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Compilation of Minimum and Maximum Isotope Ratios of Selected Elements in Naturally Occurring Terrestrial Materials and Reagents

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Conversion Factors

Multiply	By	To obtain
gram (g)	0.002 204 623	pound, avoirdupois (lb)
unified atomic mass unit (u)	$1.660\ 538\ 73 \pm 0.000\ 000\ 13 \times 10^{-27}$	kilogram (kg)

Temperature in Degrees Celsius (˚C) can be converted to degrees Fahrenheit (˚F) by using the following equation:

$˚F = (˚C \times 1.8) + 32$

List of Abbreviations Used in this Report

CAWIA	Commission on Atomic Weights and Isotopic Abundances
CDT	Cañon Diablo troilite
PDB	Peedee belemnite
IAEA	International Atomic Energy Agency
IRMM	Institute for Reference Materials and Measurements
IUPAC	International Union of Pure and Applied Chemistry
MC-ICP-MS	Multiple Collector Inductively Coupled Plasma Mass Spectrometry
NBS	National Bureau of Standards (now NIST)
NIST	National Institute of Standards and Technology
RM	Reference Material
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
SMOW	Standard Mean Ocean Water
SNIF	Subcommittee on Natural Isotopic Fractionation
SRM	Standard Reference Material
VCDT	Vienna Cañon Diablo troilite
VPDB	Vienna Peedee belemnite
VSMOW	Vienna Standard Mean Ocean Water
<	less than
>	greater than
~	approximately

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Abstract

Documented variations in the isotopic compositions of some chemical elements are responsible for expanded uncertainties in the standard atomic weights published by the Commission on Atomic Weights and Isotopic Abundances of the International Union of Pure and Applied Chemistry. This report summarizes reported variations in the isotopic compositions of 20 elements that are due to physical and chemical fractionation processes (not due to radioactive decay) and their effects on the standard atomic weight uncertainties. For 11 of those elements (hydrogen, lithium, boron, carbon, nitrogen, oxygen, silicon, sulfur, chlorine, copper, and selenium), standard atomic weight uncertainties have been assigned values that are substantially larger than analytical uncertainties because of common isotope abundance variations in materials of natural terrestrial origin. For 2 elements (chromium and thallium), recently reported isotope abundance variations potentially are large enough to result in future expansion of their atomic weight uncertainties. For 7 elements (magnesium, calcium, iron, zinc, molybdenum, palladium, and tellurium), documented isotope-abundance variations in materials of natural terrestrial origin are too small to have a significant effect on their standard atomic weight uncertainties.

This compilation indicates the extent to which the atomic weight of an element in a given material may differ from the standard atomic weight of the element. For most elements given above, data are graphically illustrated by a diagram in which the materials are specified in the ordinate and the compositional ranges are plotted along the abscissa in scales of (1) atomic weight, (2) mole fraction of a selected isotope, and (3) delta value of a selected isotope ratio.

There are no internationally distributed isotopic reference materials for the elements zinc, selenium, molybdenum, palladium, and tellurium. Preparation of such materials will help to make isotope-ratio measurements among laboratories comparable.

The minimum and maximum concentrations of a selected isotope in naturally occurring terrestrial materials for selected chemical elements reviewed in this report are given below:

Isotope	Minimum mole fraction	Maximum mole fraction
^{2}H	0.000 0255	0.000 1838
^{7}Li	0.9227	0.9278
^{11}B	0.7961	0.8107
^{13}C	0.009 629	0.011 466
^{15}N	0.003 462	0.004 210
^{18}O	0.001 875	0.002 218
^{26}Mg	0.1099	0.1103
^{30}Si	0.030 816	0.031 023
^{34}S	0.0398	0.0473
^{37}Cl	0.240 77	0.243 56
^{44}Ca	0.020 82	0.020 92
^{53}Cr	0.095 01	0.095 53
^{56}Fe	0.917 42	0.917 60
^{65}Cu	0.3066	0.3102
^{205}Tl	0.704 72	0.705 06

The numerical values above have uncertainties that depend upon the uncertainties of the determinations of the absolute isotope-abundance variations of reference materials of the elements. Because reference materials used for absolute isotope-abundance measurements have not been included in relative isotope abundance investigations of zinc, selenium, molybdenum, palladium, and tellurium, ranges in isotopic composition are not listed for these elements, although such ranges may be measurable with state-of-the-art mass spectrometry.

This report is available at the url: http://pubs.water.usgs.gov/wri014222.

Introduction

The standard atomic weights and their uncertainties tabulated by IUPAC are intended to represent most normal materials encountered in terrestrial samples and laboratory chemicals. During the meeting of the Commission on Atomic Weights and Isotopic Abundances (CAWIA) at the General Assembly of the International Union of Pure and Applied Chemistry (IUPAC) in 1985, the Working Party on Natural Isotopic Fractionation [now named the Subcommittee on Natural Isotopic Fractionation (SNIF)] was formed to investigate the effects of isotope abundance variations of elements upon their Standard Atomic Weights and atomic-weight uncertainties. The aims of the Subcommittee on Natural Isotopic Fractionation were (1) to identify elements for which the uncertainties of the standard atomic weights are larger than measurement uncertainties in materials of natural terrestrial origin because of isotope abundance variations caused by fractionation processes (excluding variations caused by radioactivity) and (2) to provide information about the range of atomic-weight variations in specific substances and chemical compounds of each of these elements. The purpose of this report is to compile ranges of isotope abundance variations and corresponding atomic weights in selected materials containing 20 chemical elements (H, Li, B, C, N, O, Mg, Si, S, Cl, Ca, Cr, Fe, Cu, Zn, Se, Mo, Pd, Te, and Tl) from published data. Because of its focus on extreme values, this report should not be viewed as a comprehensive compilation of stable isotope-abundance variations in the literature; rather, it is intended to illustrate ranges of variation that may be encountered in natural and anthropogenic material. The information in this report complements the bi-decadal CAWIA reviews of the atomic weights of the elements (Peiser and others, 1984; de Laeter and others, in press), the tabulation by De Bièvre and others (1984) of most precise measurements published on the isotopic composition of the elements, and the “Isotopic Compositions of the Elements 1997” by Rosman and Taylor (1998).

The membership of the Subcommittee on Natural Isotopic Fractionation during the period 1985–2001 has consisted of T. B. Coplen (chairman), J.K. Böhlke, C. A. M. Brenninkmeijer, P. De Bièvre, T. Ding, K. G. Heumann, N. E. Holden, H. R. Krouse, A. Lamberty, H. S. Peiser, G. I. Ramendik, E. Roth, M. Stiévenard, L. Turpin, and R. D. Vocke, Jr., with additional assistance from M. Shima.

Basic Concepts

The atomic weight of an element in a specimen can be determined from knowledge of the atomic masses of the isotopes of that element and the isotope abundances of that element in the specimen. The abundance of isotope i of element E in the specimen can be expressed as a mole fraction, $x(^{i}\mathrm{E})$. For example, the mole fraction of ^{34}S is $x(^{34}\mathrm{S})$, which is $n(^{34}\mathrm{S})/[(n(^{32}\mathrm{S}) + n(^{33}\mathrm{S}) + n(^{34}\mathrm{S}) + n(^{36}\mathrm{S})]$ or more simply $n(^{34}\mathrm{S})/\sum n(^{i}\mathrm{S})$ or $n(^{34}\mathrm{S})/n(\mathrm{S})$, where $n(^{i}\mathrm{E})$ is the amount of each isotope i of element E in units of moles. Thus, if element E is composed of isotopes ^{i}E, with mole fractions $x(^{i}\mathrm{E})$, the atomic weight, $A_{\mathrm{r}}(\mathrm{E})$, is the sum of the products of the atomic masses and mole fractions of the isotopes; that is, $A_{\mathrm{r}}(\mathrm{E}) = \sum x(^{i}\mathrm{E})\cdot A_{\mathrm{r}}(\mathrm{E})$. The atomic masses from the evaluation of 1993 (Audi and Wapstra, 1993) have been used by CAWIA and are listed in tables herein. Isotope-abundance values that have been corrected for all known sources of bias within stated uncertainties are referred to as “absolute” isotope abundances, and they can be determined by mass spectrometry through use of synthetic mixtures of isotopes. For many elements, the abundances of the isotopes are not invariant; thus, these elements have a range in atomic weight. This report includes data for 20 such elements in their natural occurrences and in laboratory reagents.

Molecules, atoms, and ions in their natural occurrences contain isotopes in varying proportions, whereby they possess slightly different physical and chemical properties; thus, the physical and chemical properties of materials with different isotopic compositions differ. This gives rise to partitioning of isotopes (isotope fractionation) during physical or chemical processes, and these fractionations commonly are proportional to differences in their relevant isotope masses. Physical isotope-fractionation processes include those in which diffusion rates are mass dependent, such as ultrafiltration or gaseous diffusion of ions or molecules. Chemical isotope-fractionation processes involve redistribution of isotopes of an element among phases, molecules, or chemical species. They either can be (1) equilibrium isotope fractionations, when forward and backward reaction rates for individual isotope-exchange reactions are equal, or (2) kinetic isotope fractionations caused by unidirectional reactions in which the forward reaction rates usually are mass dependent. In equilibrium isotope reactions, in general, the heavy isotope will be enriched in the compound with the higher oxidation state and commonly in the more condensed state. Thus, for example, ^{13}C is enriched in carbon dioxide relative to graphite, and in graphite relative to methane, and ^{2}H is enriched in liquid water relative to water vapor. In kinetic processes, statistical mechanics predicts that the lighter (lower atomic mass) of two isotopes of an element will form the weaker and more easily broken bond. The lighter isotope is more reactive; therefore, it is concentrated in reaction products, enriching reactants in the heavier isotope. Examples of reactions that produce kinetic isotope fractionation include many biological reactions, treatment of limestone with acid to liberate carbon dioxide, and the rapid freezing of water to ice. Sulfate reduction by bacteria in respiration is an example of a biologically mediated kinetic isotope-fractionation process. Kinetic isotope fractionations of biological processes are variable in magnitude and may be in the direction opposite to that of equilibrium isotope fractionations for the same chemical species.

Isotopic equilibrium between two phases does not mean that the two phases have identical mole fractions of each isotope (isotope abundances), only that the ratios of these mole fractions always are constant. Water vapor in a closed container in contact with liquid water at a constant temperature is an example of two phases in oxygen and hydrogen isotopic equilibrium; in this case, the concentrations of the heavy isotopes (^{2}H and ^{18}O) are higher in the liquid than in the vapor.

The distribution of isotopes in two substances X and Y is described by the isotope-fractionation factor $\alpha_{X,Y}$, defined by

$$\alpha_{\mathrm{X,Y}} = \frac{n_{\mathrm{X}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{X}}\left({}^{j}\mathrm{E}\right)}{n_{\mathrm{Y}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{Y}}\left({}^{j}\mathrm{E}\right)} ,$$

where $n_{X}({}^{i}E)$ and $n_{X}({}^{j}E)$ are the amounts of two isotopes, i and j, of chemical element E in substance X, in units of moles. We equally well could have used $N_{X}({}^{i}E)$ and $N_{X}({}^{j}E)$, which are the number of atoms of two isotopes, i and j, of chemical element E in substance X. In this document, the superscripts i and j denote a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. The isotope pairs used to define $n({}^{i}E)/n({}^{j}E)$ in this report are $^{2}H/^{1}H$, $^{7}Li/^{6}Li$, $^{11}B/^{10}B$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{26}Mg/^{24}Mg$, $^{30}Si/^{28}Si$, $^{34}S/^{32}S$, $^{37}Cl/^{35}Cl$, $^{44}Ca/^{40}Ca$, $^{53}Cr/^{52}Cr$, $^{56}Fe/^{54}Fe$, $^{65}Cu/^{63}Cu$, $^{66}Zn/^{64}Zn$, $^{82}Se/^{76}Se$, $^{98}Mo/^{95}Mo$, $^{110}Pd/^{104}Pd$, $^{130}Te/^{122}Te$ or $^{205}Tl/^{203}Tl$. In general, isotope-fractionation factors are near unity. For example, the value of the equilibrium $n(^{18}O)/n(^{16}O)$ fractionation factor α between water liquid and water vapor at 15 °C is 1.0102. Thus, ^{18}O is enriched in liquid water at 15 °C by 1.02 percent relative to its concentration in water vapor.

Variations in stable isotope abundance ratios typically are small. Stable isotope ratios commonly are expressed as relative isotope ratios in $\delta^{i}E$ notation (pronounced delta) according to the relation

$$\delta\,{}^{i}\mathrm{E} = \left[\frac{n_{\mathrm{X}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{X}}\left({}^{j}\mathrm{E}\right)}{n_{\mathrm{ref}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{ref}}\left({}^{j}\mathrm{E}\right)} - 1 \right] ,$$

where $\delta^{i}E$ refers to the delta value of isotope number i of element E of sample X relative to the reference ref, and $n_{X}({}^{i}E)/n_{X}({}^{j}E)$ and $n_{ref}({}^{i}E)/n_{ref}({}^{j}E)$ are the ratios of the isotope amounts in unknown X and a reference ref. A positive $\delta^{i}E$ value indicates that the unknown is more enriched in the heavy isotope than is the reference. A negative $\delta^{i}E$ value indicates that the unknown is depleted in the heavy isotope relative to the reference. In the literature, $\delta^{i}E$ values of isotope ratios have been reported in parts per hundred (% or per cent), parts per thousand (‰ or per mill), and other units. In this report, $\delta^{i}E$ values are given in per mill; thus, the expression above can be written

$$\delta\,{}^{i}\mathrm{E}\ (\text{in ‰}) = \left[\frac{n_{\mathrm{X}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{X}}\left({}^{j}\mathrm{E}\right)}{n_{\mathrm{ref}}\left({}^{i}\mathrm{E}\right)/n_{\mathrm{ref}}\left({}^{j}\mathrm{E}\right)} - 1 \right] \cdot 1000 \ .$$

because one per mill is 1/1000, and 1000 · 1/1000 = 1. Note that per mill also is spelled per mil, permil, and per mille in the literature. The International Organization for Standardization (1992) spelling is used in this report.

A single isotopic reference material defines the isotope-ratio scale of most of the elements listed in this report; however, it has been recognized that a single isotopic reference material can define only the anchor point of an isotope-ratio scale, and not the magnitude (expansion or contraction) of the scale. Two reference materials are required to define scale magnitude and anchor point, as is done for the scales of hydrogen and oxygen. Most isotopic reference materials are naturally occurring materials or are manufactured from naturally occurring materials; others have been produced from reagents whose isotopes have been artificially fractionated.

For each element E in this report, the standard atomic weight, $A_{r}(E)$, from “Atomic Weights of the Elements 1999” (Coplen, 2001) is listed with its estimated uncertainty (in parentheses, following the last significant figure to which it is attributed). For zinc and molybdenum, the new standard atomic-weight values adopted at the 41st IUPAC General Assembly in Brisbane in July 2001 are listed instead. For most elements, data are graphically illustrated by a diagram in which the materials are specified in the ordinate and the compositional ranges are plotted along the abscissa on three scales: atomic weight, mole fraction of a selected isotope, and relative isotope ratio expressed as deviation from the isotope ratio of a reference in parts per thousand. The mole fraction of a selected isotope is given in percent in figures, tables, and text in this report. Mole fractions of the selected isotope are calculated from the relative isotope ratio by using the absolute isotope-abundance measurement of the reference for the delta scale. Atomic-weight values are calculated from atomic masses and mole fractions of the isotopes, assuming mass-dependent fractionation among the isotopes. The three scales are related exactly for elements with two isotopes for which absolute isotope abundances of the references are known; however, the scales may be mismatched in some cases: (1) for some elements, the absolute isotope abundances of the reference may not be known to within the precision of the common relative isotope-ratio measurements, (2) calculations of atomic weights for polyisotopic elements are subject to additional, usually negligible, adjustments based either on additional abundance measurements or on an assumption about the mass-dependent fractionation of isotopes that are not commonly measured. The section for each element lists the isotopic composition of a real or hypothetical material with delta value of 0 ‰; commonly, this material has been used for the best absolute isotope-abundance measurement as reported by Rosman and Taylor (1998). For many elements the atomic weight derived from the best measurement is not exactly the same as the standard atomic weight. This difference results because (1) the standard atomic weight uncertainty is limited to a single digit and the two cannot match exactly, or (2) $A_r(\mathrm{E})$ was assigned to be in the center of a range of natural isotopic variation and may be greatly different than that of the best measurement substance.

With the proliferation of microprobe techniques for isotope measurements, large variations in isotopic composition have been found in source materials over distances of the order of 1 to 1000 µm (McKibben and Eldridge, 1994). Such data are excluded from this compilation, as are data from extraterrestrial materials.

Although the data presented in this report may allow reduction in the uncertainty in atomic weight of a substance, the reader is warned that when critical work is undertaken, such as assessment of individual properties, samples with accurately known isotope abundances should be obtained or suitable measurements made.

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Hydrogen $A_r(\mathrm{H}) = 1.00\ 794(7)$

Hydrogen is the third most abundant element on surface of the Earth (after oxygen and silicon), and hydrogen in combined form accounts for about 15.4 % of the atoms in the Earth's crust (Greenwood and Earnshaw, 1997). Most (97 %) of the hydrogen produced in industry is produced on site as needed, for example, for ammonia synthesis, petrochemical uses, and other uses (Greenwood and Earnshaw, 1997). In additional, large quantities of hydrogen are produced for general use (~6.5×10^{10} g^3 in the United States alone).

Reference materials and reporting of isotope ratios

The primary isotopic reference material for hydrogen-bearing materials is the IAEA (International Atomic Energy Agency) reference water VSMOW (Vienna Standard Mean Ocean Water), which is assigned a δ^2H value of 0 ‰. Since 1993, CAWIA has recommended (Coplen, 1994) that stable hydrogen relative isotope ratios be reported relative to VSMOW (also distributed by NIST as RM 8535) on a scale normalized by assigning a δ^2H value of –428 ‰ to the IAEA reference water SLAP (Standard Light Antarctic Precipitation), which also is distributed as NIST RM 8537. Sometimes δ^2H is designated δD in the literature. Hydrogen isotopic compositions are determined on gaseous hydrogen using electron impact ionization mass spectrometry and commonly are measured with a 1-σ standard deviation of ±1 ‰. The absolute hydrogen isotope abundances of VSMOW reference water have been measured by Hagemann and others (1970), De Wit and others (1980), and Tse and others (1980), and a weighted mean value is shown in table 1.

One water (GISP), 1 oil (NBS 22), 1 biotite (NBS 30), 1 polyethylene foil (PEF1, renamed IAEA-CH-7), and 3 natural gases (NGS1, NGS2, and NGS3) are secondary reference materials distributed by IAEA and (or) NIST (table 2). In addition, for tracer studies the IAEA distributes IAEA-302A water with δ^2H of +508.4 ‰ and IAEA-302B water with δ^2H of +996 ‰ (Parr and Clements, 1991).

Ranges in Isotopic Composition

Hydrogen has the largest relative mass difference among its isotopes and consequently exhibits the largest variation in isotopic composition of any element that does not have radioactive or radiogenic isotopes. Ranges in the stable isotopic composition of naturally occurring hydrogen-bearing materials are shown in table 3 and figure 1. Compilations of hydrogen isotopic variations and isotope-fractionation factors include Friedman and O'Neil (1977; 1978), Fritz and Fontes (1989), Clark and Fritz (1997), and Valley and Cole (2001).

