A_r(\mathrm{Y})$ in the seventh significant figure [147]. In 1969, CAWIA [4] found the data quoted reliable enough to add an extra decimal in $A_r(\mathrm{Y})$, which thus became equal to 88.9059(1). The atomic weight and uncertainty of Y were changed to their current values in the 1995 report of CAWIA [17] based on the atomic mass data of Wapstra and Audi [50].

$_{40}$Zr **Zirconium** $A_r(\mathrm{Zr}) = 91.224(2)$ g [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{90}Zr	89.904 7022(24)	0.5145(40)
^{91}Zr	90.905 6434(23)	0.1122(5)
^{92}Zr	91.905 0386(23)	0.1715(8)
^{94}Zr	93.906 3144(26)	0.1738(28)
^{96}Zr	95.908 275(3)	0.0280(9)

The name derives from the Arabic *zargun* for "gold-like". It was discovered in zirconia by the German chemist Martin-Heinrich Klaproth in 1789. Zirconium was first isolated by Swedish chemist Jöns Jacob Berzelius in 1824 in an impure state, and finally by the chemists D. Lely, Jr. and L. Hamburger in a pure state in 1914.

The atomic weight of Zr has been taken to be $A_r(\mathrm{Zr}) = 91.22$ since 1927, and this value was reconfirmed by the 1961 CAWIA report [22], taking into consideration existing isotope abundances by White and Cameron [128] and using atomic mass data from Everling et al. [23]. The uncertainty in 1969 [4] was assessed as $U[A_r(\mathrm{Zr})] = 0.01$. Since then, two isotopic composition measurements have been carried out by Minster and Ricard [366] yielding $A_r(\mathrm{Zr}) = 91.224$ with an estimated uncertainty of +0.002 and –0.005, and by Nomura et al. [148] yielding $A_r(\mathrm{Zr}) = 91.2235(5)$.

Shima [151] showed that the isotopic composition of nine meteoritic samples and two terrestrial standards were identical, within experimental error, to a laboratory standard. In a similar manner, Minster and Ricard [366] have shown that the isotopic composition in two meteoritic samples, one lunar sample and a terrestrial zircon are identical to a laboratory standard. In 1983, CAWIA [11], on the basis of the excellent agreement between the above mass-spectrometric measurements, refined the standard atomic weight to $A_r(\mathrm{Zr}) = 91.224(2)$. The annotation "g" refers to anomalous occurrences such as at the Oklo natural nuclear reactor.

$_{41}$Nb **Niobium** A_r(Nb) = 92.906 38(2) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{93}Nb	92.906 3762(24)	1.0000

The name derives from the Greek mythological character Niobe, who was the daughter of Tantalus (see the element tantalum), because the elements niobium and tantalum were originally thought to be identical elements. Niobium was discovered in a black mineral from America called columbite by the British chemist and manufacturer Charles Hatchett in 1801 and he called the element columbium. In 1809, the English chemist William Hyde Wollaston claimed that columbium and tantalum were identical. Forty years later, the German chemist and pharmacist, Heinrich Rose, determined that they were two different elements in 1846 and gave the name niobium because it was so difficult to distinguish it from tantalum. Finally, in 1866, the Swiss chemist Jean-Charles Galissard de Marignac separated these elements. The name columbium continued to be used in America and niobium in Europe until IUPAC adopted the name niobium in 1949. Niobium was first isolated by the chemist C. W. Blomstrand in 1846.

The 1961 CAWIA report [22] proposed A_r(Nb) = 92.906, based on atomic mass data by Everling et al. [23]. It also quoted experimental evidence from the literature concerning upper limits for the hypothetical presence of any other stable isotopes of Nb with mass numbers between 89 and 98 [127]. Such isotopes could not cause a change in the seventh significant figure of A_r(Nb). On assessment of the reliability of the data, CAWIA [4] decided in 1969 to add one significant figure to the recommended value. A_r(Nb) thus became equal to 92.9064(1). The atomic weight and uncertainty of Nb were changed to their current values in the 1985 report of CAWIA [12], based on the atomic mass data of Wapstra and Audi [50].

$_{42}$Mo **Molybdenum** A_r(Mo) = 95.94 (2) g [Since 2001]

Isotope	Atomic mass/u	Mole fraction
^{92}Mo	91.906 810(4)	0.1477(31)
^{94}Mo	93.905 0867(20)	0.0923(10)
^{95}Mo	94.905 8406(20)	0.1590(9)
^{96}Mo	95.904 6780(20)	0.1668(1)
^{97}Mo	96.906 0201(20)	0.0956(5)
^{98}Mo	97.905 4069(20)	0.2419(26)
^{100}Mo	99.907 476(6)	0.0967(20)

The name derives from the Greek *molybdos* for "lead". The ancients used the term lead for any black mineral that leaves a mark on paper. Molybdenum was discovered by the Swedish pharmacist and chemist Carl Wilhelm Scheele in 1778. It was first isolated by the Swedish chemist Peter-Jacob Hjelm in 1781.

In its 1961 report [22], CAWIA recommended A_r(Mo) = 95.94 based on the chemical ratio measurements of Hönigschmid and Wittmann [367]. Recalculation of their measurements based on current values of A_r(Ag) and A_r(Cl) [11] gives the mass ratio $MoCl_5/5Ag$ = 0.506 552 and A_r(Mo) = 95.939. In 1969, after reevaluating the uncertainties associated with this work, CAWIA recommended a value of $U[A_r(\text{Mo})]$ = 0.03 [4]. In its 1975 report [7], CAWIA evaluated five papers [368–372] dealing with mass-spectrometric determinations of the isotopic composition of Mo. Although they were judged not to be of equal reliability, their results all fall in the range of A_r(Mo) = 95.93 to 95.94 in close agreement with the chemical value. CAWIA recommended retaining the value of 95.94, but with the reduced uncertainty of $U[A_r(\text{Mo})]$ = 0.01. The uncertainty of A_r(Mo) was changed to its current value in 2001 as a result of a reevaluation of isotopic measurements by Wieser and de Laeter [373] using revised statistical guidelines. Wieser and de Laeter reported no evidence of substantial variations in the isotopic compositions in Mo in a number of molybdenites and commercial chemicals; whereas other studies have indicated minor variations in the isotopic composition of Mo that are smaller than the uncertainty of the standard atomic weight [374]. The annotation "g" refers to anomalous occurrences at the Oklo natural nuclear reactor.

$_{43}$Tc Technetium

This element has not been allocated atomic weight or isotope-abundance values as CAWIA has listed it as an element with no stable isotopes. Technetium has three radioactive isotopes: ^{96}Tc, with an atomic mass of 96.906 364(5) u and $t_{1/2}$ of 2.6 ± 0.4 × 10^6 a; ^{98}Tc, with an atomic mass of 97.907 215(4) u and $t_{1/2}$ of 4.2 ± 0.3 × 10^6 a; and ^{99}Tc with an atomic mass of 98.906 253 6(21) u and $t_{1/2}$ of 2.1 ± 0.3 × 10^5 a [375].

Convincing experimental evidence is now available that Tc occurs in "weighable" amounts resulting from the spontaneous fission of ^{238}U. It is estimated that the amount of Tc produced is approximately 2 × 10^{-12} of the amount of U present [376]. This result has yet to be accepted by CAWIA, but it seems appropriate to mention this information in the present review.

Other reasons for briefly discussing this element are the origin of its name and the way it has been discovered. The name derives from the Greek *technitos* for "artificial". Conventional wisdom is that Tc was first synthesized in 1937 by the Italian physicists C. Perrin and Emilio Segre in Palermo, Italy, who separated Tc from a sample of deuteron-bombarded Mo. However, in 1925 Noddack et al. [377] reported the discovery of element Z = 43, which they called Masurium, based on line identification of X-ray emission spectra from concentrated residues of U-rich minerals. This "discovery" was not acknowledged, and the Perrin–Segre discovery became accepted by the scientific community. A recent experiment by Armstrong and Van Assche [376] has simulated the Noddack et al. [377] experiment and given convincing proof as to the validity of the earlier discovery.

$_{44}$Ru Ruthenium A_r(Ru) = 101.07(2) g [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{96}Ru	95.907 604(9)	0.0554(14)
^{98}Ru	97.905 287(7)	0.0187(3)
^{99}Ru	98.905 9385(22)	0.1276(14)
^{100}Ru	99.904 2189(22)	0.1260(7)
^{101}Ru	100.905 5815(22)	0.1706(2)
^{102}Ru	101.904 3488(22)	0.3155(14)
^{104}Ru	103.905 430(4)	0.1862(27)

The name derives from the Latin *ruthenia* for the old name of Russia. It was discovered in a crude platinum ore by the Russian chemist Gottfried Wilhelm Osann in 1828. Osann thought that he had found three new metals in the sample, pluranium, ruthenium, and polinium. In 1844, Russian chemist Karl Karlovich Klaus was able to show that Osann's mistake was due to the impurity of the sample, and Klaus was able to isolate the ruthenium metal.

In its 1961 report [22], CAWIA changed the recommended atomic-weight value, A_r(Ru), from 101.1 to 101.07. In 1969, CAWIA [4] assigned an uncertainty $U[A_r(\mathrm{Ru})]$ of 0.03 to that value of A_r(Ru), which was based on the abundance measurements by Friedman and Irsa [378], Baldock [379], and White et al. [127], and not on the chemical determination by Gleu and Rehm [380] in view of the large uncertainties in the chemical determination. The best measurements of the isotopic composition, on which the above representative isotopic composition is based, corresponds to the work by Devillers et al. [381], yielding A_r(Ru) = 101.068(13) calculated with the atomic mass data by Wapstra and Bos [49]. The use in 1961 of earlier atomic mass data [23] does not significantly affect the magnitude of the earlier A_r(Ru) determinations. Feitknecht et al. [382] found no significant differences between three meteoritic and one terrestrial sample. Devillers et al. [381] found no significant differences between a meteoritic sample, two samples of well-defined geographic origin, and a commercial sample. In view of the excellent agreement between all the data, CAWIA [11] recommended in 1983 a reduction in $U[A_r(\mathrm{Ru})]$ from 0.03 to 0.02, and A_r(Ru) = 101.07. The annotation “g” refers to anomalous occurrences at the Oklo natural nuclear reactor.

$_{45}$Rh Rhodium A_r(Rh) = 102.905 50(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{103}Rh	102.905 504(3)	1.0000

The name derives from the Greek *rhodon* for rose because of the “rose color of dilute solutions of its salts”. It was discovered by the English chemist and physicist William Hyde Wollaston in 1803 in a crude platinum ore.

In 1961, CAWIA [22] proposed A_r(Rh) = 102.905 based on atomic mass data by Everling et al. [23]. On the basis of Leipziger’s unsuccessful search for minor stable isotopes of Rh [119], it was concluded that they could affect at most the seventh significant figure of the atomic-weight value. CAWIA changed the A_r(Rh) value to 102.9055(1) in 1969 [4]. The atomic weight and uncertainty of Rh were further changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{46}$Pd Palladium A_r(Pd) = 106.42(1) g [Since 1979]

Isotope	Atomic mass/u	Mole fraction
^{102}Pd	101.905 607(3)	0.0102(1)
^{104}Pd	103.904 034(5)	0.1114(8)
^{105}Pd	104.905 083(5)	0.2233(8)
^{106}Pd	105.903 484(5)	0.2733(3)
^{108}Pd	107.903 895(4)	0.2646(9)
^{110}Pd	109.905 153(12)	0.1172(9)

The name derives from the second largest asteroid of the solar system Pallas (named after the goddess of wisdom and arts—Pallas Athene). The element was discovered by the English chemist and physicist William Hyde Wollaston in 1803, one year after the discovery of Pallas by the German astronomer H. W. M. Olbers in 1802. The discovery was originally published anonymously by Wollaston to obtain priority, while not disclosing any details about his preparation.

In its 1961 report [22], CAWIA recommended the atomic weight of Pd to be A_r(Pd) = 106.4 based on the isotope-abundance measurements by Sites et al. [383] using atomic masses by Everling et al. [23]. The uncertainty $U[A_r(\mathrm{Pd})]$ = 0.1 was assigned by CAWIA in 1969 [4], which gave Pd the least precisely tabulated atomic weight at that time. New calibrated isotope-abundance measurements of Pd were made by Shima et al. [384], yielding A_r(Pd) = 106.415(4). No variations outside the errors of the measurements were found among three terrestrial samples. Using these new abundance values and evidence of lack of significant natural variations, CAWIA, in its 1979 report [9], recommended A_r(Pd) = 106.42(1).

In 1981, Mermelengas et al. [385] reported convincing evidence that a sample of Pd from the South African Igneous Complex was enriched in the heavier isotopes giving an atomic weight of 106.434. Further measurements by Rosman et al. [386] of other Pd samples from the same region taken from different locations and representing different stages of industrial purification of ores were unable to detect other fractionated material. The isotopically fractionated sample has, therefore, been considered “abnormal” because of its rarity, and the atomic weight remains 106.42(1). The “g” annotation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa [387] and the anomalous South African sample [386].

The possible recovery of significant quantities of nonradioactive ^{106}Pd from fission product wastes has been discussed by McDuffie [388]. This source of Pd is not likely to be available in the foreseeable future.

$_{47}$Ag Silver (Argentum) A_r(Ag) = 107.8682(2) g [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{107}Ag	106.905 093(6)	0.518 39(8)
^{109}Ag	108.904 756(3)	0.481 61(8)

The name derives from the Anglo-Saxon *seofor* and *siolfur*, which is of unknown origin. The chemical symbol, Ag derives from the Latin *argentum* and Sanskrit *argunas* from “bright”. The element was known in prehistoric times.

In its 1961 report [22], CAWIA recommended A_r(Ag) = 107.870(3) after carefully reviewing the reliability of this value. It was recognized to be of great importance because about 42 other elements had their atomic weights determined in terms of the equivalence of their halides to Ag or Ag halides. The above value for A_r(Ag) was based on seven chemical (Ag/$AgNO_3$ twice; Ag/AgI; AgI/AgCl four times), and a number of mass-spectrometric determinations, one of which was a calibrated measurement [389], using atomic masses by Everling et al. [23]. CAWIA gave equal weight to the average of these chemical determinations, A_r(Ag) = 107.8714, and the mass-spectrometric atomic weight of Shields et al. [389], of 107.8686(6).

In 1967, CAWIA [3] with news of an “absolute” isotopic composition determination for Br, saw that there was a self-consistent set of reliable “absolute” mass-spectrometric measurements for Cl, Br, and Ag. The basis for A_r(Ag) was changed to a value of A_r(Ag) = 107.868, and the uncertainty $U[A_r(\text{Ag})]$ reduced to 0.001. CAWIA pointed out that the new values gave a calculated combining ratio AgCl/Ag = 1.328 667, which is exactly the assessed best chemical ratio. Whereas this agreement corresponded to about 1 part in 10^6, the ratio AgBr/Ag showed a disparity of 19 parts in 10^6, which was thought to be due to a bias in the chemical work.

In 1981, CAWIA [10] welcomed a superior new “absolute” isotope-abundance measurement for Ag by Powell et al. [102], yielding A_r(Ag) = 107.868 15(11). These authors found no significant difference between a number of Ag metal and mineral samples with one minor exception now believed to be due to an impurity. CAWIA was able to recommend A_r(Ag) = 107.8682(3). In 1983, CAWIA retained the “g” annotation because of the Oklo occurrence [11]. In 1985, the uncertainty in the atomic weight of Ag was reduced to 0.0002 [12].

Through the greater use of mass-spectrometric determinations of atomic weights, Ag is losing some of its key role attributable to the stability of its monovalent ion. However, the atomic weight of Ag has lost none of its significance as a principal means for determining the Faraday constant. The atomic weight determination of [102] coupled with the best value of the electrochemical equivalent of Ag, has re-established the electrochemical method as the most accurate for determining the Faraday constant, and has significantly contributed to least squares adjustments of the fundamental constants.

$_{48}$Cd Cadmium A_r(Cd) = 112.411(8) g [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{106}Cd	105.906 458(6)	0.0125(6)
^{108}Cd	107.904 183(6)	0.0089(3)
^{110}Cd	109.903 006(3)	0.1249(18)
^{111}Cd	110.904 182(3)	0.1280(12)
^{112}Cd	111.902 7577(30)	0.2413(21)
^{113}Cd	112.904 4014(30)	0.1222(12)
^{114}Cd	113.903 3586(30)	0.2873(42)
^{116}Cd	115.904 756(3)	0.0749(18)

The name derives from Greek *kadmeia* for "calamine (zinc carbonate)", with which it was found as an impurity in nature. It may have been found in furnace flue dust in Thebes, a city in the Boeottia region of central Greece. The mythological king of Phoenicia, Cadmus, founded Thebes and would be a source for the name of the ore. The element was discovered and first isolated by German physician Fredrich Stromeyer in 1817.

In its 1961 report [22], CAWIA recommended A_r(Cd) = 112.40 based on seven chemical determinations by Hönigschmid and Schlee, and Baxter in cooperation with various associates, although it was noted that several isotope-abundance measurements yielded slightly higher values. Nevertheless, CAWIA in 1969 [4] assigned $U[A_r(\mathrm{Cd})] = 0.01$. In 1975, Rosman and de Laeter [390] published measurements of the isotopic composition of reagent Cd and eight terrestrial minerals. They estimated the mass discrimination by two methods. The first method interpolated the discrimination at Cd from measurements made on certified isotopic reference materials of Ag (NBS 978) and Pb (NBS 981), while the second determined it by introducing a gravimetrically prepared Cd double-spike into samples of reagent Cd. They reported A_r(Cd) = 112.410(5). In 1975, CAWIA [7] accepted this measurement as the most reliable available. It was moreover in fair agreement with earlier mass-spectrometric measurements, including those quoted in the 1961 report as well as determinations by White and Cameron [128] and Hibbs [354] yielding, respectively, A_r(Cd) = 112.43 and 112.42. As the chemical measurements, seemingly consistent with each other, had averaged 112.400 with little spread, CAWIA justified the retention of $U[A_r(\mathrm{Cd})] = 0.01$ with A_r(Cd) now 112.41. In 1985, CAWIA reexamined the data [12], taking account of a confirmatory measurement by Rosman et al. [152], which gave A_r(Cd) = 112.412. With its liberalized policy on single digit uncertainties, it then recommended an intermediate value of A_r(Cd) = 112.411(8), which has remained unchanged to the present.

It might be of some interest to note that all chemical measurements that gave an A_r(Cd) value below 112.40 depended on the purity of $CdBr_2$, for which freedom from traces of chloride at the time was hard to prove. Incidentally also, it is of interest that Rosman and de Laeter [391,392] found that Cd in the majority of meteorite samples showed no variations from the terrestrial composition although four unequilibrated ordinary chondrites exhibited enhancement of either their heavier or lighter isotopes. The "g" annotation arises from the presence of naturally occurring Cd fission products found in fossil reactors at Gabon, southwest Africa [393].

^{113}Cd is β^--active, but its half-life is so long (10^{16} a) that it does not affect A_r(Cd) measurably even over geologic time periods. It decays into the minor isotope of In, but abnormal occurrences of that element with anomalous A_r(In) from the decay of ^{113}Cd have not been reported.

$_{49}$In Indium A_r(In) = 114.818(3) [Since 1991]

Isotope	Atomic mass/u	Mole fraction
^{113}In	112.904 062(4)	0.0429(5)
^{115}In	114.903 879(40)	0.9571(5)

The name derives from the term "indigo" for the indigo-blue line in the element's spark spectrum. It was discovered in 1863 by the German physicist Ferdinand Reich and the German metallurgist Hieronymus Theodor Richter, while examining zinc blende. They isolated indium in 1867.