Water Variations in the ^{2}H content of surface waters, ground waters, and glacial ice generally are concordant with δ^{18}O variations and are caused primarily by evaporation and condensation processes (IAEA, 1981). Atmospheric moisture is depleted in ^{2}H by about 100 ‰ at 5°C relative to precipitation. The δ^2H values of naturally occurring waters range from –495 ‰ in Antarctic ice (Jouzel and others, 1987) to +129 ‰ in the Gara Diba Guelta Basin of the northwestern Sahara (Fontes and Gonfiantini, 1967). In precipitation δ^2H values decrease with increasing latitude, distance inland from a coast (Dansgaard, 1964), and increasing altitude [on the windward side of mountains only, a typical gradient in δ^2H of from –1.5 ‰ to –4 ‰ per 100 m is observed (Yurtsever and Gat, 1981)]. Precipitation is depleted in ^{2}H during winters relative to summers. Glacial-ice cores, studied to determine long-term climate change, typically are depleted in ^{2}H during full-glacial climates relative to interglacial climates. These isotopic variations permit tracing and identification of the origin and history of ground and surface waters (Coplen, 1993; Coplen, 1999). Deep oceanic water nearly is homogeneous in δ^2H, varying from –1.7 ± 0.8 ‰ in the Antarctic circumpolar region to +2.2 ± 1.0 ‰ in the Arctic (Redfield and Friedman, 1965). The δ^2H values of hydrothermal waters generally are identical to those of cold ground waters entering thermal regimes because there is little hydrogen in rocks to undergo hydrogen exchange. An unusual occurrence of water from a well in the Lacq natural gas field in France yielded δ^2H values as high as +375 ‰ (Roth, 1956). This occurrence was caused by a small amount of the water equilibrated at near ambient temperature with a much larger amount of H_2S with a δ^2H value of –430 ‰. The hydrogen

Table 1. *Hydrogen isotopic composition of VSMOW reference water*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{1}H	1.007 825 0319(6)	0.999 844 26(5)
^{2}H	2.014 101 7779(6)	0.000 155 74(5)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Hagemann and others (1970).

Table 2. *Hydrogen isotopic composition of selected hydrogen-bearing isotopic reference materials*

[Values for δ^2H given in per mill relative to VSMOW on a scale normalized such that the δ^2H of SLAP is –428 ‰ relative to VSMOW]

Reference Material	Substance	δ^2H	Reference
VSMOW	water	0 (exactly)	Gonfiantini, 1978
GISP	water	–189.73 ± 0.87	Gonfiantini and others, 1995
SLAP	water	–428 (exactly)	Gonfiantini, 1978
NBS 22	oil	–120 ± 4	Hut, 1987
NBS 30	biotite	–65.7 ± 0.27	Gonfiantini and others, 1995
NGS1	CH_4 in natural gas	–138 ± 6	Hut, 1987
NGS2	CH_4 in natural gas	–173 ± 4	Hut, 1987
NGS2	C_2H_6 in natural gas	–121 ± 7	Hut, 1987
NGS3	CH_4 in natural gas	–176 ± 10	Hut, 1987
IAEA-CH-7 (PEF1)	polyethylene	–100.33 ± 2.05	Gonfiantini and others, 1995

isotope-fractionation factor between water and H_2S is greater than 2, giving rise to water with a δ^2H value of +375 ‰. Experimentally, it is possible to produce δ^2H values in excess of +130 ‰ by evaporating water with a fan in a low humidity environment.

Most salt hydrates are depleted in ^2H relative to the coexisting liquid—for example, by 15 ‰ for gypsum. Some hydrates concentrate ^2H; $CaCl_2{\cdot}6H_2O$ and $Na_2SO_4{\cdot}10H_2O$ are enriched in ^2H by 10 ‰ and 17 ‰, respectively (Friedman and O'Neil, 1977; Friedman and O'Neil, 1978).

Agricultural food products are influenced by the isotopic composition of local meteoric waters. The enrichment of apple juice in ^2H is not as large as that in orange juice because of the lower levels of evapotranspiration occurring in the cooler northern latitudes of apple production. However, citrus trees are found in areas with subtropical climates when evaporation fractionates the water isotopes, resulting in ^2H enrichment in cellular water. For example, the ^2H content of orange juice is enriched by up to 40 ‰ relative to local meteoric water. Bricout and others (1973; also see Donner and others, 1987) showed that natural orange juice could be distinguished from orange juice reconstituted from concentrate and water added from higher latitudes because such waters typically are depleted in ^2H. The most positive δ^2H value for fruit juice and wine (+47 ‰) was reported for a sample of red wine (Martin and others, 1988).

Silicates The range of δ^2H values of silicates (table 3) is from –429 ‰ (Wenner, 1979) to +5 ‰ (Graham and Sheppard, 1980). Hydrogen isotope fractionations between most hydrogen-bearing minerals and water appear to be largely a function of the mass to charge ratio of the octahedral cation, and most hydrogen-bearing silicates are depleted in ^2H by 0 ‰ to 100 ‰. Because local meteoric water is involved in the formation or alteration of most hydrogen-bearing silicates, these silicates show a wide range in δ^2H. The extremely low value of δ^2H in pectolites [–429 ‰ to –281 ‰; (Wenner, 1979)] is not completely understood, but must result because of an unusual isotope-fractionation factor (Wenner, 1979). Analcime channel waters vary systematically with sample locality, whereas channel water in other zeolites (chabazite, clinoptilolite, laumontite, and mordenite) is largely from the ambient water vapor where the zeolites were last stored (Karlsson and Clayton, 1990). Hydrated silica (opal and diatomite) contains several types of structural water, much of which will be exchanged if temperatures reach 100 °C or at lower temperatures over geologic time.

Table 3. *Hydrogen isotopic composition of selected hydrogen-bearing materials*

[Values for δ^2H given in per mill relative to VSMOW on a scale normalized such that the δ^2H of SLAP is –428 ‰ relative to VSMOW]

Substance	Minimum δ^2H Value		Maximum δ^2H Value	
	δ^2H	Reference	δ^2H	Reference
WATER				
Sea water (deep)	–2.5	Redfield and Friedman, 1965	+3.2	Redfield and Friedman, 1965
Other (naturally occurring)	–495	Jouzel and others, 1987	+129	Fontes and Gonfiantini, 1967
Fruit juice and wine	–43	Bricout and others, 1973	+47	Martin and others, 1988
SILICATES				
$Ca_2NaH(SiO_3)$ (pectolite)	–429	Wenner, 1979	–281	Wenner, 1979
Other	–208	Friedman and O'Neil, 1978	+5	Graham and Sheppard, 1980
HYDROXIDES				
Aluminum and iron	–220	Yapp, 1993	–8	Bernard, 1978; Bird and others, 1989
ORGANIC HYDROGEN				
Non-marine organisms	–237	Schütze and others, 1982	+66	Sternberg and others, 1984
Marine organisms	–166	Schiegl and Vogel, 1970	–13	Schiegl and Vogel, 1970
Organic sediments	–103	Schiegl, 1972	–59	Oremland and others, 1988a
Coal	–162	Smith and Pallasser, 1996	–65	Redding, 1978
Crude oil	–163	Schiegl and Vogel, 1970	–80	Schiegl and Vogel, 1970
Ethanol (naturally occurring)	–272	Rauschenbach and others, 1979	–200	Rauschenbach and others, 1979
Ethanol (synthetic)	–140	Rauschenbach and others, 1979	–117	Rauschenbach and others, 1979

Table 3. *Hydrogen isotopic composition of selected hydrogen-bearing materials—Continued*

	Minimum δ^2H Value		Maximum δ^2H Value	
Substance	**δ^2H**	**Reference**	**δ^2H**	**Reference**
METHANE				
Atmospheric	–232	Snover and others, 2000	–71	Wahlen, 1993
Other (naturally occurring)	–531	Oremland and others, 1988b	–133	Schoell, 1980
HYDROGEN GAS				
Air	–136	Friedman and Scholz, 1974	+180	Gonsior and others, 1966
Other (naturally occurring)	–836	Coveney and others, 1987	–250	Friedman and O'Neil, 1978
Commercial tank gas	–813	T. B. Coplen, unpublished data	–56	J. Morrison, Micromass UK Ltd., Manchester, U.K., oral communication, 2002
Automobile exhaust and industrial contamination	–690	Gonsior and others, 1966	–147	Gonsior and others, 1966

Hydroxides The δ^2H of naturally occurring gibbsite ($Al_2O_3{\cdot}3H_2O$) and goethite [FeO(OH)] range from –220 ‰ to –8 ‰ (Yapp, 1993; Bernard, 1978) as shown in table 3. Hydroxides formed during much of the Phanerozoic in systems such as lateritic paleosols, bog ores, and other materials. Stable hydrogen and oxygen isotope ratios of hydroxides in these systems may provide information on continental paleoclimates (Yapp, 1993; Bird and others, 1989).

Organic hydrogen The hydrogen isotopic composition of organisms primarily reflects the hydrogen isotopic composition of water in the local environmental. Trees acquire their $n(^2\mathrm{H})/n(^1\mathrm{H})$ ratios from precipitation or (and) ground water. The large range in δ^2H of meteoric water gives rise to the large variation in δ^2H of vegetation (Yapp and Epstein, 1982) shown in table 3. The δ^2H values of sap from different types of trees range from –66 ‰ to –1 ‰ (White and others, 1985) with an anomalous value of +60 ‰ for sap from a poplar tree (Schiegl and Vogel, 1970). Evaporation and species-specific variations during metabolic or biochemical processes affect the hydrogen isotopic composition of organisms (Sternberg, 1988). The hydrogen isotopic composition of cellulose can be used to distinguish plants using the CAM photosynthetic pathway (δ^2H = +51 ± 10 ‰) from those using C_3 and C_4 pathways (δ^2H = –40 ± 20 ‰) according to Sternberg and others (1984). Zhang and others (1994) investigated the site-specific natural isotope fractionation of hydrogen in glucose and find that δ^2H values of glucose from C_3 plants are more negative (–106 ± 65 ‰) than those in C_4 plants (–22 ± 65 ‰); the uncertainty in the difference between the δ^2H values they report as ±16 ‰. An example of the practical use of this difference is to identify adulteration of orange juice with beet sugar (Donner and others, 1987). The organism with the lowest ^{2}H content found in the literature is algae from Lake Pomornika, Antarctica, with a δ^2H value of –237 ‰ (Schütze and others, 1982). The cellulose of *Yucca torreyi* has the highest ^{2}H content found in the literature (δ^2H = +66 ‰; Sternberg and others, 1984). Marine organisms show a smaller range in δ^2H value of between –166 ‰ and –13 ‰ (Schiegl and Vogel, 1970). The δ^2H values of organic sediments range between –103 ‰ (Schiegl, 1972) and –59 ‰ (Oremland and others, 1988a). The variation of δ^2H in coals—thought to be attributable to differing origins, maturation histories, moisture content during

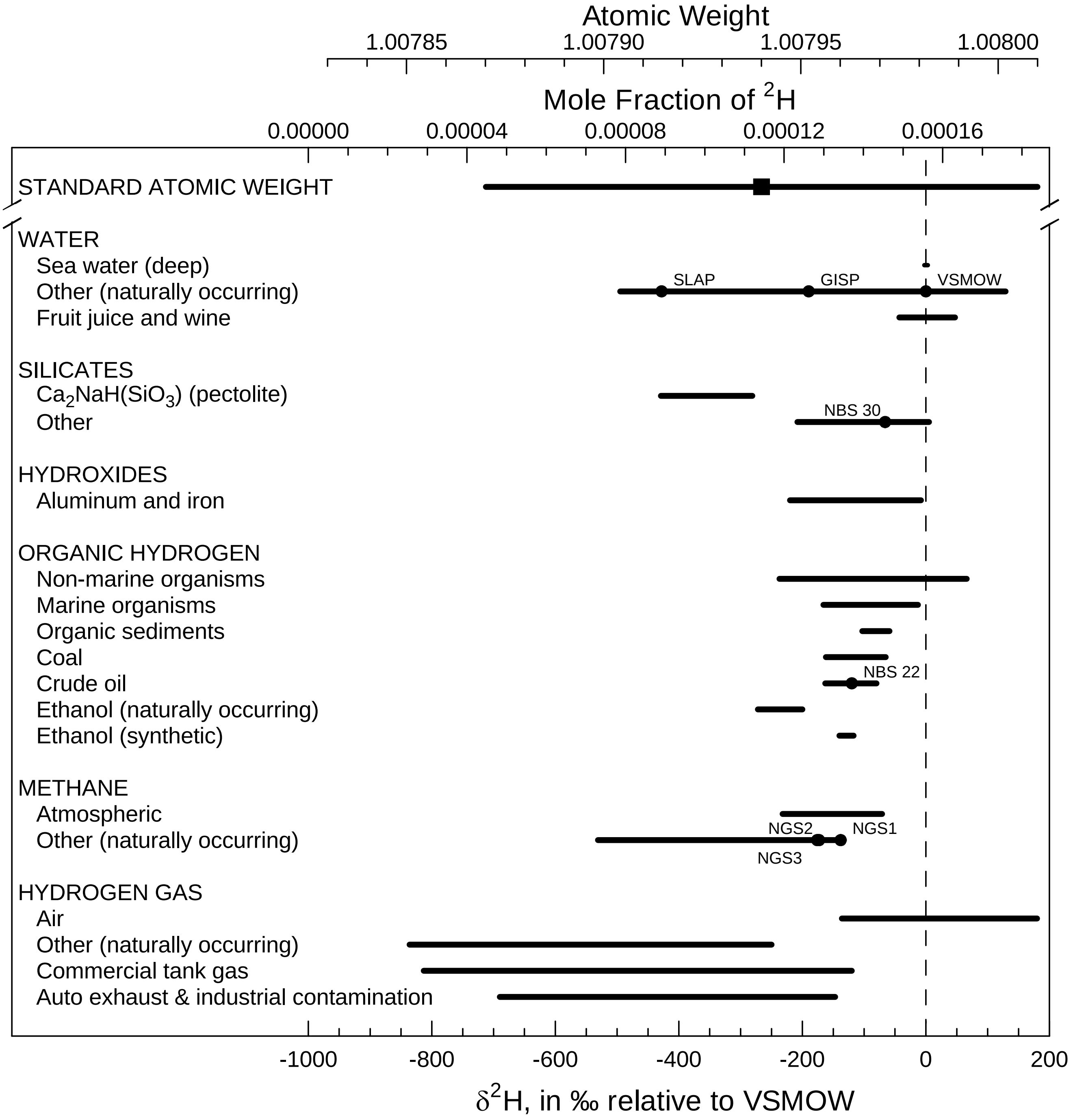

Figure 1. Hydrogen isotopic composition and atomic weight of selected hydrogen-bearing materials. The δ^2H scale and ^{2}H mole-fraction scale were matched using the data in table 1; therefore, the uncertainty in placement of the atomic-weight scale and the ^{2}H mole-fraction scale relative to the δ^2H scale is equivalent to ±0.3 ‰.

growth, and plant type—ranges from –162 ‰ (Smith and Pallasser, 1996) to –65 ‰ (Redding, 1978). Crude oil deuterium distributions (table 3) range in δ^2H from –163 ‰ to –80 ‰ (Schiegl and Vogel, 1970) with differences between the paraffin fraction and the aromatic fraction.

Hydrogen isotope ratios have been successfully used in food and beverage authentication. Rauschenbach and others (1979) note that ethanol produced from naturally occurring materials has a δ^2H ranging between –272 ‰ and –200 ‰ and is easily distinguished from synthetic ethanol, which has δ^2H values ranging between –140 ‰ and –117 ‰. According to K.P. Hom (Liquor Control Board of

Ontario, Ontario, Canada, written communication, 2001), ethanol from pure malt whisky ranges in δ^2H from –265 ‰ to –250 ‰ and bourbon is about –225 ‰. The δ^2H of amyl alcohol in pure malt whisky is similar to that of ethanol; however, in bourbon the δ^2H of amyl alcohol and isobutanol are about –190 ‰ and –165 ‰, respectively. Even in pure malt products, the δ^2H of isobutanol is relatively positive (–200 ‰). The major component of mustard oil is allyl isothiocyanate, which can be synthesized at a much lower price than its cost when extracted from mustard seeds; therefore, adulteration of natural mustard oil by adding synthetic allyl isothiocyanate is very profitable (Remaud and others, 1997). Natural and synthetic allyl isothiocyanate can be distinguished by site-specific hydrogen isotope-ratio studies because the δ^2H of the hydrogen atoms attached to the terminal carbon of the allyl group are depleted in ^{2}H by more than 150 ‰ than hydrogen in other positions (Remaud and others, 1997).

Methane The δ^2H of methane in terrestrial materials varies between –531 ‰ and –71 ‰ (table 3). The two major methane production processes are (1) diagenesis of organic matter by bacterial processes, and (2) thermal maturation of organic matter. Biogenic methane, produced by bacterial processes during the early stages of diagenesis, is formed in freshwater and marine environments, recent anoxic sediments, swamps, salt marshes, glacial till deposits, and shallow dry-gas deposits. Marine biogenic methane δ^2H values range from –250 ‰ (Nissenbaum and others, 1972) to –168 ‰ (Whiticar and others, 1986), whereas methane in freshwater sediments and swamps is more depleted in ^{2}H and ranges in δ^2H from –400 ‰ to –224 ‰ (Whiticar and others, 1986). According to Schoell (1980) and Whiticar and others (1986), methane resulting from acetate fermentation will be depleted in ^{2}H relative to that produced when CO_2 reduction predominates (Schoell, 1980; Whiticar and others, 1986) because the fractionation is larger for acetate fermentation due to the transfer of the methyl group during methanogenesis that is depleted in deuterium and accounts for three-fourths of the hydrogen in the methane.

The δ^2H of thermogenic methane not associated with oil genesis ranges from –177 ‰ to –133 ‰ (Schoell, 1980). The δ^2H of thermogenic methane that is associated with oil generation ranges from –495 ‰ (Gerling and others, 1988) to –153 ‰ Schoell (1980).

The global average δ^2H of atmospheric methane, which originates from swamps, rice paddies, ruminants, termites, landfills, fossil-fuel production, and biomass burning, is –86 ± 3 ‰ (Quay and others, 1999). Brazilian biomass burning produced methane as negative in δ^2H value as –232 ‰ (Snover and others, 2000).

Hydrocarbons are formed by a process termed "bit metamorphism" during conventional well drilling, during drilling of ultra-deep gas exploration wells, and during drilling of hard crystalline rocks. Methane produced in this way commonly is substantially depleted in ^{2}H. For example, Whiticar (1990) reports a δ^2H value of –760 ‰ for methane from a pilot gas well in Siljan Ring, Sweden.

Hydrogen gas The δ^2H value of naturally occurring gaseous hydrogen (see table 3) ranges from –836 ‰ in natural gas from a Kansas well (Coveney and others, 1987) to +180 ‰ in atmospheric hydrogen (Gonsior and others, 1966). The ^{2}H content of atmospheric hydrogen can be much higher than in any of its sources. These high concentrations are attributed to the large kinetic isotope-fractionation factor (1.65 ± 0.05) in the reaction of atmospheric hydrogen with HO:

$$H_2 + HO \rightarrow H_2O + H,$$

which preferentially enriches remaining hydrogen in ^{2}H (Ehhalt and others, 1989). Low temperature serpentinization of ophiolitic rocks generates free hydrogen along with minor amounts of methane and ethane. Fritz and others (1992) found δ^2H values of gaseous hydrogen as negative as –733 ‰. Anthropogenic hydrogen commonly is generated by automobile exhaust, and δ^2H values ranges from –690 ‰ to –147 ‰ (Gonsior and others, 1966).