In its 1961 report [22], CAWIA recommended A_r(In) = 114.82, which was the average value of two reported mass-spectrometric determinations by White and Cameron [128], and White et al. [127] calculated with atomic masses by Everling et al. [23]. The uncertainty $U[A_r(\mathrm{In})]$ was assessed to be ±0.01 in 1969 [4]. In the absence of calibrated mass-spectrometric measurements and lacking a study of possible natural variations, CAWIA did not see compelling reasons for making a change. It is not clear whether a third mass-spectrometric determination by Hibbs [354] was disregarded with cause or overlooked. However, his result of A_r(In) = 114.821, calculated with current atomic masses [51], is in excellent agreement with the other determinations.

In 1991, CAWIA [15] changed the recommended value for the atomic weight of In to A_r(In) = 114.818(3) based on high precision measurements of the metal and its compounds by Chang and Xiao [153]. The new measurement represents a significant improvement in the precision of the atomic weight and is in agreement with the previous value. The new value also agrees with the value reported by Saito et al. [394].

^{115}In is β^- active with a half-life so long, $4.41(25) \times 10^{14}$ a, that it neither affects A_r(In) nor has it given rise to recognized abnormal occurrences of tin.

$_{50}$Sn Tin (Stannum) A_r(Sn) = 118.710(7) g [Since 1983]

Isotope	Atomic mass/u	Mole fraction
^{112}Sn	111.904 822(5)	0.0097(1)
^{114}Sn	113.902 783(3)	0.0066(1)
^{115}Sn	114.903 347(3)	0.0034(1)
^{116}Sn	115.901 745(3)	0.1454(9)
^{117}Sn	116.902 955(3)	0.0768(7)
^{118}Sn	117.901 608(3)	0.2422(9)
^{119}Sn	118.903 311(3)	0.0859(4)
^{120}Sn	119.902 1985(27)	0.3258(9)
^{122}Sn	121.903 4411(29)	0.0463(3)
^{124}Sn	123.905 2745(15)	0.0579(5)

The name derives from the Anglo-Saxon *tin* of unknown origin. The chemical symbol, Sn, is derived from Latin *stannum* for alloys containing lead. The element was known in prehistoric times.

In its 1961 report [22], CAWIA recommended A_r(Sn) = 118.69 based on chemical-ratio determinations by Baxter and Starkweather [395]; Briscoe [396]; and Brauner and Krepelka [397]. From these measurements, with current values of the atomic weights of the other elements involved [11], the following atomic weights for Sn are derived: A_r(Sn) = 118.691, 118.686, and 118.701 respectively.

In 1961, CAWIA was aware that three mass-spectrometric determinations had been made that yield slightly higher atomic-weight values. Tin has 10 stable isotopes, the largest number of all elements. The isotopic composition measurements involve an unusually large number of experimentally determined ratios, each subject to uncertainty. In 1969, CAWIA [4] assessed the uncertainty to be $U[A_r(\mathrm{Sn})]$ = 0.03. CAWIA therefore preferred the chemically determined atomic-weight values. This viewpoint was reconfirmed during the years, until in 1983 CAWIA [11] was able to consider the first calibrated mass-spectrometric measurement by Devillers et al. [154] who used double spiking with a mixture prepared from Sn highly enriched in ^{116}Sn and ^{122}Sn. The authors reported a value of A_r(Sn) = 118.7099(22) and demonstrated good agreement with seven previous isotope-abundance measurements after correcting those uncalibrated measurements linearly by mass for isotope fractionation. CAWIA in 1983 [11] therefore changed the basis for the standard atomic weight of Sn to mass spectrometry and the value to A_r(Sn) = 118.710(7) with the knowledge that natural variability is very small [398].

Devillers et al. [154] identified interferences at ^{114}Sn and ^{115}Sn, which were subsequently quantified by Rosman et al. [155] and corrected, leading to the isotope abundances provided in this review. Further very high-precision measurements of refined samples of Sn and cassiterites by Rosman and McNaughton [399,400] have shown that natural isotope fractionation, if it exists, is extremely small. Only one of their samples showed evidence of fractionation (0.02 % per mass unit). Changes of this magnitude introduce a negligible change in A_r(Sn). The "g" annotation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa [387].

$_{51}$Sb Antimony (Stibium) A_r(Sb) = 121.760(1) g [Since 1993]

Isotope	Atomic mass/u	Mole fraction
^{121}Sb	120.903 8222(26)	0.5721(5)
^{123}Sb	122.904 2160(22)	0.4279(5)

The name derives from the Greek, *anti* + *monos* for "not alone or not one" because it was found in many compounds. The chemical symbol, Sb, comes from stibium, which is derived from the Greek *stibi* for "mark" because it was used for blackening eyebrows and eyelashes. The minerals stibnite (Sb_2S_3) and stibine (Sb_2H_3) are two of more than 100 mineral species, which were known in the ancient world.

In its 1961 report [22] CAWIA recommended A_r(Sb) = 121.75 based on chemical measurements by Willard and McAlpine [401], Hönigschmid et al. [402], Weatherill [403] and Krishnaswami [404]. With current values of the other atomic weights [11], these measurements yield the following results from the listed comparisons:

$SbBr_3/3Ag$ = 1.117 704	A_r(Sb) = 121.778	[401]
$SbBr_3/3AgBr$ = 0.641 682	A_r(Sb) = 121.758	[401]
$SbC_{13}/3Ag$ = 0.704 88	A_r(Sb) = 121.743	[402]
$SbC_{13}/3AgCl$ = 0.530 53	A_r(Sb) = 121.750	[402]
$SbBr_3/3Ag$ = 1.116 99	A_r(Sb) = 121.751	[402]
$SbBr_3/3AgBr$ = 0.641 67	A_r(Sb) = 121.751	[402]
$SbC_{13}/3Ag$ = 0.704 864	A_r(Sb) = 121.738	[403]
$SbBr_3/3AgBr$ = 0.641 659	A_r(Sb) = 121.745	[404]

Giving these determinations, equal weight leads to an average value for A_r(Sb) = 121.751. In 1961, CAWIA [22] was aware of the sole measurement of the isotopic composition of Sb by mass spectrometry, published by White and Cameron [128]. With current atomic mass data by Wapstra and Bos [49], that measurement yields A_r(Sb) = 121.759, in good agreement with the chemical value. The corresponding values calculated in 1961 [22] provided CAWIA with an average chemical value of A_r(Sb) = 121.750 and for the mass-spectrometric determination A_r(Sb) = 121.76. The chemical value was evidently given slight preference in the tabulated value of A_r(Sb) = 121.75, for which in 1969 [4] CAWIA assigned $U[A_r(\text{Sb})]$ = 0.03.

In 1989, CAWIA adopted an atomic weight of A_r(Sb) = 121.757(3) [14], based on the mass-spectrometric measurement by de Laeter and Hosie [405]. In 1993, CAWIA [16] changed the recommended value for the standard atomic weight to A_r(Sb) = 121.760(1), based on the calibrated mass-spectrometric determination by Chang et al. [156], which was supported by other high-quality measurements by Chang et al. [406], and by Wachsmann and Heumann [407]. A survey of five stibnite minerals and five laboratory reagents was also carried out by Chang et al. [156]. No evidence of isotope fractionation of Sb in any of the terrestrial materials was found. The "g" annotation is due to isotopic anomalies identified in the Oklo U deposit at Gabon, southwest Africa.

$_{52}$Te **Tellurium** A_r(Te) = 127.60(3) g **[Since 1969]**

Isotope	Atomic mass/u	Mole fraction
^{120}Te	119.904 026(11)	0.0009(1)
^{122}Te	121.903 0558(29)	0.0255(12)
^{123}Te	122.904 2711(20)	0.0089(3)
^{124}Te	123.902 8188(16)	0.0474(14)
^{125}Te	124.904 4241(20)	0.0707(15)
^{126}Te	125.903 3049(20)	0.1884(25)
^{128}Te	127.904 4615(19)	0.3174(8)
^{130}Te	129.906 2229(21)	0.3408(62)

The name derives from the Latin *Tellus*, who was the Roman goddess of the earth. It was discovered by the Roumanian mine director Franz Joseph Müller von Reichenstein in 1782 and overlooked for 15 years until it was isolated by the German chemist Martin-Heinrich Klaproth in 1798. The Hungarian chemist Paul Kitaibel independently discovered tellurium in 1789, prior to Klaproth's work but after von Reichenstein.

The CAWIA report in 1961 [22] recommended A_r(Te) = 127.60, based on the chemical-ratio determinations by Hönigschmid and his collaborators [408–410]. In 1969, CAWIA [4] assessed $U[A_r(\mathrm{Te})]$ to be 0.03. Recalculations of the chemical ratios with current values of the other atomic weights involved [11], yielded the following results from the listed comparisons:

$TeBr_4/4Ag = 1.036\,49$	A_r(Te) = 127.601	[408]
$TeBr_4/AgBr = 0.595\,426$	A_r(Te) = 127.602	[408]
$Ag_2Te/2Ag = 1.591\,45$	A_r(Te) = 127.597	[409]
$TeCl_4/4Ag = 0.624\,425$	A_r(Te) = 127.610	[410]
$TeCl_4/AgCl = 0.469\,960$	A_r(Te) = 127.612	[410]

Giving these chemical determinations, equal weight yields A_r(Te) = 127.604.

In 1961, CAWIA noted the mass-spectrometric measurements of Williams and Yuster [411] and White and Cameron [128], which average to a higher atomic-weight value A_r(Te) = 127.63 [22]. The later isotope-abundance measurements by Smith et al. [157], coupled with the atomic mass data by Wapstra and Bos [49], gave a value lower than that from the chemical determinations. That value, A_r(Te) = 127.586, was invariant within experimental precision for six Te mineral sources [157]. In the absence of calibrated mass-spectrometric measurements, the value of A_r(Te) = 127.60(3) was retained as the standard atomic weight of Te. The measurements by Smith et al. [157] were made with an electron multiplier and were, therefore, biased towards the lighter isotopes. In recognition of this fact, the isotope abundances measured by Smith et al. [157] were adjusted by the square root of the mass numbers to give the abundances shown here [72]. These abundances yield an atomic weight and uncertainty consistent with the standard atomic weight. They are also consistent with recent isotope-abundance measurements of de Laeter [412] made using a Faraday cup collector. Isotope fractionation in telluride minerals was reported by Smithers and Krouse [413].

^{123}Te, ^{128}Te, and ^{130}Te are radioactive; the minor isotope ^{123}Te has a long half-life of $1.3(4) \times 10^{13}$ a and transforms into ^{123}Sb without significantly affecting either element's atomic weight even over geological time. The major isotopes ^{128}Te and ^{130}Te have long half-lives of approximately 10^{24} a and 10^{21} a, respectively. These isotopes suffer double β^- decay and are responsible for detectable Xe isotopic anomalies in old Te-bearing minerals. The "g" annotation for Te arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa [414].

$_{53}$I **Iodine** A_r(I) = 126.904 47(3) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{127}I	126.904 468(4)	1.0000

The name derives from the Greek *iodes* for "violet" because of its violet vapors. It was discovered in seaweed by the French chemist Bernard Courtois in 1811. It was named by the French chemist Louis-Joseph Gay-Lussac, when he proved it was an element in 1814.

In 1961, CAWIA [22] proposed the atomic weight of I to be A_r(I) = 126.9044, based on atomic mass data by Everling et al. [23]. CAWIA had a preview of the revision of this data in a paper by Wapstra and Gove [48] that had been accepted for publication prior to CAWIA meeting in 1969 [4]. Presumably it was the new value for the mass of ^{127}I = 126.904 47 that led CAWIA to adopt the change to A_r(I) = 126.9045(1) without documenting the reasoning in the 1969 report [4]. The atomic weight and uncertainty of I were changed to their current values in the 1985 report of CAWIA [12], based on the atomic mass data of Wapstra and Audi [50].

There is little information in the literature on the hypothetical presence in normal sources of I of isotopes other than ^{127}I. Leland [158] found the upper limit of ^{129}I in normal I as 3×10^{-6}. It is a ß$^{-}$ emitter with a half-life of $1.6(1) \times 10^{7}$ a, too short for the survival in terrestrial I of significant amounts of this isotope from primordial material. If present in normal I in the concentration determined by Leland [158] to be the upper limit, ^{129}I would increase A_r(I) by six in the ninth significant figure, substantially less than the standard atomic-weight uncertainty. More recently, ^{129}I has been measured in terrestrial samples that have been exposed to cosmic radiation, and in materials that contain fallout from nuclear explosions. These measurements can be used for geochronological and environmental studies, but they also confirm the low abundance of ^{129}I in nature, and its insignificance with respect to the atomic weight of I.

$_{54}$Xe **Xenon** A_r(Xe) = 131.293(6) g, m [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{124}Xe	123.905 8954(21)	0.000 952(3)
^{126}Xe	125.904 268(7)	0.000 890(2)
^{128}Xe	127.903 5305(15)	0.019 102(8)
^{129}Xe	128.904 7799(9)	0.264 006(82)
^{130}Xe	129.903 5089(11)	0.040 710(13)
^{131}Xe	130.905 0828(18)	0.212 324(30)
^{132}Xe	131.904 1546(15)	0.269 086(33)
^{134}Xe	133.905 3945(9)	0.104 357(21)
^{136}Xe	135.907 220(8)	0.088 573(44)

The name derives from the Greek *xenos* for "the stranger". It was discovered by the Scottish chemist William Ramsay and the English chemist Morris William Travers in 1898 in a liquefied air sample.

The atomic weight of Xe is based on analyses of Xe separated from air. In its 1961 report [22], CAWIA adopted a value of A_r(Xe) = 131.30, which was recommended in 1955 and was based on the "calibrated" isotope-abundance measurements of Nier [66] and the atomic masses reported by Halsted [415]. CAWIA recognized in 1961 that this calculation was "slightly in error" and noted that with the same isotope abundances and using the atomic masses reported by Everling et al. [23], the correct calculated value was nearer to A_r(Xe) = 131.29. Despite this inconsistency, CAWIA in 1969 [4] estimated that the uncertainty $U[A_r(\mathrm{Xe})]$ was no greater than 0.01. In 1979, CAWIA [9] corrected this inconsistency and recommended $A_r(\mathrm{Xe}) = 131.29(3)$. The uncertainty was reduced to 0.02 by CAWIA in its 1985 report [12] to conform to the modified Technical Guidelines. In 1999, CAWIA adopted the analyses of Valkiers et al. [58] on a tank of purified Xe as the "best measurement" of the isotopic composition of Xe in a single source. Based on that measurement, and a reevaluation of previous data, CAWIA recommended $A_r(\mathrm{Xe}) = 131.293(6)$, which is believed to represent the value of Xe in air [19].

Xenon samples with relatively high ^{129}Xe concentrations extracted from some types of primitive volcanic rocks and from some natural gas wells have been attributed to the decay of extinct ^{129}I early in the earth's history, storage in the interior of the earth for several billion years, and subsequent release during partial degassing [416]. Other reported minor occurrences of Xe of anomalous isotopic composition have been attributed to production of the heavy isotopes ^{131}Xe to ^{136}Xe from spontaneous and induced fission of U and fission of extinct ^{244}Pu; production of ^{128}Xe and ^{130}Xe from double β^- decay of ^{128}Te and ^{130}Te; and primordial sources [237]. Not all of these variations are included within the atomic weight uncertainty, hence the annotation "g". Localized occurrences of isotopically anomalous Xe are associated with nuclear bomb test sites, and minor fractionations can occur during separation of Xe from air or other processes, hence the annotation "m".

$_{55}$Cs Caesium (Cesium) $A_r(\mathrm{Cs}) = 132.905\ 45(2)$ [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{133}Cs	132.905 447(3)	1.0000

The name derives from the Latin *caesius* for "sky blue color", which was the color of the caesium line in the spectroscope. It was discovered by the German chemist Robert Wilhelm Bunsen and the German physicist Gustav Robert Kirchhoff in 1860. It was first isolated by the German chemist Carl Setterberg in 1882.

The CAWIA report in 1961 [22] recommended $A_r(\mathrm{Cs}) = 132.905$, based on atomic mass data from Everling et al. [23]. CAWIA also cited experimental evidence from the literature indicating that the upper limit for the hypothetical existence of any other stable or quasi-stable isotope of Cs is very low [127]. When assessing the reliability of data in 1969, CAWIA [4] decided to add one significant figure and recommended $A_r(\mathrm{Cs}) = 132.9055(1)$. This value was adjusted in 1971 [5] to 132.9054(1) as a result of Wapstra and Gove's revision of atomic mass data [48]. The atomic weight and uncertainty of Cs were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{56}$Ba Barium $A_r(\mathrm{Ba}) = 137.327(7)$ [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{130}Ba	129.906 311(7)	0.001 06(1)
^{132}Ba	131.905 056(3)	0.001 01(1)
^{134}Ba	133.904 504(3)	0.024 17(18)
^{135}Ba	134.905 684(3)	0.065 92(12)
^{136}Ba	135.904 571(3)	0.078 54(24)
^{137}Ba	136.905 822(3)	0.112 32(24)
^{138}Ba	137.905 242(3)	0.716 98(42)

The name is derived from the Greek *barys* for "heavy" because it was found in the mineral heavy spar ($BaSO_4$). It was discovered by the Swedish pharmacist and chemist Carl Wilhelm Scheele in 1774 and first isolated by the British chemist and physicist Humphry Davy in 1808.

In 1961, CAWIA [22] recommended a value of A_r(Ba) = 137.34 for the atomic weight of Ba. This value was based both on the chemical data of Hönigschmid and Sachtleben [417] and on mass-spectrometric abundance measurements by Nier [418] and Thode [419]. In 1969, CAWIA [4] assigned an uncertainty so that the value became A_r(Ba) = 137.34(3). In 1975, CAWIA [7] reviewed the above data as well as new mass-spectrometric measurements by Rider et al. [420], Umemoto [421], Eugster et al. [159], and de Laeter and Date [422]. All of these measurements fell within a very narrow range, and that by Eugster et al. [159] had been calibrated by the double-spike technique. As a result, CAWIA recommended A_r(Ba) = 137.33(1). Eugster et al. [159] and de Laeter and Date [422] had reported no isotopic variations in a range of terrestrial and meteoritic samples. In 1985, CAWIA [12], under its new rules permitting the use of uncertainties from 1 to 9, again reviewed the available data and felt that an additional digit was justified and recommended A_r(Ba) = 137.327(7).

The atomic weight of Ba has carried the annotation "g" on what CAWIA has, in the past, felt were strong theoretical grounds that fission product Ba should exist in samples from the Oklo deposits. There have been numerous unsuccessful experimental attempts to measure this fission product Ba, but there is now evidence of fission product Ba in mineral separates from Oklo samples [423]. However, CAWIA judged that the isotopic composition of Ba in whole-rock Oklo samples would not be significantly different with respect to the standard atomic weight. Thus, the annotation "g" previously used for this element has been suppressed.

$_{57}$La Lanthanum A_r(La) = 138.9055(2) g [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{138}La	137.907 108(4)	0.000 90(1)
^{139}La	138.906 349(4)	0.999 10(1)

The name derives from the Greek *lanthanein* for "to be hidden or to escape notice" because it hid in cerium ore and was difficult to separate from that rare earth mineral. It was discovered by the Swedish surgeon and chemist Carl-Gustav Mosander in 1839. In 1842, Mosander separated his lanthanium sample into two oxides; for one of these he retained the name lanthanum and for the other he gave the name didymium (or twin).

In its 1961 report [22], CAWIA recommended a value A_r(La) = 138.91, based on the recalculation of two chemical determinations and the average of two mass-spectrometric determinations by Inghram et al. [424] and White et al. [127], using the atomic mass data by Everling et al. [23]. In 1969, CAWIA [4] recommended A_r(La) = 138.9055(3) based upon the same determinations, taking into account that two additional digits were justified in view of the small influence any mass discrimination could have on the atomic weight of this nearly monoisotopic element. In effect, the chemical determinations were no longer considered significant. In 1985, CAWIA reexamined the data and decided to reduce the uncertainty of the atomic weight to 0.0002 [12].

The minor isotope ^{138}La is radioactive with a half-life of $1.06(4) \times 10^{11}$ a, with ^{138}Ba and ^{138}Ce as daughter nuclides. The atomic weight of all three elements remains unaffected even over geologic time periods. The "g" annotation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{58}$Ce Cerium $A_r(\mathrm{Ce}) = 140.116(1)$ g [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{136}Ce	135.907 140(50)	0.001 85(2)
^{138}Ce	137.905 986(11)	0.002 51(2)
^{140}Ce	139.905 435(3)	0.884 50(51)
^{142}Ce	141.909 241(4)	0.111 14(51)

The name derives from the planetoid Ceres, which was discovered by the Italian astronomer Giuseppe Piazzi in 1801 and named for Ceres, the Roman goddess of agriculture and harvest. Two years later, the element was discovered by the German chemist Martin-Heinrich Klaproth, who called it ochroeite earth because of its yellow color. It was independently discovered at the same time by the Swedish chemist Jöns Jacob Bezelius and the Swedish mineralogist Wilhelm von Hisinger, who called it ceria. It was first isolated in 1875 by the American mineralogist and chemist William Frances Hillebrand and the American chemist Thomas H. Norton.

In its 1961 report [22], CAWIA recommended $A_r(\mathrm{Ce}) = 140.12$ based on the average value of the mass-spectrometric measurements by Inghram et al. [424] and Hibbs [354], which were in good agreement with earlier chemical determinations. As a result, CAWIA in 1969 [4] assessed the uncertainty $U[A_r(\mathrm{Ce})]$ to be 0.01. Consideration was also given to a determination by Umemoto [421], which, with atomic masses [49], calculates to $A_r(\mathrm{Ce}) = 140.1148$, compared with 140.1048 for Inghram et al. [424] and 140.124 5 for Hibbs [354]. Though the atomic weight of Ce of 140.11(2) might be a slightly better value, CAWIA has not seen sufficiently compelling reasons to make a change until new results became available. The above representative isotopic composition calculates to $A_r(\mathrm{Ce}) = 140.1149(20)$, which favors the lower value and higher uncertainty without compelling a change. The atomic weight and uncertainty of Ce were changed to their current values in the 1995 report of CAWIA [17], based on the isotope-abundance data of Chang et al. [161].

^{138}Ce and ^{140}Ce are the decay products of long-lived minor isotopes ^{138}La and ^{144}Nd respectively. They have a negligible effect on $A_r(\mathrm{Ce})$ in normal sources, but add justification to the “g” annotation, which also refers to the Oklo occurrence in Gabon, southwest Africa.

$_{59}$Pr Praseodymium $A_r(\mathrm{Pr}) = 140.907\,65(2)$ [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{141}Pr	140.907 648(3)	1.0000

The name derives from the Greek *prasios* for “green” and *didymos* for “twin” because of the pale green salts it forms. It was discovered by the Austrian chemist Carl Auer von Welsbach in 1885, who separated it and the element neodymium from a didymium sample. Didymium had previously been thought to be a separate element.

The CAWIA report in 1961 [22] recommended an atomic weight of $A_r(\mathrm{Pr}) = 140.907$, based on atomic mass data from Everling et al. [23]. CAWIA also examined literature evidence that placed very low limits on the possible abundances of additional stable isotopes of Pr [147]. In its assessment of the data in 1969, CAWIA [4] added one additional significant figure and recommended $A_r(\mathrm{Pr}) = 140.9077(1)$. The atomic weight and uncertainty of Pr were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{60}$Nd **Neodymium** **A_r(Nd) = 144.24(3) g** **[Since 1969]**

Isotope	Atomic mass/u	Mole fraction
^{142}Nd	141.907 719(3)	0.272(5)
^{143}Nd	142.909 810(3)	0.122(2)
^{144}Nd	143.910 083(3)	0.238(3)
^{145}Nd	144.912 569(3)	0.083(1)
^{146}Nd	145.913 113(3)	0.172(3)
^{148}Nd	147.916 889(4)	0.057(1)
^{150}Nd	149.920 887(4)	0.056(2)

The name derives from the Greek *neos* for "new" and *didymos* for "twin". It was discovered by the Swedish surgeon and chemist Carl Gustav Mosander in 1841, who called it didymium (or twin) because of its similarity to lanthanium, which he had previously discovered two years earlier. In 1885, the Australian chemist Carl Auer von Welsbach separated didymium into two elements, one of which he called neodymium (or new twin).

In its 1961 report [22], CAWIA recommended A_r(Nd) = 144.24 based on the average of the isotope-abundance measurements of Inghram et al. [425] and Walker and Thode [426] with atomic masses by Everling et al. [23]. In 1969, CAWIA [4] evaluated the uncertainty $U[A_r(\text{Nd})]$ to be 0.03.

Two isotopes of Nd (^{144}Nd and ^{145}Nd) are radioactive but with half-lives so long, $2.1(4) \times 10^{15}$ a, and more than 6×10^{16} a, respectively, that there is no measurable effect on the atomic weight comparable with the precision of the tabulated standard atomic weight. ^{143}Nd is the decay product of radioactive ^{147}Sm. Although the resulting fluctuations of $n(^{143}\text{Nd})/n(^{144}\text{Nd})$ are also too small to affect A_r(Nd), they are measurable and do permit deductions to be made in geochronology [427] and in geochemical phenomena, for instance, the mixing of ocean currents [428]. For such applications, precise measurements of isotope abundances and Sm/Nd ratios are needed, and these are greatly facilitated by comparisons with standard solutions [429]. The "g" notation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{62}$Sm **Samarium** **A_r(Sm) = 150.36(3) g** **[Since 1979]**

Isotope	Atomic mass/u	Mole fraction
^{144}Sm	143.911 996(4)	0.0307(7)
^{147}Sm	146.914 894(3)	0.1499(18)
^{148}Sm	147.914 818(3)	0.1124(10)
^{149}Sm	148.917 180(3)	0.1382(7)
^{150}Sm	149.917 272(3)	0.0738(1)
^{152}Sm	151.919 729(3)	0.2675(16)
^{154}Sm	153.922 206(3)	0.2275(29)

The name derives from the mineral samarskite, in which it was found and that had been named for Colonel Samarski, a Russian mine official. It was originally discovered in 1878 by the Swiss chemist Marc Delafontaine, who called it decipium. It was also discovered by the French chemist Paul-Emile Lecoq de Boisbaudran in 1879. In 1881, Delafontaine determined that his decipium could be resolved into two elements, one of which was identical to Boisbaudran's samarium. In 1901, the French chemist Eugène-Anatole Demarçay showed that this samarium earth also contained europium.

In its 1961 report [22], CAWIA expressed concern about disparities among several isotope-abundance measurements for Sm, while chemical measurements yielded persistently higher values. Thus, CAWIA retained A_r(Sm) = 150.35—the 1955 value based on the mass spectrometry of Inghram et al. [430], which was even lower than the average of five mass-spectrometric measurements recalculated with atomic masses by Bhanot et al. [431]. In 1969, CAWIA [4] found the evidence inadequate for the precision previously implied and corrected A_r(Sm) to 150.4(1); this value included almost all chemical and mass-spectrometric data. In 1979, CAWIA [9] undertook a thorough review of the literature. The chemical determinations by Hönigschmid and Hirschbold-Wittner [432] were found most reliable because the purity of $SmCl_3$ was proved by X-ray fluorescence and optical-emission spectrometry. Earlier work had been subject to contamination by oxychloride as correctly pointed out by Hönigschmid and Hirschbold-Wittner [432]. Their data, recalculated with the results from the listed comparison are as follows:

$SmCl_3/3Ag = 0.793\ 310$ $A_r(Sm) = 150.359$
$SmCl_3/3AgCl = 0.597\ 068$ $A_r(Sm) = 150.358$ [432]

In 1975, Lugmair et al. [433] carried out more precise mass-spectrometric measurements that, with atomic masses [49], gave A_r(Sm) = 150.366. Thus, CAWIA in 1979 [9] recommended A_r(Sm) = 150.36(3), a vindication of the 1961 value. From the previous A_r(Sm) = 150.4 this was the largest change of an atomic-weight value in CAWIA's history, although it was only 40 % of the previously estimated uncertainty.

Two isotopes, ^{147}Sm and ^{148}Sm, have very long half-lives of $1.06(1) \times 10^{11}$ a and $7(3) \times 10^{15}$ a, respectively. They cannot appreciably influence A_r(Sm) even over geologic time intervals. The applications to geochronology and geochemical phenomena are mentioned in the preceding section on Nd. The "g" notation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{63}$Eu **Europium** A_r(Eu) = 151.964(1) g [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{151}Eu	150.919 846(3)	0.4781(6)
^{153}Eu	152.921 227(3)	0.5219(6)

The name derives from the continent of Europe. It was separated from the mineral samaria in magnesium-samarium nitrate by the French chemist Eugène-Anatole Demarçay in 1896. It was also first isolated by Demarçay in 1901.

In its 1961 report [22], CAWIA recommended the atomic weight of Eu to be A_r(Eu) = 151.96 based on the mass-spectrometric determinations by Hess [434] and Collins et al. [147] and atomic masses by Bhanot et al. [431]. Owing to the fact that Eu has only two isotopes, CAWIA in 1969 [4] assessed $U[A_r(Eu)]$ at 0.01. Since that time, another confirmatory isotopic composition measurement has become available [162], but it was not a calibrated measurement. A value of A_r(Eu) = 151.965(9) was adopted in 1985 [12] when CAWIA removed the restriction requiring uncertainties to be either 1 or 3. Natural variability has not been studied and reported in the literature. The atomic weight and uncertainty of Eu were changed to their current values in the 1995 report of CAWIA [17], based on the isotope-abundance data of Chang et al. [164]. The "g" notation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{64}$Gd **Gadolinium** A_r(Gd) = 157.25(3) g [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{152}Gd	151.919 789(3)	0.0020(1)
^{154}Gd	153.920 862(3)	0.0218(3)
^{155}Gd	154.922 619(3)	0.1480(12)
^{156}Gd	155.922 120(3)	0.2047(9)
^{157}Gd	156.923 957(3)	0.1565(2)
^{158}Gd	157.924 101(3)	0.2484(7)
^{160}Gd	159.927 051(3)	0.2186(19)

The name derives from the mineral gadolinite, in which it was found, and that had been named for the Finnish rare earth chemist Johan Gadolin. It was discovered by the Swiss chemist Jean-Charles Galissard de Marignac in 1886, who produced a white oxide he called $Y_?$ in a samarskite mineral. In 1886, the French chemist Paul-Emile Lecoq de Boisbaudran gave the name gadolinium to $Y_?$.

In 1961, CAWIA [22] recommended the value of the atomic weight of Gd to be A_r(Gd) = 157.25. This value was based on the average of the isotope-abundance measurements of Hess [434] and Leland [133] using atomic masses reported by Bhanot et al. [431]. In 1969, CAWIA [4] recommended a value of A_r(Gd) = 157.25(3). The isotope-abundance measurements of Eugster et al. [165] and Holliger and Devillers [162] are considered superior, but when used with atomic masses by Wapstra and Bos [49], do not present a compelling argument for a change in the recommended values for A_r(Gd) or $U[A_r$(Gd)].

^{152}Gd has a very long half-life in excess of 10^{14} a. Within the life time of the earth, this radioactivity will not have affected the atomic weight to the precision here quoted. The "g" notation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{65}$Tb **Terbium** A_r(Tb) = 158.925 34(2) [Since 1995]

Isotope	Atomic mass/u	Molar fraction
^{159}Tb	158.925 343(3)	1.0000

The name derives from the village of Ytterby in Sweden, where the mineral ytterbite (the source of terbium) was first found. Terbium was discovered by the Swedish surgeon and chemist Carl-Gustav Mosander in 1843 in an yttrium salt, which he resolved into three elements. He called one yttrium, a rose-colored salt he called terbium, and a deep yellow peroxide he called erbium. In 1862, the Swiss chemist Marc Delafontaine reexamined yttrium and found the yellow peroxide. Because the name erbium had now been assigned to the rose colored oxide, he reintroduced the name terbium for the yellow peroxide. Thus the original names given to erbium and terbium samples are now switched.

The CAWIA report in 1961 [22] recommended the atomic weight A_r(Tb) = 158.924, based on atomic mass data from Everling et al. [23]. CAWIA also cited experimental evidence from the literature indicating that the upper limits for the abundances of other hypothetical stable or quasi-stable isotopes of Tb were very low [147]. A revision of the atomic mass data was considered by CAWIA in 1969 [4], although the relevant publication by Wapstra and Gove [48] was finalized later. The A_r(Tb) value thus became equal to 158.9254(1). The atomic weight and uncertainty of Tb were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{66}$Dy Dysprosium A_r(Dy) = 162.500(1) g [Since 2001]

Isotope	Atomic mass/u	Mole fraction
^{156}Dy	155.924 278(7)	0.000 56(3)
^{158}Dy	157.924 405(4)	0.000 95(3)
^{160}Dy	159.925 194(3)	0.023 29(18)
^{161}Dy	160.926 930(3)	0.188 89(42)
^{162}Dy	161.926 795(3)	0.254 75(36)
^{163}Dy	162.928 728(3)	0.248 96(42)
^{164}Dy	163.929 171(3)	0.282 60(54)

The name derives from the Greek *dysprositos* for "hard to get at", owing to the difficulty in separating this rare earth element from a holmium mineral in which it was found. It was discovered by the Swiss chemist Marc Delafontaine in the mineral samarskite in 1878 and called philippia. Philippia was subsequently thought to be a mixture of terbium and yttrium. It was later rediscovered in a holmium sample by the French chemist Paul-Emile Lecoq de Boisbaudron in 1886, who was then credited with the discovery. It was first isolated by the French chemist George Urbain in 1906.

In its 1961 report [22], CAWIA recommended A_r(Dy) = 162.50 based on the mass-spectrometric determinations by Inghram et al. [435] and atomic masses by Bhanot et al. [431]. In 1969, CAWIA [4] assessed $U[A_r(\mathrm{Dy})]$ as 0.03. In the absence of new calibrated mass-spectrometric measurements as well as due to lack of a study of natural variability, CAWIA found no compelling reason to make any change in these values. The isotopic measurements of Holliger and Devillers [162] confirm the existing data. The atomic weight and uncertainty of Dy were changed to their current values in 2001 as a result of the calibrated measurement by Chang et al. [166]. The "g" notation arises from the presence of naturally occurring fission products found in fossil reactors at Gabon, southwest Africa.

$_{67}$Ho Holmium A_r(Ho) = 164.930 32(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{165}Ho	164.930 319(3)	1.0000

The name derives from the Latin *holmia* for Stockholm. It was discovered in erbia earth by the Swiss chemist J. L. Soret in 1878, who referred to it as element X. It was later independently discovered by the Swedish chemist Per Theodor Cleve in 1879. It was first isolated in 1911 by Homberg, who proposed the name holmium either to recognize the discoverer Per Cleve, who was from Stockholm, or perhaps to establish his own name in history.

The CAWIA report in 1961 [22] recommended an atomic weight of A_r(Ho) = 164.930, based on atomic mass data from Bhanot et al. [431]. CAWIA also cited experimental evidence from the literature indicating that the upper limits for the abundances of other hypothetical stable isotopes of Ho were low [147]. Based on a reassessment of the available data in 1969, CAWIA [4] added one significant figure and recommended A_r(Ho) = 164.9303(1). The revision of atomic mass data by Wapstra and Gove [48] led CAWIA in 1971 [5] to revise A_r(Ho) to 164.9304(1). The atomic mass of ^{165}Ho given by Wapstra and Bos [49] favored a return to the 1969 value of A_r(Ho); however, CAWIA in 1983 [11] decided to postpone changing A_r(Ho) pending the expected publication of an updated atomic mass table and a CAWIA policy decision to limit rounding-off fluctuations in the standard atomic-weight values for the monoisotopic elements. The atomic weight and uncertainty of Ho were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{68}$Er Erbium A_r(Er) = 167.259(3) g [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{162}Er	161.928 775(4)	0.001 39(5)
^{164}Er	163.929 197(4)	0.016 01(3)
^{166}Er	165.930 290(3)	0.335 03(36)
^{167}Er	166.932 046(3)	0.228 69(9)
^{168}Er	167.932 368(3)	0.269 78(18)
^{170}Er	169.935 461(3)	0.149 10(36)

The name derives from the Swedish town of Ytterby, where the ore gadolinite (in which it was found) was first mined. It was discovered by the Swedish surgeon and chemist Carl-Gustav Mosander in 1843 in a yttrium sample. He separated the yttrium into yttrium, a rose-colored salt he called terbium and a deep yellow peroxide that he called erbium.

In its 1961 report [22], CAWIA recommended A_r(Er) = 167.26 based on the isotope-abundance measurements by Hayden et al. [436] and Leland [133], and atomic masses by Bhanot et al. [431]. In 1969, CAWIA [4] assessed $U[A_r$(Dy)] as 0.03. A subsequent confirmatory isotopic composition measurement reported by Holliger and Devillers in 1981 [162] provided support for the 1969 value and uncertainty of A_r(Er). However, the atomic weight and uncertainty of Er were changed to their current values in the 1999 report of CAWIA [19], based on the isotope-abundance data of Chang et al. [437]. The "g" notation arises from the presence of naturally occurring fission products found at the Oklo fossil reactors at Gabon, southwest Africa.

$_{69}$Tm Thulium A_r(Tm) = 168.934 21(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{169}Tm	168.934 211(3)	1.0000

The name derives from Thule, the earliest name for the northernmost part of the civilized world—Scandinavia (Norway, Sweden, and Iceland). It was discovered in 1879 by the Swedish chemist Per Theodor Cleve in a sample of erbium mineral. It was first isolated by the American chemist Charles James in 1911.

The CAWIA report in 1961 [22] proposed the atomic weight of Tm to be A_r(Tm) = 168.934 based on atomic mass data by Bhanot et al. [431]. A search by Collins et al. [147] for minor stable or quasi-stable isotopes of Tm was unsuccessful and placed the upper limit of their existence so low that they could only affect the atomic weight in the ninth significant figure. When it assessed the reliability of the data, CAWIA in 1969 [4] added one decimal figure. The A_r(Tm) value thus became 168.9342(1). The atomic weight and uncertainty of Tm were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{70}$Yb Ytterbium A_r(Yb) = 173.04(3) g [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{168}Yb	167.933 895(5)	0.0013(1)
^{170}Yb	169.934 759(3)	0.0304(15)
^{171}Yb	170.936 323(3)	0.1428(57)
^{172}Yb	171.936 378(3)	0.2183(67)
^{173}Yb	172.938 207(3)	0.1613(27)
^{174}Yb	173.938 858(3)	0.3183(92)
^{176}Yb	175.942 569(3)	0.1276(41)

The name derives from the Swedish village of Ytterby where the mineral ytterbite (the source of ytterbium) was originally found. It was discovered by the Swiss chemist Jean-Charles Galissard de Marignac in 1878 in erbium nitrate from gadolinite (ytterbite renamed).