The majority of industrial hydrogen is produced from petrochemicals. The dominant process is the catalytic steam-hydrocarbon reforming process using natural gas or oil-refinery feedstock, which typically yields hydrogen that is strongly depleted in ^{2}H (for example, δ^2H = –600 ‰). The tank hydrogen with the lowest reported ^{2}H content was from MG Industries and had a δ^2H value of –813 ‰. Hydrogen produced by electrolysis constitutes about 4 percent of industrial production and is variable in isotopic composition, but often it only is slightly depleted in ^{2}H relative to feed water (for example, δ^2H = –56 ‰; J. Morrison, Micromass UK Ltd., Manchester, U.K., oral communication, 2002). A hydrogen generator can be used to generate hydrogen of a desired isotopic composition by mixing ^2H_2O into the feed water, as necessary.

The lowest reported ^{2}H concentration in a naturally occurring terrestrial material is from hydrogen gas with a δ^{2}H value of –836 ‰, discussed above (Coveney and others, 1987). For this specimen, the mole fraction of ^{2}H is 0.000 0255 and A_r(H) = 1.007 851. The highest reported ^{2}H concentration in a naturally occurring terrestrial material is from atmospheric hydrogen gas with a δ^{2}H value of +180 ‰, discussed above (Gonsior and others, 1966). For this specimen, the mole fraction of ^{2}H is 0.000 1838 and A_r(H) = 1.008 010.

Lithium A_r(Li) = 6.941(2)

Lithium is about 10,000 times less abundant on Earth than silicon, and about 10^{-9} as abundant as hydrogen in the cosmos. Lithium is an important industrial compound in lubricating greases, aluminum alloys, brazing flux, and batteries. Lithium carbonate is the most important industrial compound of lithium and is the starting point for the production of most other lithium compounds (Greenwood and Earnshaw, 1997).

Reference materials and reporting of isotope ratios

The primary reference for the relative isotope abundance measurements of lithium isotopes is the IAEA isotopic reference material L-SVEC (NIST RM 8545), a Li_2CO_3 with an assigned δ^{7}Li value of 0 ‰. Lithium isotope-ratio measurements commonly are performed using positive ion thermal ionization mass spectrometry, and isotope ratios commonly are determined with a 1-σ standard deviation of ±1 ‰. The absolute isotope abundances of L-SVEC have been measured by Qi and others (1997a) and are shown in table 4. In accord with the recommendation of IUPAC (Coplen, 1996), δ^{7}Li values (based on $n(^{7}\mathrm{Li})/n(^{6}\mathrm{Li})$ measurements) are presented in this report, though δ^{6}Li values (based on $n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$ measurements also have been reported in the literature.

IRMM-015 and IRMM-016 lithium carbonates are internationally distributed reference materials that are available from the Institute of Reference Materials and Measurements in Geel, Belgium. The δ^{7}Li of IRMM-015 and IRMM-016, respectively, are –996 ‰ and 0 ‰. Within analytical uncertainty, IRMM-016 has isotope abundances identical to that of L-SVEC (Qi and others, 1997a).

Ranges in Isotopic Composition

Even though lithium occurs only in the +1 valence state in naturally occurring materials, lithium shows a range in δ^{7}Li of more than 50 ‰. Ranges in stable isotopic composition of naturally occurring lithium-bearing materials are shown in table 5 and figure 2.

Marine sources Lithium is supplied to the ocean primarily from two sources: (1) high temperature (> 250 °C) basalt-ocean-water reactions (Edmond and others, 1979), and (2) river input of weathering continental crust. Removal processes of lithium from the ocean include (1) low temperature (< 250°C) alteration of oceanic crust in which basalts take up lithium, (2) biogenic carbonate production—marine carbonates contain 2 mg/kg lithium on average, (3) biogenic opal and chert production—Quaternary radiolarian and diatomaceous oozes contain about 30 mg/kg Li, and (4) diagenesis of clay minerals and authigenic clay mineral production may be the most important sink for lithium (Chan and others, 1992).

Sea water is approximately homogeneous and has a δ^{7}Li value of about +33 ‰ (table 5). Using an improved procedure, You and Chan (1996) have been able to improve lithium isotope-ratio precision and reduce the amount of sample required for analysis. The δ^{7}Li of pore water from 195.7 m below the ocean

Table 4. *Lithium isotopic composition of L-SVEC lithium carbonate*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{6}Li	6.015 1223(5)	0.075 91(20)
^{7}Li	7.016 0041(5)	0.924 09(20)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Qi and others (1997a).

Table 5. *Lithium isotopic composition of selected lithium-bearing materials*

[Values for δ^7Li given in per mill relative to L-SVEC]

Substance	Minimum δ^7Li Value		Maximum δ^7Li Value	
	δ^7Li	Reference	δ^7Li	Reference
MARINE SOURCES				
Sea water	+32.4	You and Chan, 1996	+33.9	Chan and Edmond, 1988
Hydrothermal fluids	+2.6	Chan and others, 1994	+11	Chan and others, 1993
Foraminifera and carbonate sediments	–10	Hoefs and Sywall, 1997	+42	Hoefs and Sywall, 1997
Brines and pore water	+1	Vocke and others, 1990	+56.3	You and Chan, 1996
NON-MARINE SOURCES				
Surface water	+15.5	Chan and others, 1992	+34.4	Chan and Edmond, 1988
Ground and thermal water	–19	T. Bullen, U.S. Geological Survey, written communication, 2001	+10	T. Bullen, U.S. Geological Survey, written communication, 2001
Contaminated ground water	+10	T. Bullen, U.S. Geological Survey, written communication, 2001	+354	T. Bullen, U.S. Geological Survey, written communication, 2001
LITHIUM IN ROCKS				
Basalt (unaltered)	+3.4	Chan and others, 1992	+6.8	Chan and others, 1992
Basalt (altered)	–2.1	Chan and others, 1992	+13.5	Chan and others, 1995
Rhyolite	–3.5	Bullen and Kharaka, 1992	–3.5	Bullen and Kharaka, 1992
Granite	0.0	R. D. Vocke, Jr., unpublished data	+11.2	Tomascak and others, 1995
Limestone	–3.5	Bullen and Kharaka, 1992	+33.5	Hoefs and Sywall, 1997
PHOSPHATES				
$LiAlFPO_4$ (amblygonite)	–13	Cameron, 1955	+7.4	Svec and Anderson, 1965
SILICATES				
$LiAl(SiO_3)_2$ (spodumene)	–12.6	Cameron, 1955	+11.8	R. D. Vocke, Jr., unpublished data
$KLiAl_2Si_3O_{10}$ (lepidolite)	–6.6	Cameron, 1955	+7.2	Cameron, 1955

Table 5. *Lithium isotopic composition of selected lithium-bearing materials—Continued*

Substance	Minimum δ^7Li Value δ^7Li	 Reference	Maximum δ^7Li Value δ^7Li	 Reference
REAGENTS				
^{6}Li depleted compounds	+434	Qi and others, 1997a	+3013	Qi, and others, 1997a
Other	–11	Qi and others, 1997a	+23	Qi, and others, 1997a

bottom at ODP site 851A contains the highest level of ^{7}Li recorded in a natural terrestrial sample, with δ^7Li = +56.3 ‰ (You and Chan, 1996). The mole fraction of ^{7}Li in this specimen is 0.9278 and A_r(Li) = 6.9438. The δ^7Li of carbonate from the same level was about +33 ‰. Foraminifera shells from ODP site 806B showed a δ^7Li value of about +40 ‰. The foraminiferal lithium isotope data of You and Chan (1996) indicate glacial-interglacial changes in the inventory and isotopic composition of oceanic lithium. Four samples of foraminiferal tests from 2 glacial-interglacial cycles during the past 1 million years show systematic variations of lithium content and lithium isotope abundances with climate.

Non-marine sources In order to understand the global lithium cycle, Chan and others (1992) analyzed the δ^7Li values of rivers in different geologic terrains. Not surprisingly, the δ^7Li values of rivers are correlated to geologic terrains of drainage basins. The Mississippi River drains mixed volcanic and sedimentary terrains with a δ^7Li value as low as +15.5 ‰. Values as high as +19 ‰ are expected in such terrains. The Amazon River is low in lithium concentration and δ^7Li values reach values as high as +30.3 ‰, probably because the ancient shield terrains in this river basin have been almost completely weathered and most of the dissolved lithium is derived from marine evaporites, which are abundant in the Andes Mountains (Chan and others, 1992; Stallard and Edmond, 1983).

The lithium isotope abundances of thermal waters are related to geologic environment. Bullen and Kharaka (1992) analyzed thermal waters in Yellowstone National Park and found a wide range in δ^7Li value, from –12 ‰ to +2 ‰. Thermal waters from the Norris-Mammoth corridor had similar δ^7Li values, whereas thermal waters to the north were enriched in ^{7}Li. These differences are attributed to lower δ^7Li values from hydrothermally altered rocks and the higher δ^7Li values being derived from clays and other secondary minerals in marine sediments (Bullen and Kharaka, 1992). The lowest δ^7Li value in a natural sample of terrestrial origin is –19 ‰ for a ground water from a coastal aquifer of South Carolina (USA) (T. Bullen, U.S. Geological Survey, written communication, 2001). The mole fraction of ^{7}Li in this ground water is 0.9227 and A_r(Li) = 6.9387. Down gradient in the aquifer, the δ^7Li value increased to +10 ‰ after extensive dissolution of marine aragonite, but prior to major Ca-for-Na exchange on clays, which subsequently lowers δ^7Li value to approximately 0 ‰. T. Bullen (U.S. Geological Survey, written communication, 2001) reports δ^7Li values from –4 ‰ to +354 ‰ in ground water underlying West Valley Creek in Pennsylvania (USA), down gradient from a lithium processing plant. Values as high as +290 ‰ were measured in the main stem of West Valley Creek. The highest values of ^{7}Li content are probably related to removal of ^{6}Li from reagents for use in hydrogen bombs. The remaining lithium is substantially enriched in ^{7}Li and has been used in chemical and pharmaceutical manufacturing.

Lithium in rocks In order to investigate the possibility of utilizing lithium isotope ratios between co-precipitating minerals in a granite-pegmatite system, Tomascak and others (1995) analyzed lithium isotope ratios in various pegmatite albites. Wall zone albite was found to be the most enriched in ^{7}Li, but intermediate zones did not show a trend with decreasing temperature of precipitation.

Limestone shows a wide variation in δ^7Li value with values ranging from –3.5 ‰ in Paleozoic limestone in Yellowstone National Park, Wyoming (Bullen and Kharaka, 1992) to +33.5 ‰ in German limestone (Hoefs and Sywall, 1997).

Phosphates Amblygonite ($LiAlFPO_4$) is found in granite pegmatite and is mined as an ore of lithium.

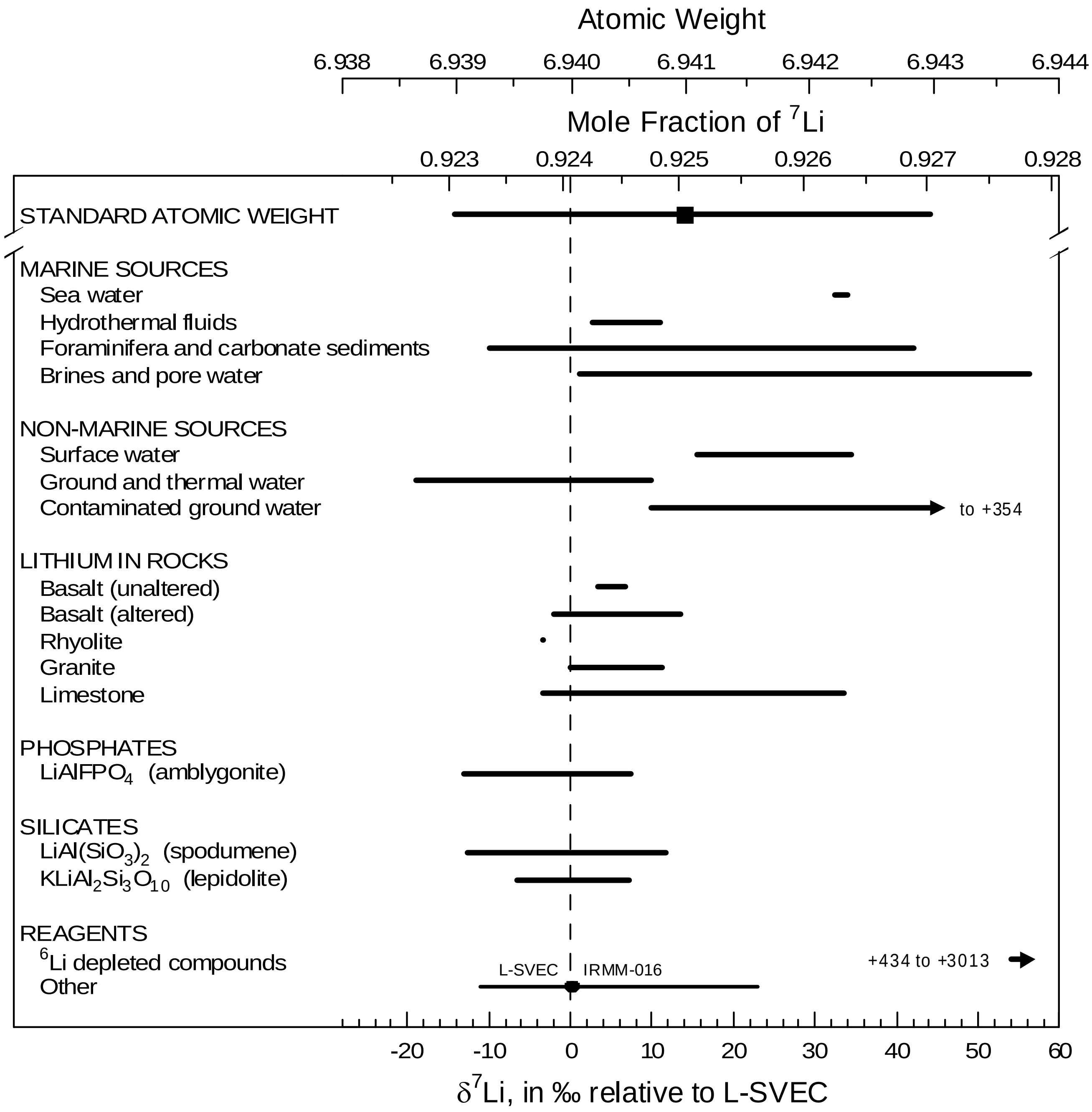

Figure 2. Lithium isotopic composition and atomic weight of selected lithium-bearing materials. The δ^7Li scale and ^{7}Li mole-fraction scale were matched using the data in table 4; therefore, the uncertainty in placement of the atomic-weight scale and the ^{7}Li mole-fraction scale relative to the δ^7Li scale is equivalent to ±3 ‰.

Published δ^7Li values of amblygonite range from –13 ‰ (Cameron, 1955) to +7.4 ‰ (Svec and Anderson, 1965).

Silicates Li-bearing silicates were among the first Li-bearing specimens to be analyzed for lithium isotopic composition. The δ^7Li of spodumene ranges between –12.6 ‰ (Cameron, 1955) and +11.8 ‰ (R. D. Vocke, Jr., unpublished data). That of lepidolite ranges between –6.6 ‰ and +7.2 ‰ (Cameron, 1955).

Reagents Of the chemical elements discussed in this report, lithium is particularly unusual because large amounts of lithium have been isotopically fractionated by removal of ^{6}Li for use in hydrogen bombs. The remaining lithium is substantially enriched in ^{7}Li and some of this lithium has found its way into laboratory reagents and into the environment. An analysis of 39 laboratory reagents (Qi and others, 1997b) indicated a δ^7Li range of between −11 ‰ (for Baker-Adamson lithium sulfate) and +3013 ‰ (for Fisher Scientific lithium hydroxide). The δ^7Li of lithium carbonate, the most common starting material for other Li-bearing reagents, ranged from 0 ‰ to +12 ‰.

Boron A_r(B) = 10.811(7)

Boron is not abundant—its average concentration in crustal rocks (9 mg/kg) is less than that of lithium (18 mg/kg). A primary commercial source is borate minerals found in commercial quantities in California (USA) and Turkey. ^{10}B is used in nuclear applications in neutron shields and control rods because of the high absorption cross-section of ^{10}B for thermal neutrons. The primary non-nuclear uses of boron are in heat resistant glasses (Pyrex), detergents, soaps, cleaners, cosmetics, porcelain enamels, synthetic herbicides and fertilizers, and abrasives.

Reference materials and reporting of isotope ratios

The primary reference for the relative abundance measurements of boron isotopes is the NIST reference material SRM 951 boric acid, which is assigned a δ^{11}B value of 0 ‰. Boron isotope-ratio measurements commonly are performed using negative ion thermal ionization mass spectrometry, and isotope ratios commonly are determined with a 1-σ standard deviation of ±1 ‰.

The absolute isotope abundances of SRM 951 have been measured by Catanzaro and others (1970) and are listed in table 6. A second reference material, IRMM-011 boric acid, is nearly identical in isotopic composition to SRM 951 (NIST, 1999a), and it is available from IRMM (Institute for Reference Materials and Measurements), Geel, Belgium. Two boric acid reference materials (IRMM-610 and SRM 952) are depleted in ^{11}B (NIST, 1999b; IRMM, 2001). The IAEA recognized the paucity of boron isotopic reference materials and has recently distributed 3 water and 5 rock reference materials to boron isotope laboratories (Tonarini and others, in press). These materials have been analyzed by negative ion thermal ionization mass spectrometry, positive ion thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry, and MC-ICP-MS. These materials are listed in table 7 and shown in fig 3.

Ranges in Isotopic Composition

Boron isotope ratios show large variations (> 90 ‰) in the terrestrial environment (table 8 and figure 3). Naturally occurring boron predominantly is found in the +3 oxidation state and does not undergo redox reactions. In solution, boric acid is enriched in ^{11}B by 20 ‰ relative to coexisting borate ions, $B(OH)_4^-$. During precipitation, borate preferentially enters the solid phase, enriching the residual solution in ^{11}B. When boron is attracted to clays or other active surfaces, the predominant species attracted is tetrahedral $B(OH)_4^-$; thus, residual dissolved boron is enriched in ^{11}B. Bassett (1990) has compiled and critically evaluated boron isotopic measurements prior to 1990.

Marine sources The δ^{11}B of sea water is relatively constant at +39.5 ‰. The values of sea water measured by Schwarcz and others (1969) have not been used because they probably are too high according to Bassett (1990). Shima's (1962; 1963) analyses of borax and ocean water differ by more than 30 ‰ from those of other researchers; thus, they are not included in this report. As sea water evaporates, salts are depleted in ^{11}B by 30 per mill in the early stages of precipitation and by 20 per mill in the latter stages of precipitation (Vengosh and others, 1992), increasing the ^{11}B content of evaporated sea water. The highest published δ^{11}B value of evaporated sea water is +58.5 ‰ from the Mediterranean Sea (Klötzli, 1992).