The atomic weight of Yb has been taken as 173.04 since 1934. This chemically determined value was reconfirmed in the 1961 CAWIA report [22]. However, from that time, A_r(Yb) was no longer based on chemical but on mass-spectrometric data by Hayden et al. [438] and by Leland [133]. The uncertainty of $U[A_r(\text{Yb})] = 0.03$ was assigned in 1969 [4] and has also remained unchanged since. A number of mass-spectrometric determinations of the isotopic composition of Yb are referenced [133,147,162,436,439]. McCulloch et al. [439] showed that the isotopic composition of eight meteoritic and four terrestrial samples were identical within experimental errors to a laboratory standard. The “g” annotation is derived from anomalous Yb in samples from the Oklo U deposit in Gabon, southwest Africa.

$_{71}$Lu Lutetium A_r(Lu) = 174.967(1) g [Since 1981]

Isotope	Atomic mass/u	Mole fraction
^{175}Lu	174.940 7682(28)	0.9741(2)
^{176}Lu	175.942 6827(28)	0.0259(2)

The name derives from Lutetia, the ancient name for the city of Paris. The discovery is credited to the French chemist George Urbain in 1907 although it had been separated earlier and independently by the Austrian chemist Carl Auer von Welsbach from an ytterbium sample. Von Welsbach had named the element cassiopeium after the constellation Cassiopeia. However, because Urbain published his results before Auer, his name for the element was adopted by IUPAC in 1949.

In its 1961 report [22], CAWIA recommended A_r(Lu) = 174.97 based on the mass-spectrometric determinations by Hayden et al. [436] and Collins et al. [147]. CAWIA noted the close agreement with the chemical determination of Hönigschmid and Wittner [440] after recalculation on the $A_r(^{12}\text{C}) = 12$ scale. In 1969, CAWIA assessed the uncertainty $U[A_r(\text{Lu})]$ as 0.01 [4]. Then, in 1977 CAWIA [8] took note of a new isotope-abundance determination by McCulloch et al. [441], which was deemed more accurate but, like its predecessors, was not calibrated. Nevertheless, as a result, the more precise A_r(Lu) = 174.967(3) was recommended. Moreover, in 1981 CAWIA [10] was able to reduce the uncertainty from $U[A_r(\text{Lu})] = 0.003$ to 0.001. This change was justified because another abundance determination by Holliger and Devillers [162] agreed very well with earlier measurements. Besides, it was pointed out that the predominance of one isotope coupled with the small mass difference between the isotopes reduces the effect of a small unrecognized mass-discrimination effect in the determination of the isotopic composition. McCulloch et al. [441] had found no significant variability for Lu from different sources.

The minor isotope, ^{176}Lu, is radioactive with a half-life of $3.57(14) \times 10^{10}$ a. In consequence, A_r(Lu) will change comparably with the current uncertainty in only about 5×10^8 a. At Oklo, the $n(^{176}\text{Lu})/n(^{175}\text{Lu})$ ratio has been used [162] as a sensitive measure of the average equilibrium temperature of the neutrons at the time of the nuclear reactions. The occurrence at this site of almost pure

(99.7 %) isotope ^{175}Lu [162] justifies the annotation “g”. The ^{176}Lu-^{176}Hf decay system is used as a geochronometer [77].

$_{72}$Hf Hafnium $A_{r(}$Hf) = 178.49(2) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{174}Hf	173.940 042(4)	0.0016(1)
^{176}Hf	175.941 403(3)	0.0526(7)
^{177}Hf	176.943 2204(27)	0.1860(9)
^{178}Hf	177.943 6981(27)	0.2728(7)
^{179}Hf	178.945 8154(27)	0.1362(2)
^{180}Hf	179.946 5488(27)	0.3508(16)

The name derives from the Latin *hafnia* for Copenhagen. An element named celtium was erroneously claimed to have been discovered in 1911 by the French chemist George Urbain in rare earth samples, until the Danish physicist Nils Bohr, predicted hafnium’s properties using his theory of electronic configuration of the elements. Bohr argued that hafnium would not be a rare earth element, but would be found in zirconium ore. It was discovered by the Dutch physicist Dirk Coster and the Hungarian physicist Georg von Hevesy in 1923, while working at Bohr’s Institute in Copenhagen.

In its 1961 report [22], CAWIA recommended A_r(Hf) = 178.49 based on isotope-abundance measurements by Hibbs [354], Reynolds [345] and White et al. [127], and atomic masses by Bhanot et al. [431]. In 1969, CAWIA [4] assessed $U[A_r$(Hf)] = 0.03. In 1985, the uncertainty associated with A_r(Hf) was revised from 178.49(3) to 178.49(2) to be consistent with the Technical Guidelines [12]. In the absence of new calibrated mass-spectrometric measurements, as well as a study of possible natural variations, CAWIA did not see sufficiently convincing reasons for making any other change since that time.

The minor isotope, ^{174}Hf, is an α-emitter with the very long half-life of 2.0(4) × 10^{15} a. It does not affect A_r(Hf) even in a geologic time frame. However, ^{176}Hf is the principal product of ^{176}Lu decay, so that small but detectable variations in ^{176}Hf abundance with geologic age and Lu association occur. These variations are overshadowed by larger uncertainties in the “absolute” value for A_r(Hf), which, however, does not preclude their use in geochronology [77]

$_{73}$Ta Tantalum A_r(Ta) = 180.9479(1) [Since 1979]

Isotope	Atomic Mass/u	Mole Fraction
^{180}Ta	179.947 466(3)	0.000 12(2)
^{181}Ta	180.947 996(3)	0.999 88(2)

The name derives from the Greek mythological character Tantalus who was banished to Hades, the region of lost souls where he was placed up to his chin in water, which receded whenever he tried to drink it, and under branches of fruit, which drew back whenever he tried to pick their fruit. This name was selected because of the insolubility of tantalum in acids; thus, when placed in the midst of acids, it is incapable of taking any of them up. It was discovered by the Swedish chemist and mineralogist Anders-Gustav Ekeberg in 1802 (see niobium).

In its 1961 report [22], CAWIA recommended A_r(Ta) = 180.948, based upon the isotope-abundance measurements by White et al. [127,442] and Palmer [443], and the atomic masses of Bhanot et al. [431]. In 1969, CAWIA [4] increased the precision of A_r(Ta) to 180.9479, recognizing the element as one whose atomic weight could be stated very precisely because of a predominant isotope. At that time $U[A_r$(Ta)] was assessed at 0.03, but lowered to 0.01 in 1979 [9]. Mass discrimination in the isotope-abundance measurements could have only a very minor effect when applied to an isotope of very low abundance and minimum mass difference.

The minor isotope, ^{180}Ta, is radioactive with a very long half-life of more than 10^{13} a. It is the last quasi-stable isotope to be discovered [127]. Its interest is heightened by the discovery [444] that it is not the ground-state isomer.

$_{74}$W Tungsten (Wolfram) A_r(W) = 183.84(1) [Since 1991]

Isotope	Atomic mass/u	Mole fraction
^{180}W	179.946 706(5)	0.0012(1)
^{182}W	181.948 205(3)	0.2650(16)
^{183}W	182.950 2242(30)	0.1431(4)
^{184}W	183.950 9323(30)	0.3064(2)
^{186}W	185.954 362(3)	0.2843(19)

The name derives from the Swedish *tungsten* for "heavy stone". The chemical symbol, W, derives from the German *wolfram*, which was found with tin and interfered with the smelting of tin. It was said to eat up tin like a wolf eats up sheep. The element was discovered by the Swedish pharmacist and chemist Carl-Wilhelm Scheele in 1781. Tungsten metal was first isolated by the Spanish chemists Don Fausto d'Elhuyar and his brother Don Juan Jose d'Elhuyar in 1783.

In 1961, CAWIA [22] recommended the value of A_r(W) = 183.85 for the atomic weight of W. This value was based on the average of the isotope-abundance measurements by Williams and Yuster [411], Mattauch and Scheld [445], White and Cameron [128], and Hibbs [354], using atomic masses reported by Bhanot et al. [431]. In 1969, after evaluating the uncertainties associated with the measurements cited above, CAWIA [4] assigned a value of $U[A_r$(W)] = 0.03. For a number of years after that, in the absence of calibrated mass-spectrometric measurements, CAWIA was concerned about a discrepancy between the recommended atomic weight and the results of earlier chemical determinations that yielded values of around A_r(W) = 183.90 as reported, for instance, in Hönigschmid and Menn [446]. In 1991, CAWIA [15] changed the recommended value for the atomic weight of W to A_r(W) = 183.84(1), based on high-precision measurements with negative thermal ionization mass spectrometry by Völkening et al. [169].

$_{75}$Re Rhenium A_r(Re) = 186.207(1) [Since 1975]

Isotope	Atomic mass/u	Mole fraction
^{185}Re	184.952 955(3)	0.3740(2)
^{187}Re	186.955 7505(30)	0.6260(2)

The name derives from the Latin *rhenus* for "the Rhine in Germany". It was discovered by X-ray spectroscopy in 1925 by German chemists Walter Noddack, Ida Tacke, and Otto Berg.

In its 1961 report, CAWIA [22] recommended the atomic weight of Re to be A_r(Re) = 186.2 based on the isotope-abundance measurements by White and Cameron [128] and the atomic mass data reported by Bhanot et al. [431]. In 1975, CAWIA [7] recommended a new value A_r(Re) = 186.207(1) that was based on the superior calibrated measurements by Gramlich et al. [170]. These authors detected no isotopic composition variations in sources of natural Re.

^{187}Re is radioactive, decaying to ^{187}Os with a half-life of 4.23(13) × 10^{10} a. Thus, it will take a billion years for the abundance of that isotope to decline by appreciably more than the uncertainty in its current value. However, the anomalies caused in the isotopic composition of some Os occurrences are of geological interest as described in the following section on Os.

$_{76}$Os Osmium A_r(Os) = 190.23(3) g [Since 1991]

Isotope	Atomic mass/u	Mole fraction
^{184}Os	183.952 491(3)	0.0002(1)
^{186}Os	185.953 838(3)	0.0159(3)
^{187}Os	186.955 7476(30)	0.0196(2)
^{188}Os	187.955 8357(30)	0.1324(8)
^{189}Os	188.958 145(3)	0.1615(5)
^{190}Os	189.958 445(3)	0.2626(2)
^{192}Os	191.961 479(4)	0.4078(19)

The name derives from the Greek *osme* for "smell" because of the sharp odor of the volatile oxide. Both osmium and iridium were discovered simultaneously in a crude platinum ore by the English chemist Smithson Tennant in 1803.

In 1961, CAWIA [22] recommended A_r(Os) = 190.2. This value was based on the isotope-abundance measurement of Nier [447] using atomic masses reported by Bhanot et al. [431]. In 1969, after reevaluating the uncertainties associated with the work cited above, CAWIA [4] recommended $U[A_r(\mathrm{Os})] = 0.1$. This was the highest "absolute" uncertainty in the Table of Standard Atomic Weights, equaled by $U[A_r(\mathrm{Pb})]$ for which element, however, the atomic weight is affected by natural variability, not applicable to Os. In 1991, CAWIA [15] considered isotope measurements by Völkening et al. [171], who used negative thermal ionization, yielding an atomic weight having a significantly improved precision, A_r(Os) = 190.23(3), which is in agreement with the value of Nier [447].

One of the minor isotopes, ^{186}Os, is radioactive with a very long half-life of 2.0×10^{15} a. It undergoes α decay into stable ^{182}W but does not affect A_r(Os) even over geologic time. ^{187}Os is the stable product of β^- active ^{187}Re decay. As a result, Os occurs with anomalous atomic weight as a trace element in Re-bearing rocks. The "g" annotation is thereby justified.

The variability of the isotopic composition of Os in nature is discussed by Faure [77]. The Re-Os decay system is used in geology for dating deposits (e.g., molybdenites) preferably with a high Re to Os ratio. Relatively low $n(^{187}\mathrm{Os})/n(^{186}\mathrm{Os})$ ratios were found in the Cretaceous/Tertiary boundary [448] and support the theory of asteroid or comet impact to explain the mass extinction of fauna on earth.

$_{77}$Ir Iridium A_r(Ir) = 192.217(3) [Since 1993]

Isotope	Atomic mass/u	Mole fraction
^{191}Ir	190.960 591(3)	0.373(2)
^{193}Ir	192.962 923(3)	0.627(2)

The name derives from the Latin *Iris*, the Greek goddess of rainbows, because of the "variety of colors in the element's salt solutions". Iridium and osmium were both discovered in a crude platinum ore in 1803 by the English chemist Smithson Tennant. Iridium was discovered independently by the French chemist H. V. Collet-Descotils, who actually published his paper one month before Tennant, but Tennant is given credit for the discovery, perhaps because he alone also found osmium in the ore.

In its 1961 report [22], CAWIA recommended the atomic weight of Ir to be A_r(Ir) = 192.2, which was based on two mass-spectrometric determinations by Sampson and Bleakney [449] and Baldock [379], and on atomic masses by Bhanot et al. [431]. In 1969, CAWIA [4] recommended a value of A_r(Ir) = 192.22(3) based on a closer uncertainty analysis of the above-mentioned mass-spectrometric determinations. In 1993, CAWIA changed the recommended value for the standard atomic weight to A_r(Ir) = 192.217(3) based on recent high-precision measurements using both positive and negative thermal ionization mass spectrometry [16]. A more recent A_r(Ir) value reported by Creaser et al. [450] was not considered by CAWIA because only a single measurement was made. Recent work by Walczyk and Heumann [172] and Chang and Xiao [451] were evaluated by CAWIA [16]. The work of Walczyk and Heumann [172] was chosen by CAWIA as the best measurement due to its better precision; however, both measurements are in agreement within stated uncertainties. The new value represents a significant improvement in the precision of the atomic weight and is in agreement with the previous measurements.

$_{78}$Pt **Platinum** A_r(Pt) = 195.078(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{190}Pt	189.959 930(7)	0.000 14(1)
^{192}Pt	191.961 035(4)	0.007 82(7)
^{194}Pt	193.962 663(3)	0.329 67(99)
^{195}Pt	194.964 774(3)	0.338 32(10)
^{196}Pt	195.964 934(3)	0.252 42(41)
^{198}Pt	197.967 875(5)	0.071 63(55)

The name derives from the Spanish *platina* for "silver". In 1735, the Spanish mathematician Don Antonio De Ulloa found platinum in Peru, South America. In 1741, the English metallurgist Charles Wood found platinum from Columbia, South America. In 1750, the English physician William Brownrigg prepared purified platinum metal.

In its 1961 report CAWIA [22], confirmed the previously recommended atomic weight of Pt to be A_r(Pt) = 195.09 based on the determinations of the isotopic composition of this element by Inghram et al. [452] and White et al. [127] with atomic masses by Bhanot et al. [431]. The uncertainty of $U[A_r(\text{Pt})] = 0.03$ was assigned by CAWIA in 1969 [4]. In 1979, CAWIA [9] corrected a small computational error by which A_r(Pt) was amended to 195.08(3). In 1995, CAWIA [17] changed the A_r(Pt) to 195.078(2) based on electron impact ionization of gaseous $Pt(PF_3)_4$ and measurement of Pt^+ ions in a mass spectrometer [173]. This measurement, although not a calibrated one, has led to a substantial improvement in the uncertainty of A_r(Pt). The minor isotope, ^{190}Pt, is radioactive with a very long half-life of $6.9(6) \times 10^{11}$ a. It does not affect the atomic weight of Pt even over geological time.

$_{79}$Au **Gold (Aurum)** A_r(Au) = 196.966 55(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{197}Au	196.966 551(3)	1.0000

The name derives from the Sanskrit *jval* to "shine", the Teutonic word *gulth* for "shining metal", and the Anglo-Saxon *gold* of unknown origin. The chemical symbol Au derives from the Latin *aurum*, for Aurora, the goddess of dawn. Gold was known and highly valued in prehistoric times.

The CAWIA report in 1961 [22] recommended A_r(Au) = 196.967, based on atomic mass data [431]. On examination of the literature in 1974, it was estimated that the uncertainty in A_r(Au) introduced by the hypothetical presence of a long-lived, but yet undiscovered isotope, is at most $+3 \times 10^{-5}$ or -1×10^{-5}. When it assessed the reliability of data, CAWIA in 1969 [4] decided to add one significant figure and the A_r(Au) value thus became 196.9665(1). The atomic weight and uncertainty of Au were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{80}$Hg **Mercury (Hydrargyrum)** A_r(Hg) = 200.59(2) [Since 1989]

Isotope	Atomic mass/u	Mole fraction
^{196}Hg	195.965 814(4)	0.0015(1)
^{198}Hg	197.966 752(3)	0.0997(20)
^{199}Hg	198.968 262(3)	0.1687(22)
^{200}Hg	199.968 309(3)	0.2310(19)
^{201}Hg	200.970 285(3)	0.1318(9)
^{202}Hg	201.970 625(3)	0.2986(26)
^{204}Hg	203.973 475(3)	0.0687(15)

The name derives from the Roman god Mercury, the nimble messenger of the gods, because the ancients used that name for the element known from prehistoric times. The chemical symbol, Hg, derives from the Greek *hydrargyrum* for "liquid silver" or quick silver.

The CAWIA report in 1961 [22] proposed A_r(Hg) = 200.59 based on the chemical determination by Hönigschmid et al. [453], to which in 1969 CAWIA assigned an uncertainty $U[A_r(\text{Hg})] = 0.03$ [4]. Recalculation of the chemical ratios [453] based on current values of the other atomic weights as they were in 1983 [11] yielded the following results from the listed comparisons:

$HgCl_2/2Ag$ = 1.258 47 A_r(Hg) = 200.592
$HgBr_2/2Ag$ = 1.670 56 A_r(Hg) = 200.593 [453]

Published measurements of the isotopic composition of Hg [66,354,454,455] agree remarkably well, giving A_r(Hg) values in the range 200.58 to 200.60. No significant variations of terrestrial sources have been reported, but Haeffner [456] observed isotope separation in a Hg column by an electric current. The lighter isotopes become enriched at the anode as for Ga (see Ga section). The isotopic composition reported by Dibeler [455] is subject to a small unresolved uncertainty because it fails to sum to 100 %. In 1985, Wapstra and Audi [50] produced a table of atomic masses, which revised the values for Hg isotopes. This change did not affect the A_r(Hg) value at the stated precision. CAWIA maintained $U[A_r(\text{Hg})] = 0.03$ in recognition of the possibility of illusory agreement between the experimental A_r(Hg) determinations. In 1989, new measurements of Hg isotope abundances by Zadnik et al. [174] led CAWIA to reexamine its atomic weight [14]. The new measurement was not calibrated with synthetic isotope mixtures, but revealed small errors in the previously accepted relative abundances. Consequently, CAWIA left A_r(Hg) = 200.59, but reduced the uncertainty from 0.03 to 0.02.

$_{81}$Tl **Thallium** A_r(Tl) = 204.3833(2) [Since 1985]

Isotope	Atomic mass/u	Mole fraction
^{203}Tl	202.972 329(3)	0.2952(1)
^{205}Tl	204.974 412(3)	0.7048(1)

The name derives from the Greek *thallos* for "green shoot or twig" because of the bright green line in its spectrum. It was discovered by the English physicist and chemist William Crookes in 1861. The metal was first isolated by the French chemist Claude-August Lamy in 1862.

CAWIA in 1961 [22] recommended A_r(Tl) = 204.37 for the atomic weight of Tl based on the chemical determinations of Hönigschmid et al. [457] and Hönigschmid and Striebel [458]. After a reevaluation of the probable uncertainties in the previous work, CAWIA in 1969 [4] recommended $U[A_r(\text{Tl})] = 0.03$. In 1979, CAWIA [9] considered the calibrated measurement of Dunstan et al. [175] and recommended A_r(T1) = 204.383(1). These authors also reported, following a comprehensive mineral survey of terrestrial material, that no natural variations were found in the Tl isotope ratio. In 1985, the atomic weight and uncertainty were revised from 204.383(1) to 204.3833(2) to be consistent with the Technical Guidelines [12]. Recent studies have indicated substantial variation in $n(^{205}\text{Tl})/n(^{203}\text{Tl})$

of natural materials [459,460], some of which are not included within the range of uncertainty of the standard atomic weight and may justify a reevaluation by CAWIA of the atomic-weight uncertainty or annotations [85].

$_{82}$Pb Lead (Plumbum) A_r(Pb) = 207.2(1) g, r [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{204}Pb	203.973 028(3)	0.014(1)
^{206}Pb	205.974 449(3)	0.241(1)
^{207}Pb	206.975 880(3)	0.221(1)
^{208}Pb	207.976 636(3)	0.524(1)

The name derives from the Anglo-Saxon *lead*, which is of unknown origin. The element was known from prehistoric times. The chemical symbol Pb is derived from the Latin *plumbum*.

The atomic weight of Pb is quite variable in nature because the three heaviest isotopes are the stable end-products of the radioactive decay of U (^{238}U to ^{206}Pb; ^{235}U to ^{207}Pb) and Th (^{232}Th to ^{208}Pb). Recognizing this, CAWIA in 1961 [22] recommended an atomic weight of 207.19 that was based on the chemical measurements of Baxter and Alter [461], Baxter et al. [462], and Hönigschmid et al. [463], and stated that "...it quite well represented the lead most likely to be encountered in normal laboratory work." However, CAWIA policy now aims for the implied range of the standard atomic weights to cover all "normal" sources of an element. In the 1969 report [4], CAWIA considered the tabulation by Brown [464] and the work of Catanzaro et al. [176] showing natural variations in the atomic weight of Pb ranging from 207.184 to 207.293 and recommended the value of A_r(Pb) = 207.2(1). These circumstances justify the annotation "r". In addition, the annotation "g" warns of the existence of abnormal sources outside the implied range.

The variability of A_r(Pb) had been incontrovertibly shown by Richards and Lembert [43] when the chemical atomic weights were thought to be constants of Nature, before the discovery of isotopes. The isotopic composition of common Pb must now be regarded as a variable mixture of primeval and radiogenic components. When an atomic-weight value of a specific sample is required to an accuracy better than the precision of the tabulated standard A_r(E) value, an isotope-abundance measurement must be made on that sample. Such measurements are facilitated by comparison with a standard reference material of known abundance, such as is available from the work of Catanzaro et al. [176].

The decay of U and Th to Pb permits geological age determinations to be made of minerals containing the heavy radioactive elements [77]. Extensive use of Pb over the history of mankind has led to widespread pollution [465], and the isotope-abundance variations reflected in the atomic weights enable historical and modern sources to be identified [181].

$_{83}$Bi Bismuth A_r(Bi) = 208.980 38(2) [Since 1995]

Isotope	Atomic mass/u	Mole fraction
^{209}Bi	208.980 384(3)	1.0000

The name derives from the German *weisse masse* for "white mass" from the color of its oxides. The ancients did not distinguish bismuth from lead. The French chemist Claude-Francois Geoffroy showed that bismuth was distinct from lead in 1753.

The CAWIA report in 1961 [22] recommended A_r(Bi) = 208.980, based on atomic mass data from Everling et al. [23]. Leipziger [119] found the upper limits for the abundances of stable or quasi-stable isotopes of Bi other than ^{209}Bi to be low. In its 1969 report [4], CAWIA decided to add a significant figure and recommended A_r(Bi) = 208.9806(1), based on the data available at that time; however, this value was adjusted in 1971 to 208.9804(1) [5] as a result of Wapstra and Gove's revision of atomic mass data [48]. This change in atomic weight, though small and seemingly insignificant to most chemists, is twice the previously estimated uncertainty and may dispel any impression that CAWIA tends to be excessively conservative in the dissemination of reliable atomic weights. The atomic weight and uncertainty of Bi were changed to their current values in the 1995 report of CAWIA [17], based on the atomic mass data of Audi and Wapstra [51].

$_{90}$Th Thorium A_r(Th) = 232.0381(1) g [Since 1969]

Isotope	Atomic mass/u	Mole fraction
^{232}Th	232.038 0495(22)	1.0000

The name derives from Thor, the Scandinavian god of thunder. It was discovered in the mineral thorite ($ThSiO_4$) by the Swedish chemist Jöns Jacob Berzelius in 1828. It was first isolated by the chemists D. Lely, Jr. and L. Hamburger in 1914.

Thorium is considered a monoisotopic element by CAWIA because only one isotope has a half-life greater than 10^{10} a. ^{232}Th is an α-emitter with a half-life of $1.40(1) \times 10^{10}$ a, decaying through a branched series to ^{208}Pb without very long-lived intermediate isotopes. ^{230}Th is a nuclide in the ^{238}U decay series. It has a half-life of $7.54(2) \times 10^4$ a, and is formed by α decay of ^{234}U. ^{230}Th also has been called ionium, as if it were a distinct element, but that name is not recognized by IUPAC. In its 1961 report [22], CAWIA recommended A_r(Th) = 232.038. In 1969, CAWIA [4] added a significant figure and recommended A_r(Th) = 232.0381(1). These values have remained unchanged since then.

By virtue of its long half-life, about 80 % of the ^{232}Th present when the earth was formed survives to this time. ^{230}Th is not generally found in substantial amounts in normal sources of Th, but it is readily detected in seawater and other substances in variable amounts relative to ^{232}Th. The annotation "g" was added on the basis of reported ^{230}Th enrichments in ocean sedimentation studies [466,467]. The ^{232}Th-^{208}Pb decay scheme is of value to geochronology [77].

$_{91}$Pa Protactinum A_r(Pa) = 231.035 88(2) [Since 1989]

Isotope	Atomic mass/u	Mole fraction
^{231}Pa	231.035 88(2)	1.0000

The name protactinium derives from the Greek πρωτος (first) for preceding the element actinium, because its most common isotope (^{231}Pa) decays to ^{227}Ac by loss of an α particle. ^{234}Pa was the first isotope of Pa to be identified in 1913 by the German chemists K. Fajans and O. H. Göhring, who proposed the name "brevium" because of that isotope's short half-life of 6.7 h. ^{231}Pa, with a longer half-life of $3.25(1) \times 10^4$ a, was identified in 1918 by the German chemist O. Hahn and the Austrian physicist L. Meitner; and, independently in Britain, by F. Soddy and J. A. Cranston. The name protactinium was adopted for Pa by IUPAC in 1949 by shortening the previous name proto-actinium, referring to its relation to the decay product of ^{231}Pa, of which the German chemist A. V. Grosse first isolated weighable quantities.

Primordial Pa has long since disappeared from the earth. The only terrestrial source of Pa is by radioactive decay of heavier elements, almost entirely from U, the ores of which contain the two isotopes ^{231}Pa and ^{234}Pa in equilibrium proportions. ^{234}Pa is a decay product in the ^{238}U series, whereas ^{231}Pa occurs in the ^{235}U series. Owing to its much longer half-life, ^{231}Pa is by far the more abundant Pa isotope even in U samples with more than 99 % ^{238}U. Chemists interested in the properties of Pa will first separate that element from its U source. A week after the separation, the remaining Pa will be essentially pure ^{231}Pa. Other Pa isotopes with short half-lives occur in the ^{241}Pu decay series (^{233}Pa with half-life 27.0 d), and are produced by transuranium isotope production in low-enrichment U fuels (^{238}Pa with half-life 2.3 m and ^{237}Pa with half-life 8.7 m).

The mean relative mass of a given sample of Pa in the presence of U depends not only on the geologically recent history of the specimen, but also on the isotopic composition of U. Consequently, in the past, CAWIA did not recommend a standard atomic weight for Pa. Subsequently, CAWIA [4] recommended A_r(Pa) = 231.0359(1) in 1969, which corresponded approximately to that of pure ^{231}Pa, but which included within its uncertainty also the average atomic weight of Pa in the presence of its radioactive U source. The atomic weight of Pa was dropped from the Table of Standard Atomic Weights in 1983 [11] because it has no long-lived stable isotopes and therefore does not fit the normal CAWIA definition of a "monoisotopic" element. Nevertheless, the atomic weight of Pa was restored to the TSAW in 1989 [14] when CAWIA recommended A_r(Pa) = 231.035 88(2), which corresponded to that of pure ^{231}Pa. The 1989 uncertainty reflects that of the atomic mass determination [50], expanded according to standard CAWIA rules for monoisotopic elements. The atomic weight of Pa isotopes in radioactive equilibrium with normal U (including both ^{231}Pa and ^{234}Pa) is not included within this uncertainty because ^{234}Pa will decay rapidly to insignificance after chemical separation of the Pa from the U.

$_{92}$U Uranium A_r(U) = 238.028 91(3) g, m [Since 1999]

Isotope	Atomic mass/u	Mole fraction
^{234}U	234.040 9447(22)	0.000 054(5)
^{235}U	235.043 9222(21)	0.007 204(6)
^{238}U	238.050 7835(22)	0.992 742(10)

The name derives from the planet Uranus, which in Roman mythology was "Father Heaven". The German chemist Martin-Heinrich Klaproth discovered the element in 1789, following the German/English astronomer William Hershel's discovery of the planet in 1781. The metal was first isolated by the French chemist Eugène-Melchior Peligot in 1841.

In its 1961 report [22], CAWIA recommended A_r(U) = 238.03(1) for the atomic weight of U based on mass-spectrometric determinations by White et al. [127] and those quoted by Greene et al. [468], with atomic masses by Everling et al. [23]. This literature included a calibrated measurement of the natural isotopic composition. The uncertainty included an allowance for up to 0.1 % variation in the ^{235}U abundance, which was interpreted as 0.007 205 ± 0.001. The actual variability in normal sources is found to be much smaller, close to 0.1 % of the abundance value, which would be 0.007 205 ± 0.000 007. In 1969, CAWIA [4] recommended A_r(U) = 238.029(1) based on the earlier measurements and a more careful analysis of the variability of U in nature. In 1979, CAWIA [9] took note of later studies of the variations of the ^{235}U abundance in normal sources by Smith and Jackson [469] and Cowan and Adler [470]. A more precise value for the standard atomic weight was considered justified, thus leading to A_r(U) = 238.0289(1). The atomic weight and uncertainty of U were changed to 238.028 91(3) in the 1999 CAWIA meeting [19] on the basis of calibrated mass-spectrometric measurements by Richter et al. [179]. That value applies to U as found in normal terrestrial sources, except as discovered in one locality in southwest Africa (Gabon at Oklo), hence the annotation "g". Uranium is used in the nuclear fuel cycle either enriched or depleted in ^{235}U, hence the annotation "m". Atomic weights of such materials must be calculated from the experimentally determined isotopic composition. Such measurements are facilitated by comparison with a reference material of known isotopic composition.

All U isotopes are α-emitters. Half-lives are: for ^{234}U: 2.454(6) × 10^5 a; for ^{235}U: 7.037(11) × 10^8 a; and for ^{238}U: 4.468(5) × 10^9 a. The latter two are primordial with the ^{235}U abundance declining very gradually in geological time because of its faster decay. ^{234}U, itself a daughter of ^{238}U, is in equilibrium established by the ratio of the half-lives. ^{235}U decays by a branched series ending with ^{207}Pb, ^{238}U (and ^{234}U) by a similar series ending in ^{206}Pb. The ^{238}U-^{206}Pb and the^{235}U-^{207}Pb decay systems are of fundamental importance in geochronology [77].

REFERENCES

1. H. A. Becquerel. *Comptes Rendus, Paris* **122**, 420–421 (1896).
2. N. E. Holden. *Chem. Intern.* **6**, 5–12 (1984).
3. "Atomic weights of the elements 1967", *Pure Appl. Chem.* **18**, 569–579 (1969).
4. "Atomic weights of the elements 1969", *Pure Appl. Chem.* **21**, 91–108 (1970).
5. "Atomic weights of the elements 1971", *Pure Appl. Chem.* **30**, 637–649 (1972).
6. "Atomic weights of the elements 1973", *Pure Appl. Chem.* **37**, 591–603 (1974).
7. "Atomic weights of the elements 1975", *Pure Appl. Chem.* **47**, 75–95 (1976).
8. "Atomic weights of the elements 1977", *Pure Appl. Chem.* **51**, 405–433 (1979).
9. N. E. Holden. "Atomic weights of the elements 1979", *Pure Appl. Chem.* **52**, 2349–2384 (1980).
10. N. E. Holden and R. L. Martin. "Atomic weights of the elements 1981", *Pure Appl. Chem.* **55**, 1101–1118 (1983).
11. N. E. Holden and R. L. Martin. "Atomic weights of the elements 1983", *Pure Appl. Chem.* **56**, 653–674 (1984).
12. "Atomic weights of the elements 1985", *Pure Appl. Chem.* **58**, 1677–1692 (1986).
13. "Atomic weights of the elements 1987", *Pure Appl. Chem.* **60**, 841–854 (1988).
14. "Atomic weights of the elements 1989", *Pure Appl. Chem.* **63**, 975–990 (1991).
15. "Atomic weights of the elements 1991", *Pure Appl. Chem.* **64**, 1519–1534 (1992).
16. "Atomic weights of the elements 1993", *Pure Appl. Chem.* **66**, 2423–2444 (1994).
17. T. B. Coplen. "Atomic weights of the elements 1995", *Pure Appl. Chem.* **68**, 2339–2359 (1996).
18. R. D. Vocke. "Atomic weights of the elements 1997", *Pure Appl. Chem.* **71**, 1593–1607 (1999).
19. T. B. Coplen. "Atomic weights of the elements 1999", *Pure Appl. Chem.* **73**, 667–683 (2001).
20. F. W. Clarke. In *The Constants of Nature*, National Academy of Sciences, Vol. XVI, Third Memoir, pp. 1–418, Government Printing Office, Washington, DC (1920).
21. A. O. Nier. *Z. Elektrochem.* **58**, 559–567 (1954).
22. A. E. Cameron and E. Wichers. *J. Am. Chem. Soc.* **84**, 4175–4197 (1962).
23. F. Everling, L. A. König, J. M. E. Mattauch, A. H. Wapstra. *Nucl. Phys.* **18**, 529–569 (1960)
24. H. S. Peiser, N. E. Holden, P. De Bièvre, I. L. Barnes, R. Hagemann, J. R. de Laeter, T. J. Murphy, E. Roth, M. Shima, H. G. Thode. *Pure Appl. Chem.* **56**, 695–768 (1984).
25. H. S. Peiser. *Anal. Chem.* **57**, 511–517 A (1985).
26. J. Dalton. *Memoirs Lit. Phil. Soc. Manchester* **1**, 271–287 (1805).
27. A. Avogadro. *J. de Physique* **73**, 58–76 (1811).
28. W. Prout and T. Thompson. *Annals Phil.* **7**, 111–113 (1815).
29. S. Cannizzaro. *Nuovo Cimento* **7**, 321–366 (1858).
30. D. I. Mendeleyev. *J. Russ. Chem. Soc.* **1**, 60–77 (1869).
31. F. W. Clarke. *J. Am. Chem. Soc.* **18**, 197–214 (1896).
32. N. E. Holden. *J. Royal Soc. West. Aust.* **79**, 21–25 (1996).
33. H. C. Urey. *J. Chem. Soc.* 562–581 (1947).
34. P. De Bièvre. *Adv. Mass Spectrom.* **7A**, 395–447 (1976).
35. P. De Bièvre. *Fresenius' J. Anal. Chem.* **337**, 766–771 (1990).
36. J. R. de Laeter, P. De Bièvre, H. S. Peiser. *Mass Spectrom. Rev.* **11**, 193–245 (1992).
37. P. De Bièvre, J. R. de Laeter, H. S. Peiser, W. P. Reed. *Mass Spectrom. Rev.* **12**, 143–172 (1993).
38. ISO, IEC, OIML, BIPM. *Guide to the Expression of Uncertainty in Measurement,* ISO, Geneva (1995).
39. W. Ramsey and F. Soddy. *Proc. Royal Soc. London* **72**, 204–207 (1905).
40. F. Soddy. *J. Chem. Soc.* **99**, 72–83 (1911).
41. G. P. Baxter and J. H. Wilson. *J. Am. Chem. Soc.* **30**, 187–195 (1908).
42. F. Soddy and H. Hyman. *J. Chem. Soc.* **105**, 1402–1408 (1914).
43. T. W. Richards and M. E. Lembert. *J. Am. Chem. Soc.* **36**, 1329–1344 (1914).