Table 6. *Boron isotopic composition of NIST SRM 951 boric acid*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{10}B	10.012 9371(3)	0.198 27(13)
^{11}B	11.009 3055(4)	0.801 73(13)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Catanzaro and others (1970)

Table 7. *Boron isotopic composition of selected boron-bearing isotopic reference materials*

[Values for δ^{11}B given in per mill relative to NIST SRM 951 boric acid]

Reference Material	Substance	δ^{11}B	Reference
SRM 951	boric acid	0 (exactly)	Catanzaro and others, 1970
IRMM-011	boric acid	–0.16	Lamberty and De Bièvre, 1991
SRM 952	boric acid	–987	NIST, 1999b
IRMM-610	boric acid solution	–987	IRMM, 2001
IAEA-B-1	surface sea water, Western Mediterranean Sea	+37.7 ± 2.1	Tonarini and others, in press
IAEA-B-2	ground water, alluvial aquifer, Cecina River, lower basin (Tuscany, Italy)	+13.6 ± 2.6	Tonarini and others, in press
IAEA-B-3	ground water, alluvial aquifer, River Cecina, upper basin (Tuscany, Italy)	–21.3 ± 0.9	Tonarini and others, in press
IAEA-B-4	tourmaline, Elba Island (Tuscan Archipelago, Italy)	–10.6 ± 3.2	Tonarini and others, in press
IAEA-B-5	basalt, Mt. Etna's main crater (Sicily), eruption July 1998	–4.2 ± 2.7	Tonarini and others, in press
IAEA-B-6	obsidian, Lipari Island, Italy (Eolian Archipelago)	–3.3 ± 1.8	Tonarini and others, in press
IAEA-B-7	Miocene marine limestone (Abruzzi, Italy)	+7.2 ± 3.9	Tonarini and others, in press
IAEA-B-8	Pliocene clay (Montelupo Fiorentino, Italy)	–5.4 ± 1.2	Tonarini and others, in press

Large-scale boron exchange between sea water and oceanic crust occurs at both high and low temperature (Spivack and Edmond, 1987). Hydrothermal solutions from 9 separate oceanic vent fields have δ^{11}B values between +30.0 ‰ and +36.8 ‰ (Spivack and Edmond, 1987). Boron extracted from basalts involved in high temperature reaction show no resolvable isotope fractionation. Serpentinites and basalts altered at low temperature are enriched in boron and have δ^{11}B values between +0.1 ‰ and +9.2 ‰. This preferential transfer of ^{10}B into altered oceanic sediments is in part responsible for the high δ^{11}B of sea water.

Because the δ^{11}B of sea water is about +40 ‰ and because the isotope fractionation between $B(OH)_3$ and $B(OH)^-_4$ is about 20 ‰ (Kakihana and others, 1977), the δ^{11}B of marine evaporites should be about +20 ‰ or higher. Swihart and others (1986) find the range to be between +18.2 ‰ and +31.7 ‰. The δ^{11}B of modern marine carbonates falls in a relatively narrow range (+22 ± 3 ‰) according to Hemming and Hanson (1992). This band is about 20 ‰ more negative than that of sea water and is explained by the fact that tetrahedral $B(OH)^-_4$, which is depleted in ^{11}B by 20 ‰ relative to $B(OH)_3$, is preferentially incorporated into the carbonate structure. The range in δ^{11}B value expands from +4.0 ‰ to +32.2 ‰ (Vengosh and others, 1991b) if hand picked foraminifera and ostracoda are included.

Non-marine sources The primary sources of boron are non-marine evaporite deposits in California (USA) and Turkey, which yield large quantities of borates. It was hypothesized that non-marine borates would reflect the isotopic composition of crustal rocks

Table 8. *Boron isotopic composition of selected boron-bearing materials*

[Values for δ^{11}B given in per mill relative to NIST SRM 951 boric acid]

	Minimum δ^{11}B Value		Maximum δ^{11}B Value	
Substance	δ^{11}B	Reference	δ^{11}B	Reference
MARINE SOURCES				
Sea water	+38.4	Vengosh and others, 1991a	+40.4	Nomura and others, 1982
Evaporated sea water	+36.5	Vengosh and others, 1991a	+58.5	Klötzli, 1992
Hydrothermal fluids	+30.0	Spivack and Edmond, 1987	+36.8	Spivack and Edmond, 1987
Evaporite minerals	+18.2	Swihart and others, 1986	+31.7	Swihart and others, 1986
Carbonates (Skeletal parts and formations)	+4.0	Vengosh and others, 1991b	+32.2	Vengosh and others, 1991b
NON-MARINE SOURCES				
Rain water	+0.8	Spivack, 1986	+35	Spivack, 1986
Brines, surface and ground waters	–21.3	Tonarini and others, in press	+59.2	Vengosh and others, 1991a
Hydrothermal fluids	–9.3	Palmer and Sturchio, 1990	+29.1	Klötzli, 1992
Evaporite minerals	–31.3	Finley and others, 1962	+7.3	Agyei and McMullen, 1968
IGNEOUS ROCKS	–17.0	Trumbull and Chaussidon, 1999	–1.7	Spivack and Edmond, 1987
METAMORPHIC ROCKS	–34.2	Wang and Xiao, 2000	+22	Swihart and Moore, 1989
SEDIMENTS	–17	Ishikawa and Nakamura, 1993	+26.2	Ishikawa and Nakamura, 1993
ORGANIC BORON	–12	Wieser and others, 2001	+29.3	Vanderpool and Johnson, 1992

and minerals, which is about 40 ‰ more negative than marine boron (Swihart and others, 1986). Except for one value at +24 ‰, the δ^{11}B of non-marine evaporites ranged between –31.3 ‰ (Finley and others, 1962) and +7.3 ‰ (Agyei and McMullen, 1968). Thus, non-marine borates are depleted in ^{11}B relative to marine borates (+18.2 ‰ to +31.7 ‰) and boron isotope ratios can be used to differentiate the two evaporite borates (Swihart and others, 1986).

The boron isotopic composition of fumarolic condensates is thought to reflect the boron isotopic composition of associated magmas (Kanzaki and others, 1979). Nomura and others (1982) measured

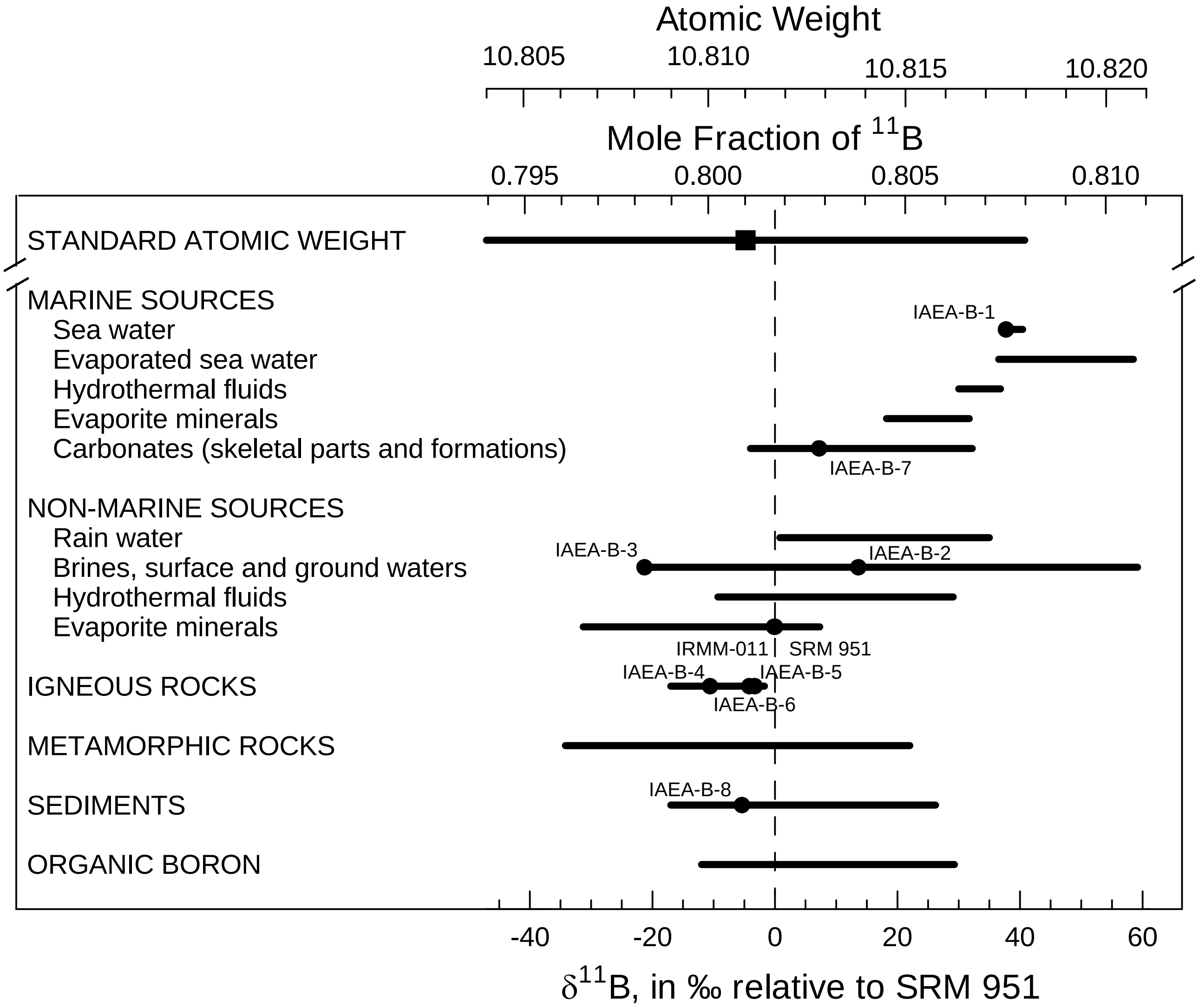

Figure 3. Boron isotopic composition and atomic weight of selected boron-bearing materials. The δ^{11}B scale and ^{11}B mole-fraction scale were matched using the data in table 6; therefore, the uncertainty in the placement of the atomic-weight scale and the ^{11}B mole-fraction scale relative to the δ^{11}B scale is equivalent to ±0.8 ‰.

40 fumarolic condensates from the Japanese island arc. Most condensates possess δ^{11}B values near +6 ‰, reflecting the boron isotopic composition of crustal rocks. However, values above +17 ‰ were found in the southernmost end of the northeastern Japanese arc, and these more positive values were attributed to interaction of magmas with sea water (δ^{11}B = +39.5 ‰). In a reconnaissance of Yellowstone National Park (Wyoming), Palmer and Sturchio (1990) found δ^{11}B values between –9.3 ‰ and +4.4 ‰. They suggest that the most negative values may be explained by leaching of boron from hydrothermally altered rhyolite. The highest δ^{11}B values in hydrothermal fluids were measured by Klötzli (1992) on Larderello geothermal field (Italy) samples (+21.8 ‰ to +29.1 ‰). These high values were attributed to meteoric waters incorporating boron from marine sediments. The δ^{11}B value of –59 ‰ obtained for Sasso Pisano 6 is not included because it cannot be satisfactorily explained (Klötzli, 1992)—it may be due to matrix effects during the isotopic analysis.

An important source of boron to the oceans for studying global boron cycling is boron in rivers. The δ^{11}B values of rivers representing 39 percent of the total world discharge of water range from –5.9 ‰ to +42.8 ‰ (Lemarchand and others, 2000).

Surface and ground waters display a wide range in boron isotopic composition. Gäbler and Bahr (1999) were able to confirm the anthropogenic input of boron in ground water north of the Harz Mountains in Germany. They identified a region with δ^{11}B values between –3 ‰ and +3 ‰ and attributed these values to perborates in detergents (exactly the range expected for perborates in the United States and Europe). Bassett and others (1995) were able to distinguish water-recharge types in an injection site of treated wastewater into an alluvial aquifer near El Paso, Texas, because the δ^{11}B of native ground water was +14 ‰; that of municipal wastewater was between +6 ‰ and +10 ‰, and that of irrigation-affected water was greater than +40 ‰. The highest δ^{11}B value found in the literature for a naturally occurring terrestrial material is +59.2 ‰ in brine from Maar lakes from southwestern Victoria, Australia (Vengosh and others, 1991a). The mole fraction of ^{11}B in this sample is 0.8107 and A_r(B) = 10.8207. Another continental brine, also of largely marine derived boron, is found in Laizhou Bay region of China with a δ^{11}B value of +57.5 ‰ (Xiao and others, 2001). Both of these brines have non-marine B/Cl ratios.

Igneous rocks The δ^{11}B of boron in the mantle is –10 ± 2 ‰, based on measurements of volcanic glasses and oceanic island basalts, which yield δ^{11}B = –9.9 ± 1.3 ‰ (Chaussidon and Marty, 1995). Unaltered mid-ocean ridge basalts from the East Pacific Rise have δ^{11}B values in the range of –4.0 ‰ to –1.7 ‰ (Spivack and Edmond, 1987; Chaussidon and Marty, 1995). As basalts undergo low temperature alteration, ^{11}B and boron concentrations are increased as discussed above. In a study in Swaziland, tourmalines in granite have a narrow range in δ^{11}B of between –17.0 ‰ and –13.5 ‰ (Trumbull and Chaussidon, 1999). In a worldwide survey of boron isotopic composition, Swihart and Moore (1989) observed a range in δ^{11}B of –12 ‰ to –5 ‰ for tourmaline in granite pegmatites.

Metamorphic rocks Tourmalines from a coarse, zoned pegmatite and hydrothermal tourmalines in a study from Swaziland ranged in δ^{11}B value from –23.0 ‰ to –16.6 ‰ (Trumbull and Chaussidon, 1999). Swihart and Moore (1989) found a range in δ^{11}B of –22 ‰ to +22 ‰ for tourmalines and metasedimentary rocks. Relatively high concentrations of ^{11}B (δ^{11}B > –1 ‰) were interpreted as indicating boron of marine or sedimentary origin. The sample of natural terrestrial origin with the lowest reported ^{11}B content in figure 3 is kornerupine $[(Mg,Fe^{2+})_4(Al,Fe^{3+})_6(SiO_4,BO_4)_5(O,OH)_2]$ from Antarctica (Wang and Xiao, 2000) with a δ^{11}B value of –34.2 ‰. The mole fraction of ^{11}B of this specimen is 0.7961 and A_r(B) = 10.8062.

Sediments The boron isotopic composition of sediments is variable. Boron isotopes are fractionated by 30 ‰ to 40 ‰ by preferential adsorption of ^{10}B of dissolved boron on clay minerals (Schwarcz and others, 1969), giving rise to low δ^{11}B values of clays. The δ^{11}B of most modern marine sediments falls in the range –6.6 ‰ to +4.8 ‰ (Ishikawa and Nakamura, 1993). The boron isotopic composition is controlled by mass balance of four major constituents: detritus of continental origin, marine smectite, biogenic carbonates, and biogenic silica. Detritus of continental origin, especially illite from eolian or fluvial transport, is the low δ^{11}B end-member of marine sediments (–13 ‰ to –8 ‰). Biogenic carbonate is the high end-member with δ^{11}B values between +8.0 ‰ and +26.2 ‰ (Ishikawa and Nakamura, 1993). These high ^{11}B concentrations are the result of equilibrium uptake of boron from sea water.

The δ^{11}B of ancient marine sediments is more negative (–17.0 ‰ to –5.6 ‰) than that of modern sediments (Ishikawa and Nakamura, 1993). The more negative δ^{11}B values can be caused by diagenesis, which promotes preferential removal of ^{11}B in calcium carbonate and silica during recrystallization, or by boron isotopic exchange during smectite/illite transition.

Organic boron Boron is an essential chemical element for the healthy development of many plants. Vanderpool and Johnson (1992) analyzed a variety of commercial produce grown in North America and found a range of –7.5 ‰ to +29.3 ‰ in δ^{11}B. Wieser and others (2001) analyzed the boron isotopic composition of *Coffee arabica* bean samples from around the world and found δ^{11}B values from –12 ‰ for Peru “organic” beans to +19 ‰ for beans from Tanzania. Wieser and others (2001) conclude that the isotopic composition of local boron sources, such as boron in the soil, fertilizer, and water, control the δ^{11}B values of the coffee beans. Thus, the boron isotopic composition of coffee can be used in quality-assurance programs as the quality depends to a large extent on the genetic and geographic origin of the coffee.

Williams and others (2001) analyzed boron content and isotopic composition of kerogen in Gulf of Mexico sediments. They found large concentrations of organically bound boron (140 mg/kg) with a δ^{11}B value of –2 ‰ that may serve as a source for boron in deep sedimentary brines with low δ^{11}B values (< approximately 25 ‰).

Carbon $A_r(C) = 12.0107(8)$

Although carbon is the fourth most abundant element in the universe after hydrogen, helium, and oxygen, its abundance in the Earth's crust is only about fourteenth. Carbon occurs as the free element (graphite and diamond), in fossil fuels (coal and petroleum), as the important atmospheric gas carbon dioxide, in carbonates of calcium and magnesium, and in living and dead plants and animals. Important uses include energy production, steel making, sugar manufacturing, water treatment, and respirators.

The continual interaction of carbon among the lithosphere, biosphere, atmosphere, and hydrosphere is called the carbon cycle. Carbon isotope ratios commonly are used to investigate carbon-cycle processes.

Reference materials and reporting of isotope ratios

Beginning in the 1950's, isotope-abundance measurements of carbon isotopes were expressed relative to Peedee belemnite (PDB), which was assigned a $\delta^{13}C$ value of 0 ‰. Because the supply of PDB is exhausted, IUPAC recommended in 1993 (Coplen, 1994; IUPAC, 1994) that carbon isotope abundances be reported relative to VPDB (Vienna PDB, the new primary reference for carbon isotope ratios having a $\delta^{13}C$ value of 0 ‰) by assigning an exact $\delta^{13}C$ value of +1.95 ‰ on the VPDB scale to the IAEA reference material NBS 19 calcium carbonate. Carbon isotope ratios are determined on gaseous CO_2 using electron impact ionization mass spectrometry and commonly are measured with a 1-σ standard deviation of ±0.1 ‰. The absolute isotope abundances of NBS 19 have been measured by Chang and Li (1990), and they calculated from this measurement the absolute isotope abundances of the zero point of the VPDB scale (table 9).

Secondary reference materials (see table 10) are distributed by IAEA and (or) NIST and include various carbonates, natural gases, sugars, and an oil (Gonfiantini and others, 1995). Reference materials in a subset of these (Parr and Clements, 1991) are variably enriched in ^{13}C and intended for use mainly in medical and biological tracer studies.

Ranges in Isotopic Composition

Carbon occurs in valence states between +4 and –4 in naturally occurring materials. Therefore, the range in isotopic variation of carbon-bearing materials is greater than 140 ‰ (table 11 and figure 4). Useful compilations of carbon isotopic variations and isotope-fractionation mechanisms include Friedman and O'Neil (1977), Schwarcz (1969), Clark and Fritz (1997) and Valley and Cole (2001).

Carbon occurs primarily in 3 reservoirs on Earth, sedimentary organic matter, the biosphere, and sedimentary carbonates. These reservoirs differ in isotopic composition because of different isotope-fractionation mechanisms. Kinetic isotope fractionation associated with photosynthesis preferentially enriches plant material in ^{12}C. This enrichment gives rise to organic sediments, coal, and crude oil with $\delta^{13}C$ values near –25 ‰ and sedimentary carbonates near 0 ‰ (figure 4).

Carbonate and bicarbonate Total dissolved inorganic carbon (DIC) consists of dissolved bicarbonate, carbonate, and carbon dioxide in aqueous solution. In most settings, such as the Earth's oceans, bicarbonate ion predominates. The primary sources of DIC are atmospheric CO_2, dissolution of carbonate, and decay of organic matter. Although the variation in $\delta^{13}C$ of ocean water is small, –0.8 ‰ to +2.2 ‰ (Kroopnick, 1985), the variation in deep sea pore waters ranges from –37.1 ‰ (Nissenbaum and others, 1972) to +37.5 ‰ (Claypool and others, 1985), the latter being the highest $\delta^{13}C$ value of a naturally

Table 9. *Carbon isotopic composition of a material with $\delta^{13}C$ = 0 ‰ relative to VPDB*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{12}C	12 u (exactly)	0.988 944(28)
^{13}C	13.003 354 838(5)	0.011 056(28)

[A] From Audi and Wapstra (1993).