44. J. J. Thomson. *Phil. Mag.* **24**, 668–693 (1912).
45. F. W. Aston. *Phil. Mag.* **39**, 449–455 (1920).
46. F. W. Aston. *Mass Spectra and Isotopes*, Edward Arnold, London (1933).
47. F. W. Aston. *Nature* **123**, 313 (1929).
48. A. H. Wapstra and N. B. Gove. *Atom. Data Nuclear Data Tables* **9**, 265–468 (1971).
49. A. H. Wapstra and K. Bos. *Atom. Data Nucl. Data Tables* **19**, 175–237 (1977).
50. A. H. Wapstra and G. Audi. *Nucl. Phys. A* **432**, 1–54 (1985).
51. G. Audi and A. H. Wapstra. *Nucl. Phys. A* **565**, 1–65 (1993).
52. P. J. Mohr and B. N. Taylor. *J. Phys. Chem. Ref. Data* **28**, 1713–1852 (1999).
53. F. DiFillipo, V. Natarajan, K. R. Boyce, D. E. Pritchard. *Phys. Rev. Let.* **73**, 1481–1483 (1994).
54. A. J. Dempster. *Science* **52**, 559 (1920).
55. A. J. Dempster. *Phys. Rev.* **18**, 415–422 (1921).
56. A. J. Dempster. *Phys. Rev.* **20**, 631–638 (1922).
57. P. De Bièvre. *J. Royal Soc. West. Aust.* **79,** 11–19 (1996).
58. S. Valkiers, Y. Aregbe, P. D. P. Taylor, P. De Bièvre. *Int. J. Mass Spectrom. Ion Proc.* **173**, 55–63 (1998).
59. S. Valkiers, H. Kipphardt, T. Ding, R. Damen, P. De Bièvre, P. D. P. Taylor. *Int. J. Mass Spectrom. Ion Proc.* **193**, 1–8 (1999).
60. P. D. P. Taylor, S. Valkiers, P. De Bièvre, U. Flegel, D. Kruck. *Anal. Chem.* **65,** 3166–3167 (1993).
61. W. F. Giauque and H. L. Johnston. *Nature* **123**, 318 (1929).
62. W. F. Giauque and H. L. Johnston. *Nature* **123**, 831 (1929).
63. H. E. Duckworth and A. O. Nier. *Int. J. Mass Spectrom. Ion Proc.* **86**, 1–19 (1988).
64. T. P. Kohman, J. H. E. Mattauch, A. H. Wapstra. *Science* **127**, 1431–1432 (1959).
65. A. O. Nier. *Phys. Rev.* **77**, 789–793 (1950).
66. A. O. Nier. *Phys. Rev.* **79**, 450–454 (1950).
67. F. L. Mohler. *Science* **122**, 334–335 (1955).
68. G. A. Uriano and C. C. Gravett. *Crit. Rev. Anal. Chem.* **6**, 361–411 (1977).
69. L. J. Powell and T. J. Murphy. *Chem. Tech.* **14**, 726–730 (1984).
70. R. Gonfiantini, P. De Bièvre, S. Valkiers, P. D. P. Taylor. *IEEE Trans Instrum. Meas.* **46**, 566–571 (1997).
71. P. De Bièvre, S. Valkiers, R. Kessel, P. D. P. Taylor, P. Becker, H. Bettin, A. Peuto, S. Pettorruso, K. Fujii, A. Waseda, M. Tanaka, R. D. Deslattes, H. S. Peiser, M. J. Kenny. *IEEE Trans. Instrum. Meas.* **50**, 593–597 (2001).
72. K. J. R. Rosman and P. D. P. Taylor. *Pure Appl. Chem.* **70**, 217–235 (1998).
73. P. De Bièvre, M. Gallet, N. E. Holden, I. L. Barnes. *J. Phys. Chem. Ref. Data* **13**, 809–891 (1984).
74. E. Roth and B. Poty (Eds.). *Nuclear Methods of Dating*, Kluwer, Dordrecht (1989).
75. A. O. Nier and E. A. Gulbransen. *J. Am. Chem. Soc.* **61**, 697–698 (1939).
76. IAEA. *Stable Isotope Hydrology, International Atomic Energy Agency, Technical Reports Series,* **210**, Vienna (1981).
77 . G. Faure. *Principles of Isotope Geology,* 2nd ed., Wiley, New York (1986).
78. J. Hoefs. *Stable Isotope Geochemistry,* 3rd ed., Springer Verlag, New York (1987).
79. H. R. Krouse and V. A. Grinenko (Eds.). *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment,* Wiley, New York (1991).
80. E. Roth. *Pure Appl. Chem.* **69**, 1753-1828 (1997).
81. P. G. Cook and A. Herczeg (Eds.). *Environmental Tracers in Subsurface Hydrology,* Kluwer, Dordrecht (1999).
82. C. R. McKinney, J. M. McCrea, S. Epstein, H. A. Allen, H. C. Urey. *Rev. Sci. Instrum.* **21**, 724–730 (1950).
83. J. H. Reynolds. *Rev. Sci. Instrum.* **27**, 928–934 (1956).

84. A. Barrie and S. J. Prosser. In *Mass Spectrometry of Soils,* T. W. Boutton and S. Yamasaki (Eds.), Marcel-Dekker, New York (1996).
85. T. B. Coplen, J. K. Böhlke, P. De Bièvre, T. Ding, N. E. Holden, J. A. Hopple, H. R. Krouse, A. Lamberty, H. S. Peiser, K. Révész, S. E. Rieder, K. J. R. Rosman, E. Roth, P. D. P. Taylor, R. D. Vocke, Jr., Y. K. Xiao. *Pure Appl. Chem.* **74**, 1987–2017 (2002).
86. H. G. Thode, J. MacNamara, F. P. Lossing, C. B. Collins. *J. Am. Chem. Soc.* **70**, 3008–3011 (1948).
87. C. C. McMullen, C. B. Cragg, H. G. Thode. *Geochim. Cosmochim. Acta* **23**, 147–149 (1961).
88. M. H. Thiemens. *Science* **283**, 341–345 (1999).
89. R. D. Loss, K. J. R. Rosman, J. R. de Laeter, D. B. Curtis, A. J. Gancarz, T. M. Benjamin, W. J. Maeck and J. E. Delmore. *Chem. Geol.* **76**, 71–84 (1989).
90. J. R. de Laeter and K. J. R. Rosman. *Proc. Intern. Symp. on the Oklo Phenomenon,* Gabon, IAEA, Vienna, 425–436 (1975).
91. P. De Bièvre and H. S. Peiser. *Pure Appl. Chem.* **64,** 1535–1543 (1992).
92. J. R. de Laeter. *Mass Spectrom. Rev.* **9**, 453–497 (1990).
93. P. De Bièvre. *Z. Anal. Chem.* **264**, 365–371 (1973).
94. H. P. Qi, T. B. Coplen, Q. Zh. Wang, Y. H. Wang. *Anal. Chem.* **69**, 4076–4078 (1997).
95. H. P. Qi, M. Berglund, P. D. P. Taylor, F. Hendrickx, A. Verbruggen, P. De Bièvre. *Fresenius' J. Chem.* **361**, 767–773 (1998).
96. R. T. Birge. *Phys. Rev*. **40**, 207–261 (1932).
97. H. S. Peiser, P. De Bièvre, P. R. Goodman, H. H. Ku. *Accred. Qual. Assur.* **1**, 67–70 (1996).
98. M. R. Moldover, J. P. M. Trusler, T. J. Edwards, J. B. Mehl, R. S. Davis. *J. Res. Natl. Bur. Stand. (U.S.)* **94**, 85–144 (1988).
99. E. R. Cohen and B. N. Taylor. *Rev. Mod. Phys.* **59**, 1121–1148 (1987).
100. E. R. Cohen and B. N. Taylor. *J. Phys. Chem. Ref. Data* **2**, 663–734 (1973).
101. V. E. Bower and R. S. Davis. *J. Res. Natl. Bur. Stand. (U.S.)* **85**, 175–191 (1980).
102. L. J. Powell, T. J. Murphy, J. W. Gramlich. *J. Res. Natl. Bur. Stand. (U.S.)* **87**, 9–19 (1982).
103. W. H. Bragg and W. L. Bragg. *Proc. Royal Soc. A* **88**, 428–438 (1913).
104. W. L. Bragg and P. Seyfried. Private communications to S. Peiser.
105. R. D. Deslattes, A. Hennins, H. A. Bowman, R. M. Schoonover, C. L. Carroll, I. L. Barnes, L. A. Machlan, L. J. Moore, W. R. Shields. *Phys. Rev. Lett.* **33**, 463–466 (1974).
106. P. Seyfried, P. Becker, A. Kozdon, F. Lüdicke, F. Spieweck, J. Stümpel, H. Wagenbreth, D. Windisch, P. De Bièvre, H. H. Ku, G. Lenaers, T. J. Murphy, H. S. Peiser, S. Valkiers. *Z. Phys. B* **87**, 289–298 (1992).
107. P. De Bièvre, S. Valkiers, R. Gonfiantini, P. D. P. Taylor, H. Bettin, F. Spieweck, A. Peuto, S. Pettorusso, M. Mosca, K. Fujii, H. Tanaka, Y. Nezu, A. Leistner, W. Giardini. *IEEE Trans. Instrum. Meas.* **46**, 592–595 (1997).
108. P. De Bièvre, S. Valkiers, P. D. P. Taylor. *Fresenius' J. Anal. Chem.* **361**, 227–234 (1998).
109. P. De Bièvre and H. S. Peiser. *Metrologia* **34**, 49–59 (1997).
110. E. Roth. *Interdisc. Sci. Rev.* **2**, 75–85 (1977).
111. T. B. Coplen and H. S. Peiser. *Pure Appl. Chem.* **70**, 237–257 (1998).
112. N. E. Holden, R. L. Martin, I. L. Barnes. *Pure Appl. Chem.* **55**, 1119–1136 (1983).
113. N. E. Holden, R. L. Martin, I. L. Barnes. *Pure Appl. Chem.* **56**, 675–694 (1984).
114. IUPAC Commission on Atomic Weights and Isotopic Abundances. *Pure Appl. Chem.* **63**, 991–1002 (1991).
115. F. Schaefer, P. D. P. Taylor, S. Valkiers, P. De Bièvre. *Int. J. Mass Spectrom. Ion Proc.* **133**, 65–71 (1994).
116. R. Hagemann, G. Nief, E. Roth. *Tellus* **22**, 712–715 (1970).
117. Y. Sano, H. Wakita, X. Sheng. *Geochem. J.* **22**, 177–181 (1988).

118. H. P. Qi, P. D. P. Taylor, M. Berglund, P. De Bièvre. *Int. J. Mass. Spectrom. Ion Proc.* **171**, 263–268 (1997).
119. F. D. Leipziger. *Appl. Spectros.* **17**, 158–160 (1963).
120. P. De Bièvre and G. H. Debus. *Int. J. Mass Spectrom. Ion Phys.* **2**, 15–23 (1969).
121. T.-L. Chang and W.-Li. *Chin. Sci. Bull.* **35**, 290–296 (1990).
122. G. Junk and H. J. Svec. *Geochim. Cosmochim. Acta* **14**, 234–243 (1958).
123. P. Baertschi. *Earth Planet. Sci. Lett.* **31**, 341–344 (1976).
124. W.-Li, D. Jin, T.-L. Chang. *Kexue Tinboa* **33**, 1610–1613 (1988).
125. F. W. Aston. *Philos. Mag.* **40**, 628 (1920).
126. D. J. Bottomley, J. D. Ross, W. B. Clarke. *Geochim. Cosmochim. Acta* **48**, 1973–1985 (1984).
127. F. A. White, T. L. Collins, F. M. Rourke. *Phys. Rev.* **101**, 1786–1791 (1956).
128. J. R. White and A. E. Cameron. *Phys. Rev.* **74**, 991–1000 (1948).
129. T. Ding, S. Valkiers, H. Kipphardt, R. Damen, P. De Bièvre, P. D. P. Taylor, R. Gonfiantini, H. R. Krouse. *Geochim. Cosmochim. Acta* **65**, 2433–2437 (2001).
130. W. R. Shields, T. J. Murphy, E. L. Garner, V. H. Dibeler. *J. Am. Chem. Soc.* **84**, 1519–1522 (1961).
131. E. L. Garner, T. J. Murphy, J. W. Gramlich, P. J. Paulsen, I. L. Barnes. *J. Res. Natl. Bur. Stand. (U.S.)* **79A**, 713–725 (1975).
132. L. J. Moore and L. A. Machlan. *Anal. Chem.* **44**, 2291–2296 (1972).
133. W. T. Leland. *Phys. Rev.* **77**, 634–640 (1950).
134. M. Shima and N. Torigoye. *Int. J. Mass Spectrom. Ion Proc.* **123**, 29–39 (1993).
135. G. D. Flesch, J. Capellen, H. J. Svec. *Advanced Mass Spectrometry III*, pp. 571–581, Leiden, London (1996)
136. W. R. Shields, T. J. Murphy, E. J. Catanzaro, E. L. Garner. *J. Res. Natl. Bur. Stand. (U.S.)* **70A**, 193–197 (1966).
137. P. D. P. Taylor, R. Maeck, P. De Bièvre. *Int. J. Mass Spectrom. Ion. Proc.* **121**, 111–125 (1992).
138. H. J. Mattraw and C. F. Pachucki. *United States Atomic Energy Commission, Rep., AECU* **1903** (1952); see also *Nucl. Sci. Abstr.* **6**, 320 (1952).
139. W. R. Shields, S. S. Goldich, E. L. Garner, T. J. Murphy. *J. Geophys. Res.* **70**, 479–491 (1965).
140. T.-L. Chang, M.-T. Zhao, W.-J. Li, J. Wang, Q.-Y. Qian. *Int. J. Mass Spectrom.* **208**, 113–118 (2001).
141. L. A. Machlan, J. W. Gramlich, L. J. Powell, G. M. Lambert. *J. Res. Natl. Bur. Stand. (USA)* **91**, 323–331 (1986).
142. O. Hönigschmid and L. Görnhardt. *Naturwissenschaften* **32**, 68 (1944).
143. E. J. Catanzaro, T. J. Murphy, E. L. Garner, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **68A**, 593–599 (1964).
144. Y. Aregbe, S. Valkiers, J. Poths, J. Norgaard, H. Kipphardt, P. De Bièvre, P. D. P. Taylor. *Int. J. Mass Spectrom.* **206**, 129–136 (2001).
145. E. J. Catanzaro, T. J. Murphy, E. L. Garner, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **73A**, 511–516 (1969).
146. L. J. Moore, T. J. Murphy, I. L. Barnes, P. J. Paulsen. *J. Res. Natl. Bur. Stand. (U.S.)* **87**, 1–8 (1982).
147. T. L. Collins, F. M. Rourke, F. A. White. *Phys. Rev.* **105**, 196–197 (1957).
148. M. Nomura, K. Kogure, M. Okamoto. *Int. J. Mass Spectrom. Ion Phys.* **50**, 219–227 (1983).
149. M. E. Wieser and J. R. de Laeter. *Int. J. Mass Spectrom.* **197**, 253–261 (2000).
150. M. Huang and A. Masuda. *Anal. Chem.* **69**, 1135 (1997)
151. M. Shima. *Int. J. Mass Spectrom. Ion Phys.* **28**, 129–140 (1978).
152. K. J. R. Rosman, I. L. Barnes, L. J. Moore, J. W. Gramlich. *Geochem. J.* **14**, 269–277 (1980).
153. T.-L. Chang and Y.-K. Xiao. *Chin. Chem. Lett.* **2**, 407 (1991).
154. C. Devillers, T. Lecomte, R. Hagemann. *Int. J. Mass Spectrom. Ion Phys.* **50**, 205–217 (1983).
155. K. J. R. Rosman, R. D. Loss, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Proc.* **56**, 281–291 (1984).

156. T.-L. Chang, Q.-Y. Qian, M.-T. Zhao, J. Wang. *Int. J. Mass Spectrom. Ion Proc.* **123**, 77–82 (1993).
157. C. L. Smith, K. J. R. Rosman, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Phys.* **28**, 7–17 (1978).
158. W. T. Leland. *Phys. Rev.* **76**, 992 (1949).
159. O. Eugster, F. Tera, G. J. Wasserburg. *J. Geophys. Res.* **74**, 3897–3908 (1969).
160. A. Makishima, H. Shimizu, A. Masudu. *Mass Spectrosc.* **35**, 64 (1987)
161. T.-L. Chang, Q.-Y. Qian, M.-T. Zhao, J. Wang, Q.-Y. Lang. *Int. J. Mass Spectrom. Ion Proc.* **142**, 125–131 (1995).
162. P. Holliger and C. Devillers. *Earth Planet. Sci. Lett.* **52**, 76–84 (1981).
163. T. L. Chang and G. S. Qiao. *Chin. Chem. Lett.* **8**, 91 (1997).
164. T.-L. Chang, Q.-Y. Qian, M.-T. Zhao, J. Wang. *Int. J. Mass Spectrom. Ion Proc.* **139**, 95–102 (1994).
165. O. Eugster, F. Tera, D. S. Burnett, G. J. Wasserburg. *J. Geophys. Res.* **75**, 2753–2768 (1970).
166. T.-L. Chang, W.-J. Li, M.-T. Zhao, J. Wang, Q.-Y. Qian. *Int. J. Mass Spectrom.* **207**, 13–17 (2001).
167. T. L. Chang, M. T. Zhao, W. J. Li, J. Wang, Q. Y. Qian, Z. Y. Chu, *Int. J. Mass Spectrom. Ion Proc.* **177**, 131–136 (1998).
168. P. J. Patchett. *Geochim. Cosmochim. Acta* **48**, 81 (1983).
169. J. Völkening, M. Köppe, K. G. Heumann. *Int. J. Mass Spectrom. Ion Proc.* **107**, 361–368 (1991).
170. J. W. Gramlich, T. J. Murphy, E. L. Garner, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **77A**, 691–698 (1973).
171. J. Völkening, T. Walczyk, K. G. Heumann. *Int. J. Mass Spectrom. Ion Proc.* **105**, 147–159 (1991).
172. T. Walczyk and K. G. Heumann. *Int. J. Mass Spectrom. Ion Proc.* **123**, 139–147 (1993).
173. P. D. P. Taylor and P. De Bièvre. *Proc. Second Nier Symposium in Inorganic Mass Spectrometry*, Atomic Energy of Canada Ltd., AECL Report **AECL-11342**, 90–93 (1996).
174. M. G. Zadnik, S. Specht, F. Begemann. *Int. J. Mass Spectrom. Ion Proc.* **89**, 103–110 (1989).
175. L. P. Dunstan, J. W. Gramlich, I. L. Barnes, W. C. Purdy. *J. Res. Natl. Bur. Stand. (U.S.)* **85**, 1–10 (1980).
176. E. J. Catanzaro, T. J. Murphy, W. R. Shields, E. L. Garner. *J. Res. Nat. Bur. Stand.* **72A**, 261–267 (1968).
177. A. J. Dempster. *Nature (London)* **136**, 120 (1936).
178. D. Brown. *Gmelin Handbuch der Anorg. Chem.* **6** (1977)
179. S. Richter, A. Alonso, W. De Bolle, R. Wellum, P.D.P. Taylor. *Int. J. Mass Spectrom. Ion Proc.* **193**, 9–14 (1999).
180. T. B. Coplen, J. A. Hopple, J. K. Böhlke, H. S. Peiser, S. E. Rieder, H. R. Krouse, K. J. R. Rosman, T. Ding, R. D. Vocke, Jr., K. M. Révész, A. Lamberty, P. Taylor, P. De Bièvre. *U.S. Geological Survey Water-Resources Investigations Report 01-4222* (2002).
181. K. J. R. Rosman and W. Chisholm. *J. Royal Soc. West. Aust.* **79**, 92–102 (1996)
182. A. B. Kersting, D. W. Efurd, D. L. Finnegan, D. J. Rokop, D. K. Smith, J. L. Thompson. *Nature* **397**, 56–59 (1999).
183. C. Guillou, J. Koziet, A. Rossman, G. J. Martin. *Anal. Chim. Acta* **388**, 137–143 (1999).
184. W. Chisholm and K. J. R. Rosman. *Anal. Chim. Acta* **311,** 141–151 (1995).
185. I. Friedman. *Geochim. Cosmochim. Acta* **4**, 89–104 (1953).
186. J. Jouzel, C. Lorius, J. R. Petit, C. Genthon, N. I. Barkov, V. M. Kotlyakov, V. M. Petrov. *Nature* **329**, 403–408 (1987).
187. J. Ch. Fontes and R. Gonfiantini. *Earth Planet. Sci. Lett.* **3**, 258–266 (1967).
188. B. Gonsior, I. Friedman, G. Lindenmayr. *Tellus* **18**, 256–261 (1966).
189. E. Roth. *C. R. Acad. Sci., Paris* **242**, 3097–3100 (1956).
190. R. M. Coveney, Jr., E. D. Goebel, E. J. Zeller, G. A. M Dreschhoff, E. E. Angino. *American Association of Petroleum Geologists Bulletin* **71**, 39–48 (1987).