[B] From Chang and Li (1990) and Rosman and Taylor (1998)

Table 10. *Carbon isotopic composition of selected carbon-bearing isotopic reference materials*

[Values for δ^{13}C given in per mill relative to VPDB, defined by assigning an exact δ^{13}C value of +1.95 ‰ to NBS 19 carbonate]

Reference Material	Substance	δ^{13}C	Reference
NBS 18	$CaCO_3$ (carbonatite)	–5.01 ± 0.06	Stichler, 1995
NBS 19	$CaCO_3$ (marble)	+1.95 (exactly)	Hut, 1987
IAEA-CO-1 (IAEA C1)	$CaCO_3$ (marble)	+2.48 ± 0.03	Stichler, 1995
IAEA-CO-8 (IAEA KST)	$CaCO_3$	–5.75 ± 0.06	Stichler, 1995
L-SVEC	Li_2CO_3	–46.48 ± 0.15	Stichler, 1995
IAEA-CO-9 (IAEA NZCH)	$BaCO_3$	–47.12 ± 0.15	Stichler, 1995
USGS24	C (graphite)	–15.99 ± 0.11	Stichler, 1995
NBS 22	oil	–29.74 ± 0.12	Gonfiantini and others, 1995
IAEA-C-6 (Sucrose ANU)	sucrose	–10.43 ± 0.13	Gonfiantini and others, 1995
NGS1	CH_4 in natural gas	–29.0 ± 0.2	Hut, 1987
NGS1	C_2H_6 in natural gas	–26.0 ± 0.6	Hut, 1987
NGS1	C_3H_8 in natural gas	–20.8 ± 1	Hut, 1987
NGS2	CH_4 in natural gas	–44.7 ± 0.4	Hut, 1987
NGS2	C_2H_6 in natural gas	–31.7 ± 0.6	Hut, 1987
NGS2	C_3H_8 in natural gas	–25.5 ± 1	Hut, 1987
NGS2	CO_2 in natural gas	–8.2 ± 0.4	Hut, 1987
NGS3	CH_4 in natural gas	–72.7 ± 0.4	Hut, 1987
NGS3	C_2H_6 in natural gas	–55.6 ± 5	Hut, 1987
IAEA-CH-7 (PEF1)	polyethylene	–31.83 ± 0.11	Gonfiantini and others, 1995
NIST RM 8562	CO_2	–3.76 ± 0.03	NIST, 1998
NIST RM 8563	CO_2	–41.56 ± 0.06	NIST, 1998
NIST RM 8564	CO_2	–10.45 ± 0.04	NIST, 1998

occurring terrestrial specimen found in the literature. The mole fraction of ^{13}C in this specimen is 0.011 466 and A_r(C) = 12.011 50.

The δ^{13}C values for igneous carbonates (carbonatites) range from –11.9 ‰ to +3.1 ‰ (Deines and Gold, 1973). A similar range of –11.9 ‰ to +0.2 ‰ usually is measured for carbonates in kimberlites as well (Khar'kiv and

Table 11. *Carbon isotopic composition of selected carbon-bearing materials*

[Values for δ^{13}C given in per mill relative to VPDB, defined by assigning an exact δ^{13}C value of +1.95 ‰ to NBS 19 carbonate]

	Minimum δ^{13}C Value		Maximum δ^{13}C Value	
Substance	**δ^{13}C**	**Reference**	**δ^{13}C**	**Reference**
CARBONATE AND BICARBONATE				
Sea water	–0.8	Kroopnick, 1985	+2.2	Kroopnick, 1985
Other water	–37.1	Nissenbaum and others, 1972	+37.5	Claypool and others, 1985
Metamorphic and igneous rock	–11.9	Deines and Gold, 1973	+24.8	Deines, 1968
Typical marine carbonate rock	–6	Land, 1980	+6	Land, 1980
Other carbonate	–64.5	Deuser, 1970	+21.1	Deuser, 1970
CARBON DIOXIDE				
Air	–8.2	Keeling and others, 1989	–6.7	Keeling, 1958
Soil gas	–31.0	Aravena and others, 1996	+6.9	Notsu and others, 2001
Volcanic gas	–37	Valyayev and others, 1985	+23	Valyayev and others, 1985
Oil, gas, coal, and landfills	–37.6	Wasserburg and others, 1963	+28	Whiticar and others, 1995
Commercial tank gas and reference materials	–54	T. B. Coplen, unpublished data	–28.76	NIST, 1998
OXALATES				
$CaC_2O_4 \cdot xH_2O$ (whewellite)	–31.7	Žák and Skála, 1993	+33.7	Hofmann and Bernasconi, 1998
CARBON MONOXIDE				
Air	–31.5	Brenninkmeijer, 1993	–22	Stevens and others, 1972

others, 1986; Mitchell, 1989); however, Deines (1968) has reported unusually high values (–10.2 ‰ to +24.8 ‰) for carbonates from a mica peridotite dike near Dixonville, Pennsylvania (USA). Calc-silicate rocks vary between –16 ‰ and +2 ‰ (Schwarcz, 1969).

The testae, skeletons, and shells of marine biota have δ^{13}C values between –12 ‰ and +5.7 ‰ (Weber and Raup, 1966; Lowenstam and Epstein, 1957; Murata and others, 1969). Marine $CaCO_3$ covers a broad δ^{13}C range from –60.6 ‰ (Hathaway and Degens, 1969) to +15.2 ‰ (Murata and others, 1969). "Typical" unaltered marine limestone tends to have δ^{13}C values between –4 ‰ and +4 ‰. Keith

Table 11. *Carbon isotopic composition of selected carbon-bearing materials—Continued*

	Minimum δ^{13}C Value		Maximum δ^{13}C Value	
Substance	**δ^{13}C**	**Reference**	**δ^{13}C**	**Reference**
ORGANIC CARBON				
Land plants (C3 metabolic process)	–35	O'Leary, 1988	–21	Smith and Turner, 1975
Land plants (C4 metabolic process)	–16	Smith and Turner, 1975	–9	Smith and Turner, 1975
Land plants (CAM metabolic process)	–34	Deines, 1980	–10	O'Leary, 1988
Marine organisms	–74.3	Paull and others, 1985	–2	Schwarcz, 1969
Marine sediments and compounds	–130.3	Elvert and others, 2000	+7	Deines 1980
Coal	–30	Deines, 1980	–19	Deines, 1980
Crude oil	–44	Sofer, 1984	–16.8	Sofer 1984
Ethanol (naturally occurring)	–32	Rauschenbach and others, 1979	–10.3	Rauschenbach and others, 1979
ELEMENTAL CARBON				
Graphite	–41	Deines, 1980	+6.2	Ghent and O'Neil, 1985
Diamonds	–34.4	Galimov, 1985	+5	Harris, 1987
ETHANE				
Hydrocarbon gas	–55.6	Hut, 1987	+6.6	Gerling and others, 1988
METHANE				
Air	–50.6	Merritt and others, 1995	–39	Bainbridge and others, 1961
Marine and other sources	–109	Whiticar and others, 1986	+12.7	Gerling and others, 1988
Fresh water sources	–86	Oremland and King, 1989	–50	Whiticar and others, 1986
Commercial tank gas	–51	K. Révész, unpublished data	–38	K. Révész, unpublished data

and Weber (1964) determined a mean of +0.56 ‰ for a selected group of 272 marine limestones. Unusual values usually are found in association with organic matter, methane, and (or) sulfur.

The carbonate of freshwater brachiopods (Abell, 1985) and mollusks (Keith and others, 1964) have δ^{13}C values between –19.4 ‰ and +7.0 ‰. Land snail shells vary between –12.0 ‰ and +0.5 ‰ (Tamers, 1970; Goodfriend and Magaritz, 1987). Freshwater CaCO$_3$ has δ^{13}C values between –17.7 ‰

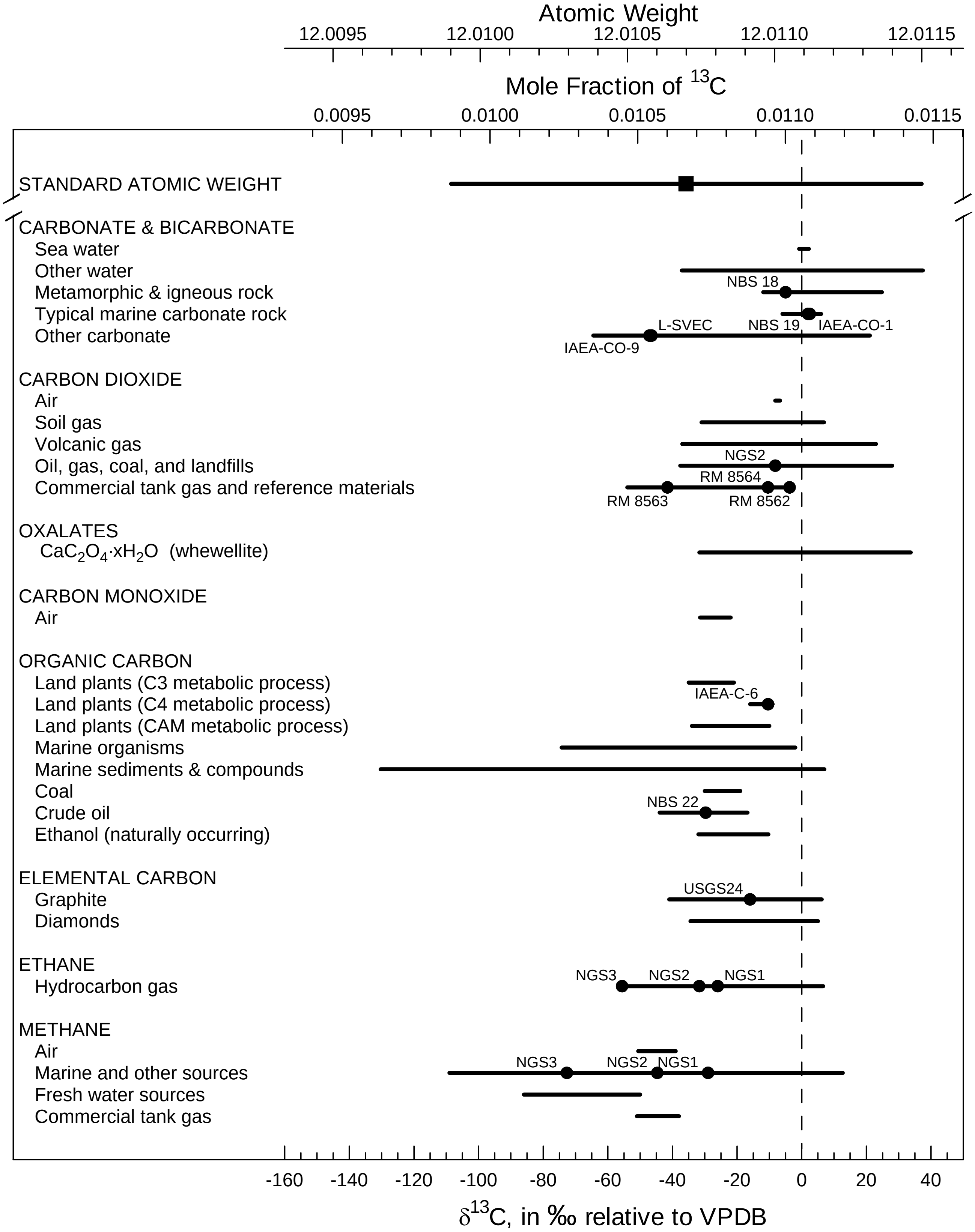

Figure 4. Carbon isotopic composition and atomic weight of selected carbon-bearing materials. The $\delta^{13}C$ scale and ^{13}C mole-fraction scale were matched using the data in table 9; therefore, the uncertainty in placement of the atomic-weight scale and the ^{13}C mole-fraction scale relative to the $\delta^{13}C$ scale is equivalent to ±2.5 ‰.

(Clayton and Degens, 1959, as cited in Murata and others, 1969) and +6.3 ‰ (O'Neil and Barnes, 1971). Keith and Weber (1964) measured an unusual value of –24.2 ‰, which they did not include in their mean of –4.93 ‰ for 158 freshwater limestone samples. Dolomite, $CaMg(CO_3)_2$, has $\delta^{13}C$ values ranging between –64.5 ‰ and +21.1 ‰ (Deuser, 1970). Most platform dolomites have $\delta^{13}C$ values within a smaller range between –6 ‰ and +6 ‰ (Land, 1980). Dolomite with unusual isotopic compositions tends to be associated with organic matter or hydrocarbons (Land, 1980). Marbles have $\delta^{13}C$ values between about –12 ‰ and +13 ‰ (Palin and Rye, 1987; Baker and Fallick, 1989). Components of human kidney stones have $\delta^{13}C$ values between approximately –22 ‰ and –14 ‰ (Krouse and others, 1987a). The common, low temperature mineral, goethite (α-FeOOH), contains small amounts of an $Fe(CO_3)OH$ component in apparent solid solution (Yapp, 1987a) with $\delta^{13}C$ values between –21.7 ‰ and +3.3 ‰.

Carbon dioxide The N_2O-corrected $\delta^{13}C$ values of "global" atmospheric CO_2 ranged from –8.2 ‰ to –7.0 ‰ during the years from 1977 to 1988 (Mook, 1986; Keeling and others, 1989). A range of –7.5 ‰ to –6.7 ‰ was measured in 1956 (Keeling, 1958). The air samples were collected at sites where industrial and photosynthetic processes have a minimal effect. Two principal global trends have been observed: a long-term gradual decrease in $\delta^{13}C$ values and much larger seasonal fluctuation. In both trends, $\delta^{13}C$ values tend to decrease with increasing CO_2 concentrations (Keeling and others, 1984). The gradual $\delta^{13}C$ decrease seems to be primarily because of fossil-fuel combustion (Mook, 1986). Relative to atmospheric CO_2, the released CO_2 is depleted in ^{13}C (estimated average $\delta^{13}C$ values = –27 ‰) reflecting its sources (Tans, 1981). Keeling and others (1979) noted a 0.55 ‰ decrease over the 22-year period from 1956 to 1978; the mean, seasonally adjusted $\delta^{13}C$ value changed from –6.7 ‰ to –7.2 ‰ as the CO_2 concentration increased from 314 mg/kg to 334 mg/kg in the Northern Hemisphere. Cement use and production also may make a minimal contribution of CO_2 with approximate $\delta^{13}C$ values of –15 ‰ and +1 ‰, respectively (Mook, 1986). The yearly cycle can be as large as 1.2 ‰ (Mook, 1986) and is caused by seasonal variations in the metabolic activities of plants, fossil-fuel combustion, organic decay, and temperature-dependent CO_2 solubility in the oceans (Mook, 1986; Oeschger and Siegenthaler, 1978).

Values of $\delta^{13}C$ for atmospheric CO_2 can be substantially more negative—values as negative as –27 ‰ were measured by Mook (1986)—in air near cities and industrial areas, in plant populations, and in rivers. CO_2 respired by humans ranges between –23.5 ‰ and –18.7 ‰ (Epstein and Zeiri, 1988). In addition, $\delta^{13}C$ values between –42.2 ‰ and –28.2 ‰ have been measured for CO_2 in a cave in the Ukraine (Klimchuk and others, 1981).

The $\delta^{13}C$ of soil CO_2 is a function of the isotopic composition of the CO_2 released during plant respiration, decomposition of organic matter, dissolution of carbonates, mixing with atmospheric CO_2, and diffusional processes (Cerling, 1984). The $\delta^{13}C$ values correlate strongly with the $\delta^{13}C$ of the local vegetation: CO_2 depleted in ^{13}C generally is found in areas with C3 plant cover, whereas CO_2 with more positive $\delta^{13}C$ values is observed where C4 plants predominate (Parada and others, 1983; Deines, 1980). Overall the soil CO_2 tends to be 3 ‰ to 9 ‰ more positive than soil organic matter and plant cover because of the contributions of atmospheric CO_2 and diffusion effects (Rightmire and Hanshaw, 1973). The $\delta^{13}C$ values of CO_2 within soils tend to become more negative as CO_2 concentration increases (Amundson, 1989; Cerling, 1984). Seasonal variations of as much as 13 ‰ have been observed, which generally are attributed to the varying effect of atmospheric CO_2 isotopic composition and differences in the peak activity times of C3 and C4 plants (Rightmire, 1978; Parada and others, 1983). For example, $\delta^{13}C$ values especially tend to be positive during winters and dry summers.

The $\delta^{13}C$ values of most CO_2 from volcanic and hydrothermal sources range between –12 ‰ and +2 ‰ (Deines, 1980; Taylor, 1986). Valyayev and others (1985) reported that CO_2 from mud volcanoes in the U.S.S.R. had $\delta^{13}C$ values ranging from –37 ‰ to +23 ‰; more than one third of the samples were more positive than 0 ‰. Values more negative than –12 ‰ have been reported for a wider variety of CO_2 samples (Jeffrey and others, 1986; Deines, 1980; Janik and others, 1983; Batard and others, 1982; Wasserburg and others, 1963).

The $\delta^{13}C$ values of CO_2 released from CO_2 fluid inclusions during fusion and (or) step heating of rocks and minerals range between about –35 ‰ and +10 ‰ (Taylor, 1986). Values more positive than –2 ‰ are relatively unusual (Taylor, 1986) and determination of $\delta^{13}C$ values for CO_2 fluid inclusions is complicated; the released CO_2 can arise from endogenous carbonates, graphite, dissolved carbon, and CO_2 fluid inclusions as well as from contamination during sampling, storage, and analysis (Taylor, 1986; Kyser, 1987). The "true" $\delta^{13}C$ range for CO_2 in fluid inclusion may be substantially smaller for a given sample type than the range indicated above (–35 ‰ and +10 ‰).

The $\delta^{13}C$ values of CO_2 from oil, gas, coal, landfills, and marine sediments range from –38 ‰ to about +28 ‰ (Valyayev and others, 1985; Deines, 1980; Whiticar and others, 1995; Wasserburg and others, 1963). However, most values fall between –24 ‰ and +2 ‰ (Valyayev and others, 1985).

Oxalates The oxalate, whewellite ($CaC_2O_4{\cdot}H_2O$), is a relatively rare mineral found with carbonaceous materials. Whewellite formation seems to be related to mobilization of oxalates released during decomposition of organic matter (Žák and Skála, 1993). Whewellites from low temperature hydrothermal veins had $\delta^{13}C$ values as negative as –31.7 ‰. Much more positive values can be associated with bacterial processes. The most positive value is +33.7 ‰ (S. Bernasconi, Geologisches Institut, ETH-Zentrum, Zuerich, Switzerland, written communication, 1997).

Carbon monoxide Carbon monoxide is an important atmospheric trace gas and also a major pollutant in most large cities (Brenninkmeijer, 1993). Principal sources of carbon monoxide (Seiler, 1974) include oxidation of methane and non-methane hydrocarbons, biomass burning (mostly tropical forests and savanna), transportation, industry, heating, oceans, and vegetation. The primary sinks of atmospheric methane are oxidation by the hydroxyl radical (OH) and uptake by soils. Its average residence time in the atmosphere is about 2 months; however, its global budget is complex. Brenninkmeijer (1993) measured the $\delta^{13}C$ of carbon monoxide in the atmosphere in Antarctica in order to obtain the isotopic composition of unpolluted atmospheric carbon monoxide and found $\delta^{13}C$ values between –31.5 ‰ and –27 ‰. The range reported by Stevens and others (1972) is between –31 ‰ and –22 ‰.