191. A. O. C. Nier. Private communication, quoted in *Nucl. Data Tables*, K. Way (Ed.), U.S. Government Printing Office, Washington, DC (1959).
192. B. A. Mamyrin, I. N. Tolstikhin, G. S. Anufriyev, I. L. Kamenskiy. *Trans. From Geokhimiya* **Ser. 5**, 595 (1969).
193. W. B. Clarke, W. J. Jenkins, Z. Top. *Int. J. Appl. Radiat. Isot.* **27**, 515–522 (1976).
194. B. A. Mamyrin and L. N. Tolstikhin. *Helium Isotopes in Nature*, Elsevier, Amsterdam (1984).
195. E. R. Dobbs. *Helium Three,* Oxford University Press, Oxford (2000).
196. T. W. Richards and H. H.Willard. *J. Am. Chem. Soc.* **32**, 4 (1910).
197. A. E. Cameron. *J. Am. Chem. Soc.* **77**, 2731–2733 (1955).
198. H. J. Svec and A. R. Anderson. *Geochim. Cosmochim. Acta* **29**, 633–641 (1965).
199. G. D. Flesch, A. R. Anderson, H. J. Svec. *Int. J. Mass Spectrom. Ion Phys.* **12**, 265–272 (1973).
200. E. L. Callis, A. E. Essling, G. Reedy, R. J. Meyer. *Proc. 28th Ann. Meeting American Society of Mass Spectrometry*, p. 202, New York (1980).
201. E. Michiels and P. De Bièvre. *Int. J. Mass Spectrom. Ion Phys.* **49**, 265–274 (1983).
202. C.-F. You and L.-H. Chan. *Geochim. Cosmochim. Acta* **60**, 909–915 (1996).
203. H. O. Finley, A. R. Eberle, C. J. Rodden. *Geochim. Cosmochim. Acta* **26**, 911–914 (1962).
204. H. P. Schwarcz, E. K. Agyei, C. C. McMullen. *Earth Planet. Sci. Lett.* **6**, 1–5 (1969); see also E. K. Agyei, Ph.D. thesis, McMaster Univ. (1968).
205. E. J. Catanzaro, C. E. Champion, E. L. Garner, G. Marinenko, K. M. Sappenfield, W. R. Shields. *NBS Special Publication* **260–17**, U.S. Printing Office (1970).
206. P. De Bièvre, G. H. Debus, J. Spaepen. *React. Technol. (J. Nucl. Energy A/B)* **17**, 349 (1963).
207. M. Nomura, T. Kanzaki, T Ozawa, M. Okamoto, H. Kakihana. *Geochim. Cosmochim. Acta* **46**, 2403–2406 (1982).
208. G. Wang and Y. K. Xiao. *Rock Mineral Anal.* **19**, 169–172 (2000).
209. A. Vengosh, A. R. Chivas, M. T. McCulloch, A. Starinsky, Y. Kolodny. *Geochim. Cosmochim. Acta* **55**, 2591–2606 (1991).
210. H. Craig. *Geochim. Cosmochim. Acta* **12**, 133–149 (1957).
211. H. Craig. *Geochim. Cosmochim. Acta* **3**, 53–92 (1953).
212. G. Hut. *Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*, International Atomic Energy Agency, Vienna, Austria (1987).
213. G. E. Claypool, C. N. Threlkeld, P. N. Mankiewicz, M. A. Arthur, T. F. Anderson. *Initial Reports of the Deep Sea Drilling Project* **84**, 683–691 (1995).
214. M. Elvert, E. Suess, J. Greinert, M. J. Whiticar. *Org. Geochem.* (2001).
215. M. Stuiver and H. A. Polach. *Radiocarbon* **19**, 355–363 (1977).
216. T. Hoering. *Science* **122**, 1233–1234 (1955).
217. A. Mariotti. *Nature* **303**, 685–687 (1983).
218. T. B. Coplen, H. R. Krouse, J. K. Böhlke. *Pure. Appl. Chem.* **64**, 907–908 (1992).
219. P. De Bièvre, S. Valkiers, H. S. Peiser, P. D. P. Taylor, P. Hansen. *Metrologia* **33**, 447–455 (1996).
220. H. D. Freyer, K. Kobel, R. J. Delmas, D. Kley, M. R. Legrand. *Tellus* **48B**, 93–105 (1996).
221. E. Wada, R. Shibata, T. Torii. *Nature* **292**, 327–329 (1981).
222. T. H. E. Heaton. *Atmos. Envir.* **21,** 843–852 (1987).
223. M. Dole, G. A. Lane, D. P. Rudd, D. A. Zaukelies. *Geochim. Cosmochim. Acta* **6**, 65–78 (1954).
224. P. Kroopnick and H. Craig. *Science* **175**, 54–55 (1972).
225. J. Santrock, S. Studley, J. M. Hayes. *Anal. Chem.* **57**, 1444–1448 (1985).
226. H. A. J. Meijer and W. J. Li. *Isotopes Environ. Health Stud.* **34**, 349–369 (1998).
227. H. Bao, M. H. Thiemens, J. Farquhar, D. A. Campbell, C. C. Lee, K. Heine, D. B. Loope. *Nature* **406**, 176–178 (2000)
228. G. Michalski and M. H. Thiemens. *EOS, Transactions of the American Geophysical Union* **81**, F120 (2000).
229. H. Craig. *Science* **133**, 1702–1703 (1961).

230. T. Yoshinari, M. A. Altabet, S. W. A. Naqvi, L. Codispoti, A. Jayakumar, M. Kuhland, A. Devol. *Marine Chem.* **56**, 253–264 (1997).
231. L. Aldaz and S. Deutsch. *Earth Planet. Sci. Lett.* **3**, 267–274 (1967).
232. G. P. Baxter and H. W. Starkweather. *Proc. Nat. Acad. Sci. USA* **14**, 50 (1928).
233. G. P. Baxter. *J. Am. Chem. Soc.* **50**, 603 (1928).
234. P. Eberhardt, O. Eugster, K. Marti. *Z. Naturforsch.* **20a**, 623–624 (1965).
235. J. R. Walton and A. E. Cameron. *Z. Naturforsch.* **21a**, 115–119 (1966).
236. G. W. Wetherill. *Phys. Rev.* **96**, 679–683 (1954).
237. M. Ozima and F. A. Podosek. *Noble Gas Geochemistry*, Cambridge University Press, Cambridge (1983).
238. B. M. Kennedy, H. Hiyagon, J. H. Reynolds. *Earth Planet. Sci. Lett.* **98**, 277–286 (1990).
239. E. J. Catanzaro, T. J. Murphy, E. L. Garner, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **70A**, 453–458 (1966).
240. E. J. Catanzaro and T. J. Murphy. *J. Geophys. Res.* **71**, 1271–1274 (1966).
241. V. S. Lepin, G. S. Plyusnin, S. B. Brandt. *Yearbook of the Erzheg. Inst. Geokhim. Sibir. Otdel. Akad. Nauk SSSR*, 267–271 (1969).
242. D. N. Schramm, F. Tera, G. J. Wasserburg. *Earth Planet. Sci. Lett.* **10**, 44–59 (1970).
243. V. T.-C. Chang, A. Galy, R. K. O'Nions. In *Eleventh Annual V. M. Goldschmidt Conference,* Abstract 3426: LPI Contribution **No. 1088**, Lunar and Planetary Institute, Houston (2001).
244. W. Hampel, J. Takagi, K. Sakamoto, S. Tanaka. *J. Geophys. Res.* **80**, 3757–3760 (1975).
245. I. L. Barnes, L. J. Moore, L. A. Machlan, T. J. Murphy, W. R. Shields. *J. Res. Natl. Bur. Stand. (U.S.)* **79A**, 727–735 (1975).
246. C. B. Douthitt. *Geochim. Cosmochim. Acta* **46**, 1449–1458 (1982).
247. S. Valkiers, P. De Bièvre, G. Lenaers, H. S. Peiser. *J. Res. Natl. Inst. Stand. Technol.* **96**, 617–619 (1991).
248. P. De Bièvre, S. Valkiers, H. S. Peiser. *J. Res. Natl. Inst. Stand. Technol.* **99**, 201–202 (1994).
249. T. Ding, D. Wan, J. Li, S. Jiang, H. Song, Y. Li, Z. Li. *Kuangchang Dixhi (Mineral Deposits)* **7**, 90–95 (1988).
250. P. De Bièvre, S. Valkiers, H. S. Peiser, P. Becker, F. Lüdicke, F. Speiweck, J. Stümpel. *IEEE Trans. Instrum. Meas.* **44**, 530–532 (1995).
251. R. D. Deslattes. *Proc. of the International School of Physics, Enrico Fermi* **68**, 38 (1980).
252. P. De Bièvre, G. Lenaers, T. J. Murphy, H. S. Peiser, S. Valkiers. *Metrologia* **32**, 103–110 (1995).
253. P. Bradt, F.L. Mohler, V. H. Dibeler. *J. Res. Natl. Bur. Stand. (U.S.)* **57**, 223–225 (1956).
254. J. MacNamara and H. G. Thode. *Phys. Rev.* **78**, 307–308 (1950).
255. K. Rankama. *Isotope Geology*, McGraw Hill, New York (1954).
256. H. E. Duckworth. *Mass Spectroscopy*, Cambridge University Press, Cambridge (1958).
257. T. Ding, R. Bai, Y. Li, D. Wan, X. Zou, Q. Chang. *Science in China*, Series D **42**, 45–51 (1999).
258. T. Ding, S. Valkiers, H. Kipphardt, C. Quétel, P. De Bièvre, P. D. P. Taylor, R. Gonfiantini. *Int. J. Mass Spectrom.* **197**, 131–137 (2000).
259. W. U. Ault and M. L. Jensen. *Biogeochemistry of Sulfur Isotopes*, M. L. Jensen (Ed.), pp. 16–29, U.S. National Science Foundation (1963).
260. B. W. Robinson. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, International Atomic Energy Agency, Vienna, IAEA-TECDOC-825, 47–48 (1995).
261. H. R. Krouse and T. B. Coplen. *Pure Appl. Chem.* **69**, 293–295 (1997).
262. G. Beaudoin, B. E. Taylor, D. Rumble III, M. Thiemens. *Geochim. Cosmochim. Acta* **58**, 4253–4255 (1994).
263. M. D. Rudnicki, H. Elderfield, B. Spiro. *Geochim. Cosmochim. Acta* **65**, 777–789 (2001).
264. J. H. E. Mattauch, W. Thiele, A. H. Wapstra. *Nucl. Phys.* **67**, 1–120 (1965).
265. A. Long, C. J. Eastoe, R. S. Kaufmann, J. G. Martin, L. Wirt, J. B. Finley. *Geochim. Cosmochim. Acta* **57**, 2907–2912 (1993).

266. Y. K. Xiao, Y. Zhou, Q. Wang, H. Wei, W. Liu, C. J. Eastoe. *Chem. Geol.* **182**, 655–661 (2002).
267. M. Lamotte, H. J. Dewey, R. A. Keller, J. J. Ritter. *Chem. Phys. Lett.* **30**, 165–170 (1975).
268. B. Ransom, A. J. Spivack, M. Kastner. *Geology* **23**, 715–718 (1995).
269. A. J. Magenheim, A. J. Spivack, P. J. Michael, J. M. Gieskes. *Earth Planet. Sci. Lett.* **131**, 427–432 (1995).
270. H. W. Bentley, F. M. Phillips, S. N. Davis. In *Handbook of Environmental Isotope Geochemistry*, P. Fritz and J.-Ch. Fontes (Eds.), **2B**, pp. 427–480, Elsevier, Amsterdam (1986).
271. R. H. Steiger and E. Jäger. *Earth Planet. Sci. Lett.* **36**, 359–362 (1977).
272. J. J. Irwin and J. H. Reynolds. *Geochim. Cosmochim. Acta* **59**, 355–369 (1995).
273. G. Marinenko. *Talanta* **16**, 1339–1340 (1969).
274. R. G. Bates and E. J. Wichers. Res. *Natl. Bur. Stand. (U.S.)* **59**, 9–17 (1957).
275. R. W. Hinton, R. N. Clayton, E. J. Olsen, A. M. Davis. *Abstracts 18th Lunar Planet Sci. Conf.*, pp. 429–430, Houston (1987).
276. M. Humayun and R. N. Clayton. *Geochim. Cosmochim. Acta* **59**, 2115–2130 (1995).
277. N. E. Holden. *Pure Appl. Chem.* **62**, 941–958 (1990).
278. O. Hönigschmid and K. Kempter. *Z. Anorg. Allg. Chem.* **195**, 1–14 (1931).
279. A. O. Nier. *Phys. Rev.* **53**, 282–286 (1938).
280. R. D. Deslattes, H. S. Peiser, J. A. Bearden, J. S. Thomsen. *Metrologia* **2**, 104–114 (1966).
281. W. A. Russell, D. A. Papanastassiou, T. A. Tombrello. *Geochim. Cosmochim. Acta* **42**, 1075–1090 (1978).
282. M. Skulan and D. J. DePaolo. *Proc. Natl. Acad. Sci. USA* **96**, 13709–13713 (1999).
283. C. L. De La Roche and D. J. DePaolo. *Science* **289**, 1176–1178 (2000).
284. K. S. Kozier, K. S. Sharma, R. C. Barber, J. W. Barnard, R. J. Ellis, V. P. Derenchuk, H. E. Duckworth. *Can. J. Phys.* **57**, 266–270 (1979).
285. G. P. Baxter and A. A. Butler. *J. Am. Chem. Soc.* **48**, 3117–3121 (1926).
286. G. P. Baxter and A. A. Butler. *J. Am. Chem. Soc.* **50**, 408–419 (1928).
287. R. F. Hibbs. *United States Atomic Energy Commission, Rep. Y-646* (1956).
288. H. J. Mattraw and C. F. Pachucki. *United States Atomic Energy Commission, Rep., Nucl. Sci. Abstr.* **6**, 320 (1952).
289. J. E. Hogg. *Can. J. Chem.* **32**, 1039–1043 (1954).
290. V. H. W. Darwin. *Nuklionik* **1**, 109–112 (1958).
291. H. A. Belsheim. Iowa State University, *United States Atomic Energy Commission, Rep. IS-T-217* (1968).
292. H. R. Heydegger, J. J. Foster, W. Compston. *Nature (London)* **278**, 704–707 (1979).
293. F. R. Niederer, D. A. Papanastassiou, G. J. Wasserburg. *Lunar Planet. Sci. XI*, **Part 2 240**, L73–L77 (1980).
294. D. C. Hess and M. G. Inghram. *Phys. Rev.* **76**, 1717 (1949).
295. W. T. Leland. *Phys. Rev.* **76**, 1722–1723 (1949).
296. H. Balsiger, J. Geiss, M. E. Lipschutz. *Earth Planet. Sci. Lett.* **6**, 117–122 (1969).
297. H. Balsiger, M. D. Mendia, I. Z. Pelly, M. E. Lipschutz. *Earth Planet. Sci. Lett.* **28**, 379–384 (1976).
298. G. D. Flesch, H. J. Svec, H. G. Staley. *Geochim. Cosmochim. Acta* **20**, 300–309 (1960).
299. A. S. Ellis, T. M. Johnson, T. D. Bullen. *Science* **295**, 2060–2062 (2002).
300. M. Imamura, T. Inoune, K. Nishizumi, S. Tanaka. *16th Int. Cosmic Ray Conf.* **2**, 304 (1979).
301. G. E. Valley and H. H. Anderson. *Phys. Rev.* **59**, 113 (1941).
302. G. E. Valley and H. H. Anderson. *J. Am. Chem. Soc.* **69**, 1871 (1947).
303. P. D. P. Taylor, R. Maeck, F. Hendirckx, P. De Bièvre. *Int. J. Mass Spectrom. Ion. Proc.* **128**, 91–97 (1993).

304. P. R. Dixon, D. R. Janecky, R. E. Perrin, D. J. Rokop, P. L. Unkefer, W. D. Spal. *"Unconventional Stable Isotopes: Iron", Water-Rock Interaction, Vol. 2, Moderate and High Temperature Environments*, Y. K. Kharaka and A. S. Maest (Eds.), pp. 915–918, A. A. Balkema, Rotterdam (1992).
305. T. D. Bullen and P. M. McMahon. *EOS* **78**, S173 (1997).
306. B. L. Beard, C. M. Johnson, L. Cox, H. Sun, K. H. Nealson, C. Aquilar. *Science* **285**, 1889–1892 (1999).
307. T. Walczyk. *Fresenius' J. Anal. Chem.* **370**, 444–453 (2001).
308. B. L. Beard and C. M. Johnson. *Geochim. Cosmochim. Acta* **63**, 1653–1660 (1999).
309. T. L. Collins, A. O. Nier, W. H. Johnson, Jr. *Phys. Rev.* **86**, 408–412 (1952).
310. G. P. Baxter and L. W. Parsons. *J. Am. Chem. Soc.* **43**, 507–518 (1921).
311. G. P. Baxter and F. A. Hilton. *J. Am. Chem. Soc.* **45**, 694–700 (1923).
312. G. P. Baxter and J. Ishimaru. *J. Am. Chem. Soc.* **51**, 1729 (1929).
313. M. G. Inghram and D. C. Hess. *Argonne Natl. Lab. Rep.* **4120** (1948).
314. I. L. Barnes, E. L. Garner, J. W. Gramlich, L. A. Machlan, J. R. Moody, L. J. Moore, T. J. Murphy, W. R. Shields. *Geochim. Cosmochim. Acta* Suppl. 4, **2**, 1197–1207 (1973).
315. J. W. Gramlich, L. A. Machlan, I. L. Barnes, P. J. Paulsen. *J. Res. Natl. Inst. Stand. Technol. (U.S.)* **94**, 347–356 (1989).
316. J. W. Gramlich and L. A. Machlan. *Anal. Chem.* **57**, 1788–1790 (1985).
317. O. Hönigschmid and K. Johannsen. *Z. Anorg. Allg. Chem.* **252**, 364–370 (1944).
318. R. Reur and K. Bode. *Z. Anorg. Allg. Chem.* **137**, 101–114 (1924).
319. W. R. Shields, T. J. Murphy, E. L. Garner. *J. Res. Natl. Bur. Stand. (U.S.)* **68A**, 589–592 (1964)
320. N. H. Gale, A. P. Woodhead, Z. A. Stos-Gale, A. Walder, I. Bowen. *Int. J. Mass Spectrom.* **184**, 1–9 (1999).
321. C. N. Maréchal, P. Télouk, F. Albarède. *Chem. Geol.* **156**, 251–273 (1999).
322. O. Hönigschmid and M. von Mack. *Z. Anorg. Allg. Chem.* **246**, 363–369 (1941).
323. G. P. Baxter and M. R. Grose. *J. Am. Chem. Soc.* **38**, 868–873 (1916).
324. G. P. Baxter and J. H. Hodges. *J. Am. Chem. Soc.* **43**, 1242–1251 (1921).
325. D. C. Hess, M. G. Inghram, R. J. Hayden. *Phys. Rev.* **74**, 1531–1532 (1948).
326. W. T. Leland and A. O. Nier. *Phys. Rev.* **73**, 1206 (1948).
327. G. Marinenko and R. T. Foley. *J. Res. Natl. Bur. Stand. (U.S.)* **75A**, 561–564 (1971).
328. K. J. R. Rosman. *Geochim. Cosmochim. Acta* **36**, 801–819 (1972).
329. T. W. Richards and W. M. Craig. *J. Am. Chem. Soc.* **45**, 1155–1167 (1923).
330. G. E. F. Lundell and J. I. Hoffman. *J. Res. Natl. Bur. Stand. (U.S.)* **15**, 409–420 (1935).
331. M. G. Inghram, D. C. Hess, H. S. Brown, E. Goldberg. *Phys. Rev.* **73**, 180 (1948).
332. M. G. Inghram, D. C. Hess, H. S. Brown, E. Goldberg. *Phys. Rev.* **74**, 343–344 (1948).
333. G. J. Marinenko. *Res. Natl. Bur. Stand. (U.S.)* **8lA**, 1–4 (1977).
334. J. R. de Laeter and K. J. R. Rosman. *Int. J. Mass Spectrom. Ion Phys.* **21**, 403–409 (1976).
335. J. R. de Laeter. *Geochim. Cosmochim. Acta* **36**, 735–743 (1972).
336. G. Nief and E. Roth. *C. R. Acad. Sci., Paris* **239**, 162–164 (1954).
337. B. W. Mangum. *Temperature* **5**, 299–309 (1982).
338. G. P. Baxter and W. C. Cooper. *J. Phys. Chem.* **28**, 1049 (1924).
339. G. P. Baxter and W. C. Cooper. *J. Phys. Chem.* **29**, 1364 (1925).
340. O. Hönigschmid, K. Wintersberger, F. Wittner. *Z. Anorg. Allg. Chem.* **225**, 81 (1935).
341. O. Hönigschmid and K. Wintersberger. *Z. Anorg. Allg. Chem.* **227**, 17 (1936).
342. A. J. Dempster, A. E. Shaw, M. G. Inghram, D. C. Hess Jr, R. J. Hayden. *Argonne Natl. Lab. Rep. Plutonium Project* **ANL-4082** (1947).
343. R. F. Hibbs, J. W. Redmond, H. R. Gwinn, W. D. Harman. *Phys. Rev.* **75**, 533–534 (1949).
344. R. P. Graham, J. Macnamara, I. H. Crocker, R. B. MacFarlane. *Can. J. Chem.* **29**, 89–102 (1951).
345. J. H. Reynolds. *Phys. Rev.* **90**, 1047–1049 (1953).