Organic carbon The biological assimilation of carbon by plants generally results in depletion of ^{13}C in the organism's tissues relative to the carbon sources (CO_2 and HCO_3^-). The magnitude of the ^{13}C depletion depends on the species and the carbon fixation pathways utilized, environmental factors such as temperature, CO_2 availability, light intensity, pH of water, humidity, water availability, nutrient supply, salinity, cell density, age of photosynthesizing tissue, and oxygen concentration (Berry, 1988).

Plants assimilate carbon using 2 different pathways, which leads to a classification of 3 photosynthetic groups. The predominant fixation reaction is carboxylation of ribulosebisphosphate (RuBP) to the C_3-product phosphoglycerate, which generally results in $\delta^{13}C$ of plants between –34 ‰ and –24 ‰ (Winkler, 1984), but as low as –35 ‰ (O'Leary, 1988) and as high as –21 ‰ (Smith and Turner, 1975). C3 plants tend to grow in cool, moist, shaded areas (Ambrose and DeNiro, 1989) and comprise 80 to 90 percent of plants. All trees, most shrubs, some grasses from temperate regions and tropical forests, and common crops such as wheat, rice, oats, rye, sweet potatoes, beans, and tubers utilize the C3 pathway (Winkler, 1984).

A second reaction is carboxylation of phosphoenolpyruvate to the C_4 product oxalacetic acid. This fixation is more efficient leading to less depletion in ^{13}C; the $\delta^{13}C$ of C4 plants ranges between –16 ‰ and –9 ‰ (Smith and Turner, 1975). C4 plants, such as maize, sugar cane, sorghum, and grasses in Australia, Africa, and other subtropical, savannah, and arid regions, tend to grow in hot, dry, sunny environments (Winkler, 1984; Ambrose and DeNiro, 1989).

Plants that fix carbon by Crassulacean Acid Metabolism (CAM) can utilize either the C3 or C4 cycles (Schidlowski, 1987; Deines, 1980; O'Leary, 1988); thus their $\delta^{13}C$ values cover the range of both C4 and C3 plants (–34 ‰ to –10 ‰). Succulents such as agave, prickly pear, yucca, and pineapple and some submerged aquatic plants utilize CAM carbon fixation. The isotopic composition of CAM plants especially is sensitive to factors such as water supply, light intensity, and temperature, since CAM plants can utilize either the C4 or C3 cycles depending on environmental conditions (Deines, 1980).

Animals and microbial heterotrophs generally have $\delta^{13}C$ values within 2 ‰ of their food supply; however, the $\delta^{13}C$ values of various organs and tissues within a single organism can have a wider range (Fry and Sherr, 1984). The $\delta^{13}C$ values of fresh tissues and the collagen and hydroxyapatite from bones and teeth have been applied to food web studies and reconstructions of prehistoric diet and vegetation patterns (Fry and Sherr, 1984; Tieszen and Boutton, 1988; Ambrose and DeNiro, 1989). For example, geographic variations of the $\delta^{13}C$ values of hair in humans compares favorably with the ^{13}C depleted diets of Germans ($\delta^{13}C$ = –23.6 ‰), the seafood and corn diets of Japanese ($\delta^{13}C$ = –21.2 ‰), and the corn diets of Americans ($\delta^{13}C$ = –18.1 ‰), according to Nakamura and others (1982).

Isotope-ratio analyses of organisms found in the literature primarily have been confined to analysis of molecules or whole tissues. Brenna (2001) points out that, “Natural isotopic variability, particularly on an intramolecular level, is likely to retain more physiological history. Because of ubiquitous isotope fractionation, every sterochemically unique position in every molecule has an isotope ratio that reflects the processes of synthesis and degradation.” Brenna (2001) makes a strong case that future studies of physiological isotope fractionation should involve position-specific isotope analysis and should reveal the relationship of diet and environment to observed isotope ratio. A remarkable example that shows that physiological isotope-abundance variations are preserved in some materials for extended periods is the study by Slatkin and others (1985) that compared the δ^{13}C of human cerebellar autopsy tissue from American-born Americans, European-born Americans (immigrants residing in the U.S. for an average of 46 years), and European-born Europeans. Cerebellar DNA from European-born Europeans (δ^{13}C = –20.34 ± 0.30 ‰) was similar to that of European-born Americans (δ^{13}C = –19.55 ± 0.37 ‰), but substantially different than that of American-born Americans (δ^{13}C = –16.05 ± 0.33 ‰). Slatkin and others (1985) conclude “that a large proportion of the DNA in small neurons of the cerebellum undergoes no metabolic turnover during the human life-span.” Because the brain is known to develop perinatally, these data suggest that neuronal DNA retains the isotopic signature of conditions prevailing during the perinatal period.

The δ^{13}C of marine and freshwater organisms generally fall within the –31 ‰ to –7 ‰ range (Van der Merwe, 1982; Schwarcz, 1969; Rau, 1981). Marine organisms unusually depleted in ^{13}C have been discovered in deep-sea hydrothermal vent communities; these mussels, clams, and tube worms have δ^{13}C values from –70 ‰ to –10 ‰ and seem to be living in symbiosis with chemotropic bacteria (Rau, 1981; Paull and others, 1989). Most eukaryotic algae, cyanobacteria (“blue-green algae”), and some marine plants such as sea grasses fix carbon by the C3 cycle; these organisms, however, can have much more positive δ^{13}C values than typical terrestrial C3 plants because of the low diffusion rates and higher concentrations of the carbon sources in aqueous environments. Furthermore, some algae and cyanobacteria also use special CO_2-concentrating mechanisms (Berry, 1988) and closed-system metabolism, which decrease the expected C3 isotope-fractionation effect. The strong dependence of δ^{13}C values on the environment is demonstrated by variations of as much as 25 ‰ in a pondweed species found in slow rather than fast-moving streams (Fry and Sherr, 1984). Freshwater organisms tend to have more negative δ^{13}C values than those from marine environments; this may result from the lower pH values and thus higher CO_2 concentrations found in freshwater settings (Schwarcz, 1969). Plankton tends to be more depleted in ^{13}C than sessile plants in the same environment (Deines, 1980), possibly because of the higher concentration of ^{13}C-depleted lipids in plankton (Schwarcz, 1969).

Methanogenic bacteria grown in the laboratory under varying and sometimes extreme conditions have had δ^{13}C values ranging from –41 ‰ to +6 ‰ (Schidlowski, 1987). Zyakun and others (1981) determined that methane oxidizing bacteria were depleted in ^{13}C by 10 ‰ to 20 ‰ relative to the source methane. The range of δ^{13}C values of chemoautotrophic bacteria in natural settings probably is very broad because of the large variation in δ^{13}C values in CO_2 and CH_4.

The δ^{13}C value of sedimentary organic matter is affected by the local flora and fauna, the environmental conditions, secondary processes, recycling of older carbon-bearing sediments, and anthropogenic wastes (Deines, 1980). During diagenesis, the biopolymers of newly deposited sediments are biochemically degraded by microorganisms. Most of the organic matter is oxidized to CO_2 and H_2O or reused as biomolecules within living organisms. Within limited settings, terrestrial plant sediments tend to be more depleted in ^{13}C than marine plankton sediments; for example, river sediments, with an average δ^{13}C value of about –26 ‰, tend to become enriched in ^{13}C at the river mouth, presumably because of increasing amounts of marine plankton (as opposed to terrestrial C3 plant) input (Deines, 1980). Some of the degradation products polymerize to form heterogeneous fulvic acids, humic acids, and finally kerogen after compaction and dewatering and some loss of functional groups. During subsequent catagenesis (50°C to 150°C) and metagenesis (150°C to 250°C), kerogen is thermally degraded, functional groups are lost as CO_2, H_2O, and CH_4, and mobile, hydrogen-rich fractions separate as petroleum. During the final stage, which is metamorphism, intense alteration occurs until the carbon is in elemental form as graphite. The high δ^{13}C values observed for some Precambrian kerogen and graphite samples seem to be due to high temperature carbon exchange with coexisting sedimentary carbonates (Valley and O’Neil, 1981). The unusually low ^{13}C contents (δ^{13}C as low as –84 ‰) of some sediment and kerogen samples have been attributed to the activities of chemoautotrophic bacteria in modern deep sea vent (Paull and others,

1989) and localized Archean (Schoell, 1988) communities. Furthermore, organic matter substantially depleted in ^{13}C has been found near sulfur deposits with $\delta^{13}C$ values from –89.3 ‰ to –82.5 ‰ (Kaplan and Nissenbaum, 1966). The material of natural terrestrial origin with the lowest ^{13}C content found in the literature is crocetane (2,6,11,15-tetramethylhexadecane), produced at cold seeps of the eastern Aleutian subduction zone, with a value of –130.3 ‰ (Elvert and others, 2000). The mole fraction of ^{13}C of this specimen is 0.009 629 and $A_r(C)$ = 12.009 66.

The isotopic composition of petroleum is constrained primarily by the kerogen ^{13}C content and the sedimentary environment (Sofer, 1984). The $\delta^{13}C$ of petroleum tends to be a few per mill more negative than the source kerogen (Deines, 1980) and ranges from –44 ‰ to about –17 ‰ (Sofer, 1984).

Rauschenbach and others (1979) analyzed the $\delta^{13}C$ of ethanol in a variety of alcoholic beverages and found a range from –32 ‰ to –10.3 ‰. This range is similar to the range found in C3 and C4 plants used to produce these beverages. According to K.P. Hom (Liquor Control Board of Ontario, Ontario, Canada, written communication, 2001) ethanol from pure malt whisky ranges from –26 ‰ to –25 ‰, and bourbon is about –12 ‰. In pure malt products, the $\delta^{13}C$ of isobutanol is –30 ‰; thus, a combination of carbon and hydrogen isotope ratios is useful in investigating adulteration of alcohols.

Elemental carbon As organic matter undergoes burial and thermal alteration, functional groups of organic compounds are lost, H_2O and CO_2 are produced, and methane is evolved. The final product of this reduction is graphite, whose $\delta^{13}C$ ranges between –41 ‰ and +6.2 ‰ (Deines, 1980; Ghent and O'Neil, 1985).

The $\delta^{13}C$ of diamonds has been used to ascertain information about their origin. Recently, Deines and others (2001) observed that variations in $\delta^{13}C$ of diamonds from Venetia, South Africa (–15.6 ‰ to –4.4 ‰) are consistent with depth-related variations in the mantle. After studying over 700 isotopic analyses Galimov (1985) also concluded that at least some of the variations in $\delta^{13}C$ might be explained in terms of a depth zonation in the upper mantle or lithosphere. Galimov (1985) reported a $\delta^{13}C$ range between –34.4 ‰ and +2.4 ‰, although most values fall between –9 ‰ and –2 ‰, the most negative value being from a diamond from a kimberlite pipe from East Siberia. The highest $\delta^{13}C$ reported value for a diamond is +5 ‰ (Harris, 1987).

Ethane Low temperature serpentinization of ophiolitic rocks generates free hydrogen along with minor amounts of methane and ethane. A study by Fritz and others (1992) finds $\delta^{13}C$ values of ethane as high as –11.4 ‰. Hydrocarbons are entrapped in the Zechstein evaporites of northern Germany. Gases in the potash layers are highly enriched in ^{13}C with $\delta^{13}C$ values as positive as +6.6 ‰ (Gerling and others, 1988). The mode of formation is still uncertain although hypotheses include (1) maturation of organic matter rich in ^{13}C, (2) transformation of CO_2 enriched in ^{13}C to CH_4, (3) unknown bacterial isotope fractionation, and (4) abiotic gas formation during halokinesis. The most negative $\delta^{13}C$ found in the literature for a bacterially formed ethane is –55 ‰. The $\delta^{13}C$ of the ethane component of the NGS3 natural gas reference material discussed by Hut (1987) is –55.6 ‰.

Methane The two major methane production processes are (1) diagenesis of organic matter by bacterial processes, and (2) thermal maturation of organic matter. Biogenic methane, produced by bacterial processes during the early stages of diagenesis, is formed in freshwater and marine environments, recent anoxic sediments, swamps, salt marshes, glacial till deposits, and shallow dry-gas deposits. There are 2 major pathways for biogenic methane production (Whiticar and others, 1986): (1) CO_2 reduction, which dominates in marine environments, and (2) acetate fermentation, which dominates in fresh-water environments. Marine methane $\delta^{13}C$ values range from –109 ‰ (Whiticar and others, 1986) to 0 ‰ (Whiticar and others, 1999), whereas methane in freshwater sediments and swamps is on average more enriched in ^{13}C, but have a smaller range in carbon isotopic composition, with $\delta^{13}C$ values range from –86 ‰ (Oremland and King, 1989) to –50 ‰ (Whiticar and others, 1986).

Thermogenic methane is found in a wide variety of geologic settings and sedimentary basins, with a wide range of isotopic composition. These isotopic compositions are affected by the geological history of the basins and they depend on such factors as the extent of conversion of organic matter and the timing of gas expulsion, migration, and trapping (Schoell, 1988). The $\delta^{13}C$ of thermogenic methane that is associated with natural gas ranges from –74 ‰ (Deines, 1980) to +12.7 ‰ (Gerling and others, 1988). The mode of formation of this extremely positive $\delta^{13}C$ is unknown as discussed in the section on ethane above and as discussed by Whiticar (1989).

Methane is an important atmospheric greenhouse gas with major natural and anthropogenic sources including swamps, rice paddies, ruminants, termites, landfills, fossil-fuel production, and biomass burning. The $\delta^{13}C$ of atmospheric methane is relatively constant, generally ranging between –50.58 ‰ and –46.44 ‰ (Merritt and others, 1995) although values as positive as –39 ‰ have been reported (Bainbridge and others, 1961). Two commercial tanks of methane measured during this study by K. Révész (unpublished data) had $\delta^{13}C$ values of –51 ‰ and –38 ‰.

Nitrogen $A_r(N) = 14.0067(2)$

Although nitrogen is about twenty-fifth in crustal abundance, it comprises 78.1 percent of the atmosphere by volume. A primary use of nitrogen gas is as an inert atmosphere in iron and steel production and in the chemical and metallurgical industry (Greenwood and Earnshaw, 1997). Large quantities of nitrogen are used in fertilizers and chemical products. More moles of anhydrous ammonia are produced worldwide than any other nitrogen-bearing compound. The continual interaction of nitrogen among the lithosphere, biosphere, atmosphere, and hydrosphere is called the nitrogen cycle. Nitrogen isotope ratios commonly are used to investigate nitrogen-cycle processes.

Reference materials and reporting of isotope ratios

The primary reference for relative isotope abundance measurements of nitrogen isotopes is atmospheric N_2, which is homogeneous with respect to analytical uncertainties with common analytical techniques (Mariotti, 1983) and is assigned a $\delta^{15}N$ value of 0 ‰. Nitrogen isotope ratios are determined on gaseous N_2 using electron impact ionization mass spectrometry and commonly are measured with a 1-σ standard deviation of ±0.1 ‰.

The absolute isotope ratio, $n(^{14}N)/n(^{15}N)$, of atmospheric nitrogen was measured by Junk and Svec (1958) as 272.0(3). The ^{14}N and ^{15}N fractional isotope abundances (table 12) previously have been rounded to 0.996 34(1) and 0.003 66(1), respectively (Holden and others, 1984), corresponding to $n(^{14}N)/n(^{15}N) = 272.22$. The difference between the two sets of values corresponds to a $\delta^{15}N$ difference of 0.8 ‰, which is about 10 times the measurement precision of many laboratories. To eliminate possible confusion in the reporting of nitrogen-isotope analyses, IUPAC recommended in 1992 that the value of 272 be used for the $n(^{14}N)/n(^{15}N)$ value of N_2 in air for calculating the fraction of ^{15}N from measured $\delta^{15}N$ values (Coplen and others, 1992). De Bièvre and others (1996) reported uncalibrated measurements corrected for mass spectrometer inlet fractionation effects that yield a $n(^{14}N)/n(^{15}N)$ ratio for atmospheric nitrogen of 271.87 ± 0.11, in agreement with the recommended value of 272.

Table 13 lists 6 ammonium sulfates (IAEA-N1, IAEA-N2, USGS25, USGS26, IAEA-305A, and IAEA-305B), 2 potassium nitrates (IAEA-N3 and USGS32), 2 ureas (IAEA-310A and IAEA-310B), and 1 tank of purified N_2 gas (NSVEC) that are secondary isotopic reference materials internationally distributed by IAEA and (or) NIST. "Provisional certified $\delta^{15}N$ values" have been reported for IAEA-305A, IAEA-305B, IAEA-310A, and IAEA-310B, which are enriched in ^{15}N and intended for use mainly in medical and biological tracer studies (Parr and Clements, 1991). A comparison test was completed for the others, which have been distributed mainly to geologic, hydrologic, and soils science laboratories (Böhlke and Coplen, 1995).

Ranges in Isotopic Composition

Naturally occurring nitrogen-bearing materials have widely varying isotopic compositions ranging over more than 200 ‰, in large part because of redox transformations among the wide range of valence states (from –3 to +5). Ranges in the stable isotopic composition of naturally occurring nitrogen-bearing materials are shown in table 14 and figure 5. Compilations of nitrogen isotope-abundance variations and isotope-fractionation mechanisms include Letolle (1980), Heaton (1986), Hübner (1986), Owens (1987), and Kendall (1998).

Nitrate Limited data indicate that nitrate in precipitation generally has $\delta^{15}N$ values near 0 ‰ or slightly higher. Major studies in Germany and South Africa both indicate that $\delta^{15}N$ values of nitrate in rain are higher in cold seasons than in warm seasons (Heaton, 1987; Freyer, 1978a). The range of nitrate $\delta^{15}N$ values reported for Pacific sea water by Cline and Kaplan (1975), +5 ‰ to +19 ‰, is matched almost exactly by the range reported for estuaries by Mariotti and others (1984), +2 ‰ to +20 ‰, and by Horrigan and others (1990), +4 ‰ to +20 ‰. The high values are attributed to denitrification (microbial reduction of nitrate to N_2) in the water column. Marine values less than 0 ‰ have been attributed locally to incomplete nitrification (microbial oxidation of ammonium to nitrate) in sediments (Ostrom, 1992).

Table 12. *Isotopic composition of atmospheric nitrogen*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{14}N	14.003 074 0074(18)	0.996 337(4)
^{15}N	15.000 108 973(12)	0.003 663(4)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Junk and Svec (1958).

Most studies of ground waters with high nitrate concentrations indicate average δ^{15}N values between approximately 0 ‰ and +20 ‰. Values lower than about +8 ‰ are typical of agricultural areas where artificial fertilizers are used, whereas values higher than +8 ‰ commonly result from nitrification of animal wastes such as sewage and manure. Published values greater than +20 ‰ are becoming increasingly common, especially in isotopically fractionated residual nitrate from waters that have been partially denitrified. For example, Schroeder and others (1991) reported a value of +102 ‰ for nitrate in a groundwater from a well in the Imperial Valley, California (USA), and Böhlke and others (2000) report a value of +103 ‰ for nitrate in contaminated groundwater in Massachusetts (USA). It is likely that increasing numbers of δ^{15}N values higher than these will be obtained from future analyses of nitrate-contaminated waters undergoing denitrification. Even higher δ^{15}N values (to +150 ‰) were reported for nitrate in Antarctic ice, where partial evaporation of HNO_3 may have caused isotope fractionation (Freyer and others, 1996). This is the naturally occurring terrestrial material with the highest ^{15}N content found in the literature. The mole fraction of ^{15}N in this nitrate is 0.004 210 and A_r(N) = 14.007 27. Extraction procedures for nitrate in soils are variable and potentially isotopically fractionating (Lindau and Spalding, 1984); therefore, the results of different studies of nitrates in soils may not be directly comparable. The most highly concentrated natural accumulations of nitrate minerals on the Earth's surface (desert “caliche” deposits in the Atacama Desert of Chile) have average δ^{15}N values near 0 ‰. With few exceptions, nitrates in synthetic fertilizers and laboratory chemicals have δ^{15}N between –6 ‰ and +6 ‰, and average between 0 ‰ and +4 ‰.

Nitrite Relatively few data are available for nitrogen isotopes in nitrite reagents and environmental samples. Values of δ^{15}N ranging from –80 ‰ to +4 ‰ have been obtained for nitrite reagents from various sources (J.K. Böhlke, unpublished data). Böhlke and others (2000) report a range of δ^{15}N values in nitrite from sewage-contaminated ground water from about –30 ‰ to +55 ‰.

Nitrogen oxide gases The sources, sinks, and fluxes of nitrogen oxides in the atmosphere are not well known, nor are their isotopic compositions. Limited data indicate that atmospheric N_2O is enriched in ^{15}N relative to atmospheric N_2, whereas atmospheric NOx may be relatively depleted in ^{15}N. Anthropogenic NOx has a large range of isotopic compositions that overlaps the ranges reported for NOx in relatively “clean” air. Dissolved N_2O in near-surface sea water is isotopically similar to atmospheric N_2O; higher values are reported for some deeper sea-water samples. Ueda and others (1991) report that N_2O in ground waters is depleted in ^{15}N relative to nitrate in the same samples, and suggest that the N_2O probably was produced by nitrification. Böhlke and others (2000) report a range of δ^{15}N in N_2O from sewage-contaminated ground water undergoing denitrification from about –55 ‰ to +53 ‰, consistently more negative than the δ^{15}N values of coexisting nitrate, which range from about +12 ‰ to +103 ‰. The value of –55 ‰ is the lowest δ^{15}N value of a naturally occurring terrestrial material found in the literature. The mole fraction of ^{15}N in this sample is 0.003 462 and A_r(N) = 14.006 53. Extremely low δ^{15}N values may result from fractionation by vapor-liquid exchange in nitric acid production facilities (table 14).

Nitrogen gas Numerous studies have indicated that natural variations in δ^{15}N of atmospheric N_2 are not larger than analytical uncertainties of several tenths per mill. The 1-σ standard deviation of 32 samples of atmospheric N_2 collected at various times and localities in the Northern Hemisphere is reported to be ±0.026 ‰ (Mariotti, 1983). This result indicates that atmospheric N_2 is isotopically homogeneous with

Table 13. *Nitrogen isotopic composition of selected nitrogen-bearing isotopic reference materials*

[Values for $\delta^{15}N$ given in per mill relative to N_2 in air]

Reference Material	Substance	$\delta^{15}N$	Reference
NSVEC	N_2 gas	–2.77 ± 0.05	Böhlke and Coplen, 1995
NBS-14	N_2 gas	–1.18	Kendall and Grim, 1990
IAEA-N-1	$(NH_4)_2SO_4$	+0.43 ± 0.07	Böhlke and Coplen, 1995; Gonfiantini and others, 1995
IAEA-N-2	$(NH_4)_2SO_4$	+20.32 ± 0.09	Böhlke and Coplen, 1995; Gonfiantini and others, 1995
IAEA-NO-3 (IAEA-N-3)	KNO_3	+4.69 ± 0.09	Böhlke and Coplen, 1995; Gonfiantini and others, 1995
IAEA-305A	$(NH_4)_2SO_4$	+39.8 ± 0.5	Parr and Clements, 1991
IAEA-305B	$(NH_4)_2SO_4$	+375.3 ± 2.3	Parr and Clements, 1991
IAEA-310A	$CO(NH_2)_2$	+47.2 ± 1.3	Parr and Clements, 1991
IAEA-310B	$CO(NH_2)_2$	+244.6 ± 0.8	Parr and Clements, 1991
IAEA-311	$(NH_4)_2SO_4$	+4693 ± 57	Parr and Clements, 1991
USGS25	$(NH_4)_2SO_4$	–30.25 ± 0.38	Böhlke and Coplen, 1995
USGS26	$(NH_4)_2SO_4$	+53.62 ± 0.25	Böhlke and Coplen, 1995
USGS32	KNO_3	+179.2 ± 1.3	Böhlke and Coplen, 1995

respect to common analytical procedures. N_2 in surface waters and shallow ground waters generally is dominated by dissolved atmospheric N_2, which is fractionated only slightly during dissolution. Some anoxic ground waters contain an additional N_2 component derived from denitrification that is isotopically distinct from the atmospheric component. N_2 gases emanating from volcanoes and hot springs generally are mixtures of atmospheric N_2 and N_2 from the Earth's mantle and (or) crust (including sediments, if present at depth). Isotope fractionation of N_2 in volcanic and geothermal environments may occur in response to mineral devolatilization, oxidation-reduction reactions involving aqueous ammonia, and other reactions. N_2 from sedimentary basins, including oil and hydrocarbon gas deposits, has a large range of reported isotopic compositions, only part of which can be attributed to variations in organic

Table 14. *Nitrogen isotopic composition of selected nitrogen-bearing materials*

[Values for $\delta^{15}N$ given in per mill relative to N_2 in air]

	Minimum $\delta^{15}N$ Value		Maximum $\delta^{15}N$ Value	
Substance	**$\delta^{15}N$**	**Reference**	**$\delta^{15}N$**	**Reference**
NITRATE				
Air (aerosols and precipitation)	–16	Heaton, 1987	+18	Moore, 1977
Sea water and estuaries	–6	Ostrom, 1992	+20	Mariotti and others, 1984; Horrigan and others, 1990
Ground water and ice	–7	Mariotti and others, 1988	+150	Freyer and others, 1996
Soil extracts	–23	Wada and others, 1981	+46	Kreitler, 1975
Desert salt deposits	–5	Böhlke and others, 1997	+15	Densmore and Böhlke, 2000
Synthetic reagents and fertilizers	–23	Freyer and Aly, 1974	+15	Shearer and others, 1974
NITRITE				
Ground waters	–30	Böhlke and others, 2000	+55	Böhlke and others, 2000
Synthetic reagents	–80	Böhlke, unpublished data	+4	Böhlke, unpublished data
NITROGEN OXIDE GASES				
N_2O in air (troposphere)	0	Moore, 1974	+10	Yoshida and Matsuo, 1983
N_2O in sea water	+3	Yoshida and others, 1989	+38	Yoshinari and others, 1997
N_2O in ground water	–55	Böhlke and others, 2000	+53	Böhlke and others, 2000
NOx in air	–15	Moore, 1977	+5	Heaton, 1987
NOx from nitric acid plant	–150	Heaton, 1987		

source materials. Isotope fractionation of natural gases may be caused by biological activity, thermal reaction kinetics, and physical processes including diffusion.

Organic nitrogen Organisms that fix (metabolize) atmospheric N_2 commonly have $\delta^{15}N$ values between –3 ‰ and 0 ‰. Most other plants and essentially all animals have $\delta^{15}N$ greater than 0 ‰. Some of the lowest organic $\delta^{15}N$ values

Table 14. *Nitrogen isotopic composition of selected nitrogen-bearing materials—Continued*

	Minimum δ^{15}N Value		Maximum δ^{15}N Value	
Substance	δ^{15}N	Reference	δ^{15}N	Reference
NITROGEN GAS				
Air	0	Mariotti, 1983	0	Mariotti, 1983
Ground waters	–3	Vogel and others, 1981	+5	Smith and others, 1991
Volcanic gases and hot springs	–10	Marty and others, 1991	+16	Allard, 1983
Sedimentary basins	–49	Stroud and others, 1967	+46	Eichmann and others, 1971
Commercial tank gas	–5	Shearer and Legg, 1975	+3	Zschiesche, 1972
ORGANIC NITROGEN				
Plants and animals	–49	Wada and others, 1981	+31	Wada and others, 1981
Marine particulate organic matter	–3	Altabet and McCarthy, 1985	+46	Altabet and McCarthy, 1985
Bituminous sediments, peat, and coal	–3	Hoering, 1955	+13	Rigby and Batts, 1986
Crude oil	+1	Hoering and Moore, 1958	+7	Hoering and Moore, 1958; Eichmann and others, 1971
Soils	–29	Wada and others, 1981	+38	Mizutani and others, 1986
Synthetic reagents and fertilizers	–3	Shearer and others, 1974	+6	Shearer and others, 1974
Biological fertilizers	+3	Shearer and others, 1974	+15	Shearer and others, 1974
NITROGEN IN ROCKS				
Metamorphic rocks	+1	Bebout and Fogel, 1992	+17	Haendel and others, 1986
Igneous rocks	–36	Mattey and others, 1985	+31	Mayne, 1957
Diamonds	–37	Mattey and others, 1985	+14	Mattey and others, 1985

Table 14. *Nitrogen isotopic composition of selected nitrogen-bearing materials—Continued*

Substance	Minimum δ^{15}N Value		Maximum δ^{15}N Value	
	δ^{15}N	Reference	δ^{15}N	Reference
AMMONIUM				
Air (ammonia gas)	–15	Heaton, 1987	+28	Moore, 1977
Air (aerosols and precipitation)	–14	Freyer, 1978a	+14	Moore, 1974
Sea water and estuaries	+2	Velinsky and others, 1991	+42	Velinsky and others, 1989
Soil extracts	–7	Freyer, 1978b	+50	Mizutani and others, 1986
Volcanic gas condensates	–31	Volynets and others, 1967	+13	Hoering, 1955; Volynets and others, 1967
Synthetic reagents and fertilizers	–5	Shearer and others, 1974	+11	Drechsler, 1976

(< –8 ‰) are reported for microorganisms that appear to consume dissolved ammonium from acid hot springs (Estep, 1983) or dissolved nitrate from saline lakes (Wada and others, 1981). Animals generally have higher δ^{15}N values than their diets, such that there is a fairly consistent increase in δ^{15}N with trophic level in a given setting. There is evidence for minor isotope fractionation of nitrogen in some coals and sedimentary rocks that have been partially devolatilized by high temperature metamorphism. However, much of the isotopic variation in these materials probably is related to the type and source of organic matter preserved. The δ^{15}N values reported from crude oils are relatively uniform compared to the more variable data from modern organisms and organic-rich sediments. Soil organic nitrogen in most natural and agricultural settings is slightly enriched in ^{15}N relative to air N_2; average values of δ^{15}N typically are between 0 ‰ and +10 ‰. Unusually high and low values of δ^{15}N have been reported from soils in Antarctica (Wada and others, 1981). Wada and others reported a δ^{15}N value of –49 ‰ for epibenthic algae from a saline pond in Antarctica. Organic N in synthetic fertilizers and reagents averages approximately 0 ‰.

Nitrogen in rocks The concentration and isotopic composition of nitrogen in the core and mantle of the earth are not well known, in part because of analytical difficulties with N-poor samples. Basalt glasses from the seafloor and other presumably mantle-derived igneous rocks have reported δ^{15}N values from –36 ‰ to +20 ‰. Rocks in the Earth's continental crust, including granitic igneous rocks and metamorphosed sedimentary rocks, have a range of δ^{15}N values similar to that of most bituminous sediments and soils, probably because most nitrogen in crustal rocks represents transformed and redistributed organic matter. The nitrogen in most granitic and metamorphic rocks occurs largely as ammonium substituting for potassium in silicate minerals such as micas and feldspars. Because of isotope fractionation by devolatilization reactions (rock ammonium → fluid N_2), δ^{15}N values of metamorphic rocks tend to increase with metamorphic grade.

Ammonium Particulate ammonium in air apparently has δ^{15}N higher than that of "normal" atmospheric ammonia gas. However, ammonia gas collected above barnyard soils and in animal shelters has variable ^{15}N concentration because volatilization of ammonia from mineralized organic nitrogen causes a large isotope fractionation. Most studies of ammonium in rain yield average δ^{15}N values near 0 ‰ or slightly lower. The δ^{15}N values of ammonium in sea water and estuaries are variable; high values have been attributed to fractionation by

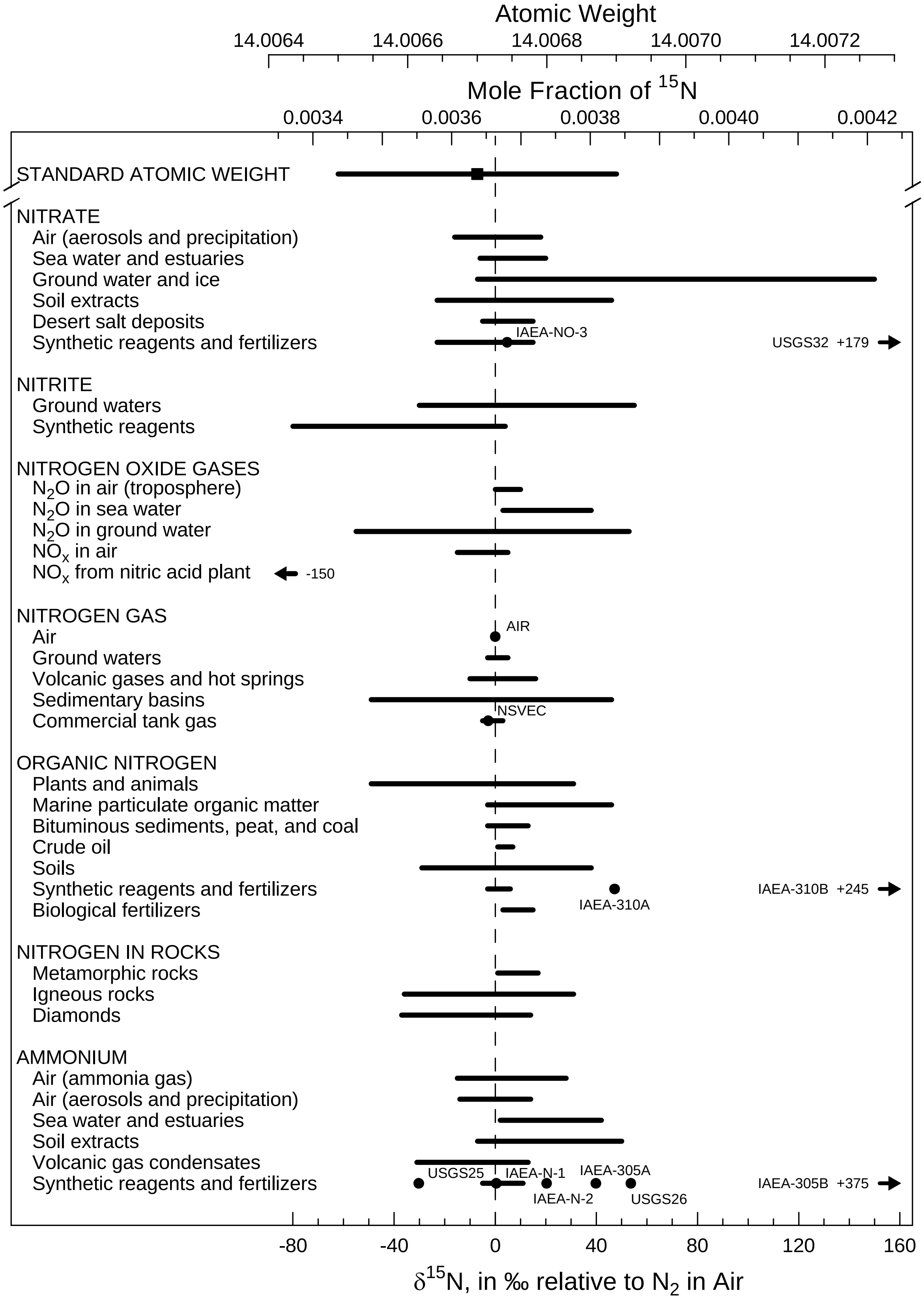

Figure 5. Nitrogen isotopic composition and atomic weight of selected nitrogen-bearing materials. The δ^{15}N scale and ^{15}N mole-fraction scale were matched using the data in table 12; therefore, the uncertainty in placement of the atomic-weight scale and the ^{15}N mole-fraction scale relative to the δ^{15}N scale is equivalent to ±1.1 ‰.

nitrification, assimilation, and (or) organic matter mineralization. Data for ammonium extracted from soils and for salts precipitated from condensed volcanic steam also are highly variable. Average δ^{15}N values of synthetic ammonium reagents and fertilizer are slightly lower than those of synthetic nitrate chemicals in general, but there is much overlap.

Oxygen $A_r(\mathrm{O}) = 15.9994(3)$

Oxygen is the most abundant element in the Earth's crust, occurring both as the free element and in numerous compounds. Oxygen gas and liquid are produced on a large scale by fractional distillation of liquid air. Only nitrogen (liquid and gas) and sulfuric acid are produced in the United States on a larger scale. Important uses of purified oxygen include steel manufacturing in the Bessemer process, oxy-gas welding and metal cutting, chemical production (TiO_2, ethylene oxide, and other compounds), hospital oxygen tents, and oxidant for rocket fuels.

Reference materials and reporting of isotope ratios

Relative oxygen isotope ratios are based on $n(^{18}\mathrm{O})/n(^{18}\mathrm{O})$ measurements. Since 1993, the Commission has recommended that oxygen isotope ratios be reported relative to VSMOW water or relative to VPDB (defined by adopting an exact δ^{18}O value of –2.2 ‰ for NBS 19 $CaCO_3$) on a scale normalized such that the exact δ^{18}O of SLAP water is –55.5 ‰, relative to VSMOW (IUPAC, 1994; Coplen, 1994). Using the data in Coplen and others (1983) and given a value of –2.2 ‰ for the δ^{18}O value of NBS 19 relative to VPDB, the VPDB scale can be related to the VSMOW scale by

$$\delta^{18}\mathrm{O}_{\mathrm{x-VPDB}} = 0.97001\delta^{18}\mathrm{O}_{\mathrm{x-VSMOW}} - 29.99.$$

Oxygen-bearing gases also are sometimes reported relative to atmospheric oxygen. $^{18}\mathrm{O}/^{16}\mathrm{O}$ isotope ratios are determined on gaseous CO_2, O_2, or CO using electron impact ionization mass spectrometry and commonly are measured with a 1-σ standard deviation of ±0.1 ‰.

Although no investigator has measured the absolute abundances of all three oxygen isotopes, Baertschi (1976) measured the $n(^{18}\mathrm{O})/n(^{16}\mathrm{O})$ abundance ratio of VSMOW reference water and Li and others (1988) measured the absolute ^{17}O concentration in VSMOW reference water. From these measurements, the absolute isotope abundances of VSMOW reference water can be determined (table 15).