346. M. Shima. *J. Geophys. Res.* **68**, 4289–4292 (1963).
347. R. G. Artakuni, A. M. Kolchin, G. M. Panchenkov. *Zh. Khim.* **37**, 893 (1963).
348. A. Smakula and V. Sils. *Phys. Rev.* **99**, 1744–1746 (1955).
349. M. D. Green, K. J. R. Rosman, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Proc.* **68**, 15–24 (1986).
350. H. Kipphardt, S. Valkiers, F. Hendrickx, P. De Bièvre, P. D. P. Taylor, G. Tölg. *Int. J. Mass Spectrom.* **189**, 27–37 (1999).
351. T.-L. Chang, W.-J Li, G.-S Qiao, Q.-Y. Qian, Z.-Y Chu. *Int. J. Mass Spectrom.* **189**, 205–211 (1999).
352. T. Hirata. *Geochim. Cosmochim. Acta* **61**, 4439–4448 (1997).
353. O. Hönigschmid and W. Kapfenberger. *Z. Anorg. Allg. Chem.* **212**, 198 (1933).
354. R. F. Hibbs. *United States Atomic Energy Commission*, *Rep. A.E.C.U. 556* (1949).
355. M. Wachsmann and K. G. Heumann. *Adv. Mass Spectrom.* **11B**, 1828–1829 (1989).
356. H. R. Krouse and H. G. Thode. *Can. J. Chem.* **40**, 367–375 (1962).
357. O. Hönigschmid and E. Xintl. *Julius Liebigs Ann. Chem.* **433**, 201 (1923).
358. A. E. Cameron and E. L. Lippert. *Science* **121**, 136–137 (1955).
359. J. R. Walton, A. E. Cameron, R. L. Walker, T. L. Hebble. *Int. J. Mass Spectrom. Ion Phys.* **12**, 439–453 (1973).
360. M. Ozima. *Rev. Geophys.* **32**, 405–426 (1994).
361. E. H. Archibald, J. G. Hooley, N. Phillips. *J. Am. Chem. Soc.* **58**, 70–72 (1936).
362. E. H. Archibald and J. G. Hooley. *J. Am. Chem. Soc.* **58**, 618–619 (1936).
363. W. R. Shields, E. L. Garner, C. E. Hedge, S. S. Goldich. *J. Geophys. Res.* **68**, 2331–2334 (1963).
364. W. Compston, B. W. Chappell, P. A. Arriens, M. J. Vernon. *Geochim. Cosmochim. Acta* **33**, 753–759 (1969).
365. J. Mattauch. *Naturwissenschaften* **25**, 189 (1937).
366. J. F. Minster and L. Ph. Ricard. *Int. J. Mass Spectrom. Ion Phys.* **37**, 259–272 (1981).
367. O. Hönigschmid and G. Wittmann. *Z. Anorg. Allg. Chem.* **229**, 65–75 (1936).
368. V. R. Murthy. *Geochim. Cosmochim. Acta* **27**, 1171–1178 (1963).
369. E. A. C. Crouch and T. A. Tuplin. *Nature (London)* **202**, 1282–1284 (1964).
370. G. W. Wetherill. *J. Geophys. Res.* **69**, 4403–4408 (1964).
371. C. M. Stevens. *Int. J. Mass Spectrom. Ion Phys.* **8**, 251–257 (1972).
372. L. J. Moore, L. A. Machlan, W. R. Shields, E. L. Garner. *Anal. Chem.* **46**, 1082–1089 (1974).
373. M. E. Wieser and J. R. de Laeter. *Int. J. Mass Spectrom.* **197**, 253–261 (2000).
374. C. Siebert, T. F. Nagler, F. von Blankenburg, J. D. Kramers. *EOS*, *Transactions of the American Geophysical Union* **82**, F1324-F1325 (2001).
375. R. D. Vocke. *Pure Appl. Chem.* **71**, 1593–1607 (1998).
376. J. T. Armstrong and P. H. M. Van Assche. *Proc. Microscopy and Microanalysis,* Springer, **5**, 84–85 (1999).
377. W. Noddack, I. Tacke, O. Berg. *Naturwissen.* **13**, 567 (1925).
378. L. Friedman and A. P. Irsa. *J. Am. Chem. Soc.* **75**, 5741–5743 (1953).
379. R. Baldock. *Oak Ridge Natl. Lab. Rep.* 1719–1722 (1954).
380. K. Gleu and K. Rehm. *Z. Anorg. Allg. Chem.* **235**, 352–362 (1938).
381. C. Devillers, T. Lecomte, M. Lucas, R. Hagemann. *Adv. Mass Spectrom.* **7A**, 553–564 (1978).
382. J. Feitknecht, W. Herr, W. HoffmeisteR. *Helv. Phys. Acta* **35**, 289–291 (1962).
383. J. R. Sites, G. Consolazio, R. Baldock. *Phys. Rev.* **92**, 1096 (1953).
384. M. Shima, C. E. Rees, H. G. Thode. *Can. J. Phys.* **56**, 1333–1339 (1978).
385. N. Mermelengas, K. J. R. Rosman, J. R. de Laeter. *Int. J. Mass Spectrom. Ion Phys.* **37**, 1–11 (1981).
386. K. J. R. Rosman, J. R. de Laeter, N. Kempt. *Int. J. Mass Spectrom. Ion Proc.* **93**, 107–114 (1989).
387. R. D. Loss, J. R. de Laeter, K. J. R. Rosman, T. M. Benjamin, D. B. Curtis, A. J. Gancarz, J. E. Delmore and W. J. Maeck. *Earth Planet. Sci. Lett.* **89**, 193–206 (1988).

388. H. F. McDuffie. *Oak Ridge Natl. Lab. Rep.* **TM-6654** (1979).
389. W. R. Shields, D. N. Craig, V. H. Dibeler. *J. Am. Chem. Soc.* **82**, 5033–5036 (1960).
390. K. J. R. Rosman and J. R. de Laeter. *Int. J. Mass Spectrom. Ion Phys.* **16**, 385–394 (1975).
391. K. J. R. Rosman and J. R. de Laeter. *J. Geophys. Res.* **83**, 1279–1287 (1978).
392. K. J. R. Rosman and J. R. de Laeter. *Earth Planet. Sci. Lett.* **89**, 163–169 (1988).
393. J. R. de Laeter and K. J. R. Rosman. International Atomic Energy Agency **SM204/1**, 499–508 (1975).
394. T. Saito, H. Shimizu, A. Masuda. *Geochem. J.* **21**, 237–245 (1987).
395. G. P. Baxter and H. W. Starkweather. *J. Am. Chem. Soc.* **42**, 905–917 (1920).
396. H. V. A. Briscoe. *J. Chem. Soc.* **107**, 63–86 (1915).
397. B. Brauner and J. Krepelka. *J. Am. Chem. Soc.* **42**, 917–925 (1920).
398. J. R. de Laeter and P. M. Jeffery. *Geochim. Cosmochim. Acta* **31**, 969–985 (1967).
399. K. J. R. Rosman and N. J. McNaughton. *Int. J. Mass Spectrom. Ion Proc.* **75**, 91–98 (1987).
400. N. J. McNaughton and K. J. R. Rosman. *Geochim. Cosmochim. Acta* **55**, 499–504 (1991).
401. H. H. Willard and R. K. McAlpine. *J. Am. Chem. Soc*. **43**, 797(1921).
402. O. Hönigschmid, E. Zintl, M. Linhard. *Z. Anorg. Allg. Chem.* **136**, 257 (1924).
403. P. F. Weatherill. *J. Am. Chem. Soc.* **46**, 2437–2445 (1924).
404. K. R. Krishnaswami. *J. Chem. Soc.* **2,** 2534 (1927).
405. J. R. de Laeter and D. J. Hosie. *Int. J. Mass Spectom. Ion Proc.* **83**, 311–318 (1988).
406. T.-L Chang., Q.-Y. Qian, M.-T. Zhao. *Science in China (Series B)* **32** (12), 1409–1414 (1989).
407. M. Wachsmann and K. G. Heumann. *Int. J. Mass Spectrom. Ion Proc.* **108**, 75–86 (1991).
408. O. Hönigschmid, R. Sachtleben, K. Wintersberger. *Z. Anorg. Allg. Chem.* **212**, 242 (1933).
409. O. Hönigschmid. *Z. Anorg. Allg. Chem.* **214**, 281–288 (1933).
410. O. Hönigschmid and H. Baudrexler. *Z. Anorg. Allg. Chem.* **223**, 91–100 (1935).
411. D. Williams and P. Yuster. *Phys. Rev.* **69**, 556–567 (1946).
412. J. R. de Laeter. *Astrophys. J.* **434**, 695–697 (1994).
413. M. R. Smithers and H. R. Krouse. *Can. J. Chem.* **46**, 583–591 (1968).
414. J. R. de Laeter, K. J. R. Rosman, C. L. Smith. *Earth Planet. Sci. Lett.* **50**, 238–246 (1980).
415. R. E. Halsted. *Phys. Rev.* **88**, 666–672 (1952).
416. J. H. Reynolds. *J. Geophys. Res.* **68**, 2939–2956 (1963).
417. O. Hönigschmid and R. Sachtleben. *Z. Anorg. Allg. Chem.* **178**, 1–32 (1929).
418. A. O. Nier. *Phys. Rev.* **54**, 275–278 (1938).
419. H. G. Thode. Private communication cited in *Nucl. Data Tables*, K. Way (Ed.) Supt. of Documents, U.S. Government Printing Office, Washington, DC (1959).
420. B. F. Rider, J. P. Peterson, Jr., C. P. Ruiz. *General Electric Company Rep.* **GEAP-4008** (1962).
421. S. Umemoto. *J. Geophys. Res.* **67**, 375–379 (1962).
422. J. R. de Laeter and R. Date. *Int. J. Mass Spectrom. Ion Phys.* **12**, 455–463 (1973).
423. H. Hidaka, P. Holliger, A. Masuda. *Earth Planet. Sci. Lett.* **114**, 391–396 (1993).
424. M. G. Inghram, R. J. Hayden, D. C. Hess, Jr. *Phys. Rev.* **72**, 967–970 (1947).
425. M. G. Inghram, D. C. Hess, Jr., R. J. Hayden. *Phys. Rev.* **74**, 98–99 (1948).
426. W. H. Walker and H. G. Thode. *Phys. Rev.* **90**, 447–448 (1953).
427. S. B. Jacobsen and G. J. Wasserburg. *J. Geophys. Res.* **84**, 7411–7427 (1979).
428. D. J. Piepgras and G. J. Wasserburg. *Science* **217**, 207–214 (1982).
429. G. J. Wasserburg, S. B. Jacobsen, D. J. DePaolo, M. T. McCulloch, T. Wen. *Geochim. Cosmochim. Acta* **45**, 2311–2323 (1981).
430. M. G. Inghram, D. C. Hess, Jr., R. J. Hayden. *Phys. Rev.* **73**, 180 (1948).
431. V. B. Bhanot, W. B. Johnson, A. O. Nier. *Phys. Rev.* **120**, 235–251 (1960).
432. O. Hönigschmid and Fr. Hirschbold-Wittner. *Z. Physik. Chem.* **A189**, 38–43 (1941).
433. G. W. Lugmair, N. B. Scheinin, K. Marti. *Proc. Lunar Sci. Conf., 6th Geochim. Cosmochim. Acta Suppl.* **6**, 1419–1429 (1975).

434. D. C. Hess, Jr. *Phys. Rev.* **74**, 773–778 (1948).
435. M. G. Inghram, R. J. Hayden, D. C. Hess, Jr. *Phys. Rev.* **75**, 693–694 (1949).
436. R. J. Hayden, D. C. Hess, Jr., M. G. Inghram. *Phys. Rev.* **77**, 299 (1950).
437. T.-L. Chang, M.-T. Zhao, W.-J. Li, J. Wang, Q.-Y. Qian. *Int. J. Mass Spectrom.* **177**, 131–136 (1998).
438. R. J. Hayden, D. C. Hess, M. G. Inghram. *Phys. Rev.* **75**, 322–323 (1950).
439. M. T. McCulloch, K. J. R. Rosman, J. R. de Laeter. *Geochim. Cosmochim. Acta* **41**, 1703–1707 (1977).
440. O. Hönigschmid and F. Wittner. *Z. Anorg. Allg. Chem.* **240**, 284 (1939).
441. M. T. McCulloch, J. R. de Laeter, K. J. R. Rosman. *Earth Planet. Sci. Lett.* **28**, 308–322 (1976).
442. F. A. White, T. L. Collins, Jr., F. M. Rourke. *Phys. Rev.* **97**, 566–567 (1955).
443. G. H. Palmer. *J. Nucl. Energy* **7**, 1–12 (1958).
444. K. S. Sharma, R. J. Ellis, V. P. Derenchuk, R. C. Barber, H. E. Duckworth. *Phys. Lett.* **91B**, 211–213 (1980).
445. J. Mattauch and H. Scheld. *Z. Naturforsch.* **3a**, 105–114 (1948).
446. O. Hönigschmid and W. Menn. *Z. Anorg. Allg. Chem.* **229**, 49 (1936).
447. A. O. Nier. *Phys. Rev.* **52**, 885 (1937).
448. J. M. Luck and K. K. Turekian. *Science* **222**, 613–615 (1983).
449. M. P. Sampson and W. Bleakney. *Phys. Rev.* **50**, 732–735 (1936).
450. R. A. Creaser, D. A. Papanastassiou, G. J. Wasserburg. *Geochim. Cosmochim. Acta* **55**, 397–401 (1991).
451. T.-L. Chang and Y.-K. Xiao. *Chin. Chem. Lett.* **3**, 731–734 (1992).
452. M. G. Inghram, D. C. Hess, Jr., R. J. Hayden. *Arnonne Natl. Lab. Rep. ANL-4012* (1947); cited in *Nucl. Data Tables* (1959).
453. O. Hönigschmid, L. Birckenbackand, N. Steinheil. *Ber. Dtsch. Chem. Ges.* **56B**, 1212 (1923).
454. M. G. Inghram, D. C. Hess, Jr., R. J. Hayden. *Phys. Rev.* **71**, 561–562 (1947).
455. V. H. Dibeler. *Anal. Chem.* **27**, 1958–1959 (1955).
456. E. Haeffner. *Nature (London)* **172**, 775–776 (1953).
457. O. Hönigschmid, L. Birckenbach, E. Kothe. *Sitzungsber. Bayer. Akad. Wiss. Jahrb.* 179 (1922).
458. O. Hönigschmid and H. Striebel. *Z. Anorg. Allg. Chem.* **194**, 293 (1930).
459. M. Rehkämper and A. N. Halliday. *Geochim. Cosmochim. Acta* **63**, 935–944 (1999).
460. M. Rehkämper, M. Frank, A. N. Halliday, J. R. Hein. *European Union of Geosciences, 11th Biannual Symposium, Strassbourg, Book of Abstracts*, 689 (2001).
461. G. P. Baxter and C. M. Alter. *J. Am. Chem. Soc.* **55**, 1445–1448 (1933).
462. G. P. Baxter, J. H. Faull, F. D. Tuemmler. *J. Am. Chem. Soc.* **59**, 702–705 (1937).
463. O. Hönigschmid, R. Sachtlebenand, H. Baudrexler. *Z. Anorg. Allg. Chem.* **214**, 104–110 (1933).
464. J. S. Brown. *Econ. Geol.* **57**, 673–720 (1962).
465. C. C. Patterson. *Lead in the Human Environment.* Report prepared by the Committee on Lead in the Human Environment, National Academy of Sciences, Washington, DC (1980).
466. M. P. Bacon. *Isot. Geosci.* **2**, 97–111 (1984).
467. B. F. Anerson, M. P. Bacon, P. G. Brewer. *Earth Planet. Sci. Lett.* **66**, 73–90 (1983).
468. R. E. Greene, C. A. Kienberger, A. E. Meservey. *Nucl. Data Tables* (1959).
469. R. F. Smith and J. M. Jackson. *United States Atomic Energy Commission, Rep. KY-581* (1969).
470. G. A. Cowan and H. H. Adler. *Geochim. Cosmochim. Acta* **40**, 1487–1490 (1976).

APPENDIX A: SOURCES OF REFERENCE MATERIALS

IAEA Reference and intercomparison samples such as VSMOW, SLAP, GISP, LSVEC, NSVEC, NBS18, and NBS19 may be purchased from:
International Atomic Energy Agency
Section of Isotope Hydrology, P.O. Box 100, 1400 Vienna, Austria
<http://www.iaea.org/programmes/aqcs/>

NIST NIST Standard Reference Materials and VSMOW, SLAP, GISP, LSVEC, NSVEC, NBS18, and NBS19 may be purchased through:
Standard Reference Material Program
National Institute of Standards and Technology, Room 204, Building 202,
Gaithersburg, MD 20899-0001, USA
<http://ts.nist.gov/srm/>

IRMM Reference Materials may be obtained from:
Institute for Reference Measurements and Materials, Commission of the
European Communities-JRC, B-2440 Geel, Belgium
<http://www.irmm.jrc.be/>

CEA CEA distributes stable isotopes through its daughter company:
EUROISO-TOP
Parc des Algorithmes (Bat. Homère), F-91194 St Aubin, France
<http://www.eurisotop.fr/>
For nuclear reference materials, see also:
CETAMA
CEA/DCC
Centre d'Etudes Nucléaires de Fontenay aux Roses, BP 6, F 92265
Fontenay aux Roses, France

NBL Standards may be obtained through:
U.S. Department of Energy
New Brunswick Laboratory, 9800 S. Cass Ave., Argonne, IL 60439, USA
<http://www.nbl.doe.gov/crms/crm.htm>