Table 16 and figure 6 list various carbonates, a silica sand, three sulfates, three carbon dioxide gases, and a biotite that are secondary isotopic reference materials for environmental, geochemical, and hydrological studies. These are distributed by IAEA and (or) NIST. The reference material, NBS 127 barium sulfate, is plotted in figure 6 as a sulfate mineral although technically the sulfate was derived from ocean water. Silicates are among the most difficult materials to analyze because of the strong silicon-oxygen bonds in these molecules. During the last decade a CO_2-laser-based method has produced good results, agreeing with a δ^{18}O value of +9.59 ‰ for NBS 28 (Spicuzza and others, 1998; Hut, 1987). “Provisional certified δ^{18}O values” have been reported for IAEA-304A and IAEA-304B waters, which are enriched in ^{18}O and intended for use mainly in medical and biological tracer studies (Parr and Clements, 1991). Note that these reference materials were made with ^{18}O enriched water; thus, the relative abundances of ^{16}O, ^{17}O, and ^{18}O may not

Table 15. *Oxygen isotopic composition of VSMOW reference water*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass^A	Mole Fraction^B
^{16}O	15.994 914 6223(25)	0.997 6206(5)
^{17}O	16.999 131 50(22)	0.000 3790(9)
^{18}O	17.999 1604(9)	0.002 0004(5)

^{A} From Audi and Wapstra (1993).

^{B} From Baertschi (1976) and Li and others (1988).

Table 16. *Oxygen isotopic composition of selected oxygen-bearing isotopic reference materials*

[Values for $\delta^{18}O$ given in per mill relative to VSMOW or VPDB on scales normalized such that the $\delta^{18}O$ of SLAP is –55.5 ‰ relative to VSMOW; the VPDB scale is defined (Hut, 1987) by assigning an exact $\delta^{18}O$ value of –2.2 ‰ to NBS 19 carbonate; ºC = degrees Celsius]

Reference Material	Substance	$\delta^{18}O$	Relative to	Reference
VSMOW	water	0 (exactly)	VSMOW	Gonfiantini, 1978
GISP	water	–24.78 ± 0.08	VSMOW	Gonfiantini and others, 1995
SLAP	water	–55.5 (exactly)	VSMOW	Gonfiantini, 1978
NIST RM 8562	CO_2	–8.45 ± 0.11	VPDB	NIST, 1998
NIST RM 8563	CO_2	–23.72 ± 0.11	VPDB	NIST, 1998
NIST RM 8564	CO_2	+0.19 ± 0.10	VPDB	NIST, 1998
NBS 30	biotite	+5.24 ± 0.25	VSMOW^A	Gonfiantini and others, 1995
NBS 18	$CaCO_3$ (carbonatite)	–23.00 ± 0.06	VPDB	Coplen and others, 1983; Gonfiantini and others, 1995; Stichler, 1995
NBS 19	$CaCO_3$ (calcite)	–2.2 (exactly)	VPDB	Hut, 1987
IAEA-CO-1	$CaCO_3$	–2.44 ± 0.07	VPDB	Stichler, 1995
IAEA-CO-8 (IAEA KST)	$CaCO_3$	–22.67 ± 0.19	VPDB	Stichler, 1995
IAEA-CO-9 (IAEA NZCH)	$BaCO_3$	–15.28 ± 0.09	VPDB	Stichler, 1995
L-SVEC	Li_2CO_3	–26.64 ± 0.25	VPDB	Stichler, 1995
NBS 28	SiO_2 (silica sand)	+9.58 ± 0.09	VSMOW^A	Gonfiantini and others, 1995
IAEA-NO-3	KNO_3	+25.3 ± 0.7	VSMOW^A	Kornexl and others, 1999
NBS 127	$BaSO_4$	+8.7 ± 0.2	VSMOW^A	Kornexl and others, 1999
IAEA-SO-5	$BaSO_4$	+12.0 ± 0.2	VSMOW^A	Kornexl and others, 1999
IAEA-SO-6	$BaSO_4$	–11.0 ± 0.2	VSMOW^A	Kornexl and others, 1999

[A] Using an oxygen isotope-fractionation factor between gaseous CO_2 and H_2O of 1.0412 at 25 ºC.

vary systematically with mass as they do in normal terrestrial samples. As a result, the abundance of $C^{16}O^{17}O$ during mass-spectrometric measurements may be low and may require special corrections during isotopic data reduction.

Ranges in Isotopic Composition

Oxygen exhibits a large variation in isotopic composition (> 160 ‰), partly because it is found in valence states between –2 and 0 in naturally occurring materials (table 17 and figure 6). Compilations of isotopic variations and isotope-fractionation mechanisms of oxygen-bearing materials include

Table 17. *Oxygen isotopic composition of selected oxygen-bearing materials*

[Values for δ^{18}O given in per mill relative to VSMOW on a scale normalized such that the δ^{18}O of SLAP is –55.5 ‰ relative to VSMOW]

	Minimum δ^{18}O Value		Maximum δ^{18}O Value	
Substance	**δ^{18}O**	**Reference**	**δ^{18}O**	**Reference**
OXYGEN GAS				
Air	+23.8	Kroopnick and Craig, 1972	+23.8	Kroopnick and Craig, 1972
WATER				
Sea water	–1	Craig, 1967	+0.6	Craig, 1967
Continental water	–62.8	Aldaz and Deutsch, 1967	+31.3	Fontes and Gonfiantini, 1967
Fruit juice and wine	–4.4	Bricout and others, 1973	+15.3	Caldwell, 1995
CARBON MONOXIDE				
Air	–6.9	Brenninkmeijer, 1993	+1.7	Brenninkmeijer, 1993
Commercial tank gas	–229	W.J. Showers, North Carolina State University, Raleigh, North Carolina, written communication, 2002	+7.6	R. A. Werner, Max-Planck-Institute for Biogeochemistry, Jena, Germany, written communication, 2001
CARBON DIOXIDE				
Air	+40	Francey and Tans, 1987	+53.0	Thiemens and others, 1991
Commercial tank gas	+3.9	Coplen and others, 1983	+22.2	NIST, 1998
CARBONATES				
Typical marine carbonate	+26	Murata and others, 1969	+34	Murata and others, 1969
Igneous (carbonatite)	–1.3	Garlick, 1969	+7.7	Suwa and others, 1975
Other carbonate	–20.5	Faure and others, 1988	+36.4	Makhnach and others, 1994
NITROGEN OXIDES				
N_2O (air and water)	+20	Pérez and others, 2000	+109	Yoshinari and others, 1997
Nitrate (air and water)	–2.5	Amberger and Schmidt, 1987	+76	Williard and others, 2001

Table 17. *Oxygen isotopic composition of selected oxygen-bearing materials—Continued*

	Minimum $\delta^{18}O$ Value		Maximum $\delta^{18}O$ Value	
Substance	**$\delta^{18}O$**	**Reference**	**$\delta^{18}O$**	**Reference**
OXIDES				
Al and Fe oxides	–15.5	Yapp, 1993	+16	Bird and others, 1989
Chert	+9.4	Knauth and Lowe, 1978	+45	Labeyrie and others, 1986
PHOSPHATES				
Skeletal parts	+6	Kolodny and others, 1983	+26.7	Bryant and others, 1994
Phosphorite rocks	+8.6	Longinelli and Nuti, 1968	+25.1	Shemesh and others, 1983
SILICATES	–16.2	Blattner and others, 1997	+34.9	Böhlke and others, 1984
SULFATES				
Air	–19	Norman and Krouse, 1992	+14.1	Mizutani and Rafter, 1969
Sea water	+9.3	Longinelli, 1989	+9.6	Longinelli, 1989
Other water	–19.8	Hendry and others, 1989	+23.2	Longinelli and Craig, 1967
Minerals	–10.0	Yonge and Krouse, 1987	+31.2	Cecile and others, 1983; Sakai, 1971
PLANTS AND ANIMALS				
Cellulose, lipids, and tissue	–4.3	Dunbar and Wilson, 1982	+37.0	Sternberg and others, 1984

Garlick (1969), Friedman and O'Neil (1977), Valley and others (1986), Kyser (1987), Clark and Fritz (1997), Valley and Cole (2001), and Schmidt and others (2001). Values of $\delta^{17}O$, which are based on $n(^{17}O)/n(^{16}O)$ measurements, and $\delta^{18}O$ are expressed relative to VSMOW in this report unless otherwise specified.

Oxygen isotope fractionations in naturally occurring materials generally are mass dependent. For example, Meijer and Li (1998) find $\delta^{17}O$ values to be 0.5281 ± 0.0015 times $\delta^{18}O$ values in natural waters on the VSMOW scale. However, mass-independent $\delta^{17}O$ and $\delta^{18}O$ isotopic variation has been observed in atmospheric O_3, O_2, N_2O, H_2O_2, CO, CO_2, sulfate aerosols, and nitrate aerosols (Thiemens and others, 1991; Thiemens and others, 1995; Johnson and others, 2001; Thiemens, 2001). For ozone, this effect may be caused in part by discrimination between symmetric and asymmetric isotopic species during photochemical reaction (Gao and Marcus, 2001). Bao and others (2000) report $\delta^{17}O$ and $\delta^{18}O$ values of +11.1 ‰ and +12.5 ‰ for sulfate in sand crystals from Scotts Bluff, Nebraska (USA), a 4.6 ‰ enrichment in ^{17}O relative to the expected mass-dependent value. This is the first sulfate deposit on the Earth's surface reported to be enriched in ^{17}O. ^{17}O enrichments in excess of

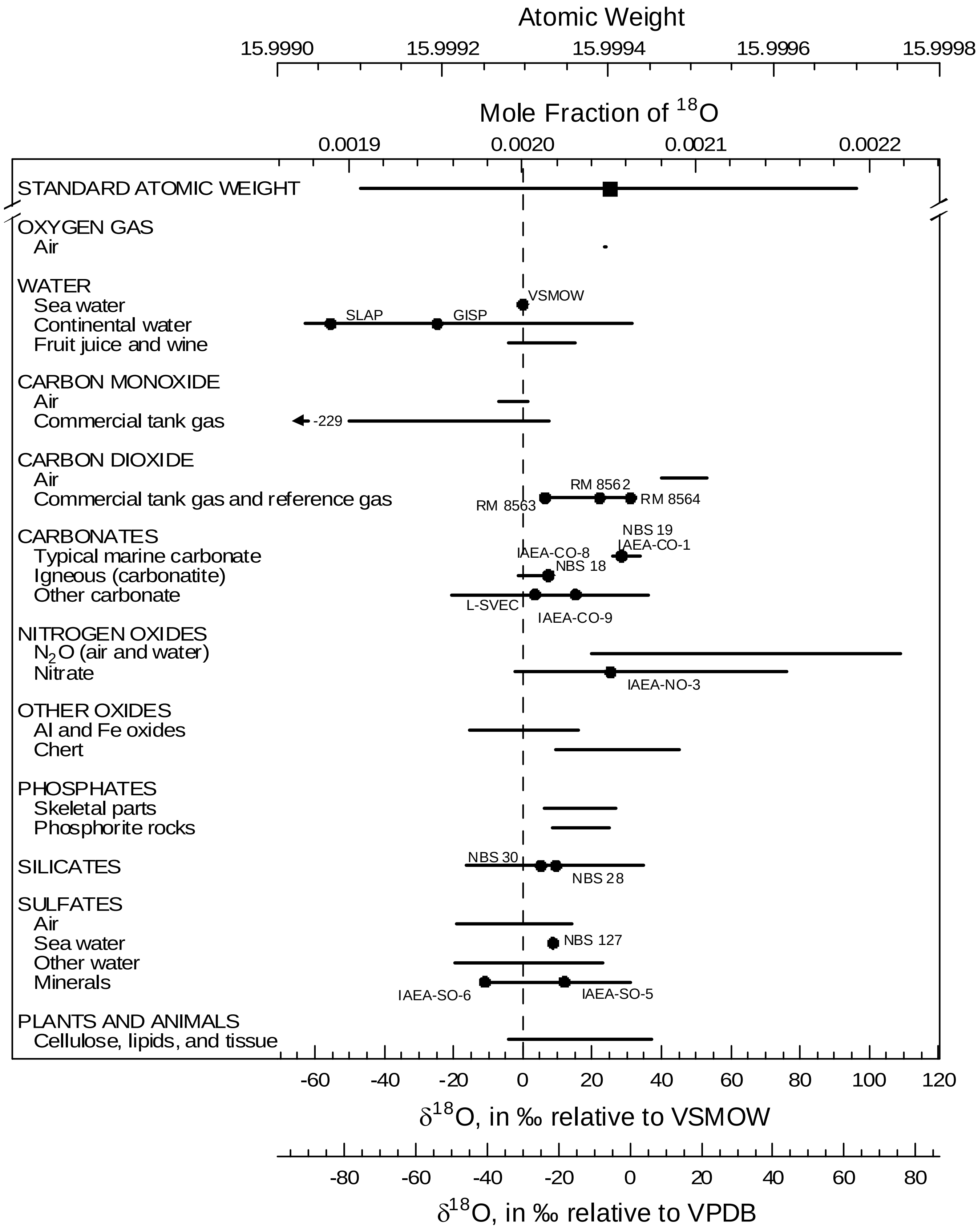

Figure 6. Oxygen isotopic composition and atomic weight of selected oxygen-bearing materials. The δ^{18}O scale and ^{18}O mole-fraction scale were matched using the data in table 15; therefore, the uncertainty in placement of the atomic-weight scale and the ^{18}O mole-fraction scale relative to the δ^{18}O scale is equivalent to ±0.3 ‰.

10 ‰ (relative to mass-dependent values) have been determined for atmospheric nitrate (Galanter and others, 2000; Michalski and Thiemens, 2000) and in excess of 20 ‰ for nitrate from the Atacama Desert, Chile (J.K. Böhlke, unpublished data).

Oxygen gas Dole and others (1954) observed that atmospheric oxygen is constant in ^{18}O content. Kroopnick and Craig (1972) determined a δ^{18}O value for atmospheric oxygen of +23.5 ‰ using an oxygen isotope-fractionation factor between water and CO_2 of 1.0409. However, that isotope-fractionation factor appears to be too low and we use herein an oxygen isotope-fractionation factor between water and CO_2 of 1.0412 recommended by Friedman and O'Neil (1977). Thus, δ^{18}O of atmospheric oxygen relative to VSMOW is +23.8 ± 0.3 ‰. If atmospheric oxygen were in isotopic equilibrium with ocean water, the δ^{18}O of atmospheric oxygen would be +6 ‰. Thus, atmospheric oxygen cannot be in isotopic equilibrium with ocean water; this isotopic enrichment of atmospheric oxygen in ^{18}O is called the Dole effect (Dole, 1935). The primary cause of the Dole effect is the preferential uptake of ^{16}O during respiration of terrestrial and marine plants and animals (Lane and Dole, 1956). Dissolved oxygen exhibits variations in δ^{18}O that are related to photosynthesis and respiration in surface water and ground water.

Water Variations in the ^{18}O content of surface waters, ground waters, and glacial ice generally are concordant with δ^{2}H variations and are caused primarily by evaporation and condensation processes. For example, atmospheric moisture is depleted in ^{18}O by about 11 ‰ at 5 °C relative to precipitation. The δ^{18}O of naturally occurring waters ranges from –62.8 ‰ in Antarctic ice (Aldaz and Deutsch, 1967) to +31.3 ‰ in the Gara Diba Guelta Basin, Western Sahara (Fontes and Gonfiantini, 1967). ^{18}O abundance decreases with increasing latitude, distance inland from a coast (Dansgaard, 1964), and increasing altitude [on the windward side of mountains only, a typical δ^{18}O gradient of –0.15 ‰ to –0.5 ‰ per 100 m is observed (Yurtsever and Gat, 1981)]. Precipitation is depleted in ^{18}O during cold seasons relative to warm seasons. Glacial ice cores, studied to determine long-term climate change, are depleted in ^{18}O during full-glacial climates relative to interglacial climates. These isotopic variations enable tracing and identification of the origin and history of ground and surface waters (Coplen, 1993; Coplen, 1999). Deep oceanic water is nearly homogeneous in δ^{18}O, varying from –1 ‰ to +0.6 ‰ (Craig, 1967). Hydrothermal waters commonly are enriched in ^{18}O relative to cold ground waters recharging thermal regimes because oxygen in rock exchanges with oxygen in water (Valley and others, 1986).

Agricultural food products have δ^{18}O values that are related to those of the meteoric waters in the growing area. However, citrus trees are found in areas with subtropical climates and undergo extensive evaporation, resulting in ^{18}O enrichment in cellular water. Bricout and others (1973) showed that natural orange juice could be distinguished from orange juice reconstituted from concentrate and water from higher latitudes containing less ^{18}O.

The lowest δ^{18}O value in naturally occurring terrestrial material is –62.8 ‰, found in Antarctic ice (Aldaz and Deutsch, 1967). The mole fraction of ^{18}O in this sample is 0.001 875 and A_r(O) = 15.999 04.

Carbon monoxide The δ^{18}O of carbon monoxide in air ranges between –6.9 ‰ and –0.4 ‰ (Brenninkmeijer, 1993). Compressed tank carbon monoxide is used for a reference gas in isotope-ratio mass spectrometry for oxygen-bearing materials analyzed with a reactor at ~1,400 ºC. The δ^{18}O of this compressed gas can vary greatly and is dependent upon the method of preparation. It has been observed that the tanks of carbon monoxide available in Europe commonly have δ^{18}O values near 0 ‰. R. A. Werner (Max-Planck-Institute for Biogeochemistry, Jena, Germany, written communication, 2001) has measured a δ^{18}O value of +7.6 ‰ for commercial carbon monoxide gas. The δ^{18}O of carbon monoxide available in the United States is as negative as –229 ‰ (W.J. Showers, North Carolina State University, Raleigh, North Carolina, written communication, 2002).

Carbon dioxide The δ^{18}O of atmospheric carbon dioxide is expected to be about +41 ‰ because it is in approximate isotopic equilibrium with sea water. Francey and Tans (1987) report a large asymmetric meridional gradient in δ^{18}O of atmospheric carbon dioxide from 6 remote stations with differences of as much as 2 ‰. These variations indicate that large quantities of carbon dioxide (~200 Gt a^{-1}) must be exchanged annually to maintain the observed isotopic gradient. Francey and Tans (1987) argue that this gradient is maintained by exchange with plant leaf water and possibly soil water. Thiemens and others (1991) collected carbon dioxide samples between 26 and 35.5 km and found δ^{18}O values as high as +53 ‰. They attributed ^{18}O enrichment to photochemical exchange between carbon dioxide and ozone, which produced δ^{18}O variation and mass independent δ^{17}O and variation, leading to ^{17}O enrichment as discussed above.

Carbonates At 20 ºC calcium carbonate precipitating from water is enriched in ^{18}O by about 30 ‰; thus, the δ^{18}O of typical marine carbonate ranges from +26 ‰ to +34 ‰ (Murata and others, 1969). Igneous carbonatites commonly are associated with kimberlite pipes, and they inherit their oxygen isotopic composition from the mantle. Consequently, on average, their ^{18}O content is substantially lower than other carbonates, and unaltered carbonatites range in δ^{18}O composition between –1.3 ‰ (Garlick, 1969) and +7.7 ‰ (Suwa and others, 1975). However, altered carbonatites can have δ^{18}O values as high as +29 ‰ (Suwa and others, 1975).

The range in δ^{18}O of non-marine carbonates is much greater than that of marine carbonates because the oxygen isotopic composition of continental water controls the isotopic content of carbonates and varies substantially (table 6). The lowest δ^{18}O value (–20.5 ‰) is found in calcite crystals ablating out of the ice at the Elephant Moraine, Antarctica, and these low ^{18}O concentrations are attributed to precipitation of calcite from aqueous solutions discharged by hot springs under the East Antarctic ice sheet (Faure and others, 1988). The carbonate with the highest ^{18}O content found in the literature is from saline deposits of the Pripyat Trough, Belarus, with δ^{18}O values as high as +36.4 ‰ (Makhnach and others, 1994).

Nitrogen oxides With a greenhouse effect 180 times as strong as that of carbon dioxide on a per molecule basis, nitrous oxide is an important greenhouse gas and it is increasing in abundance in the atmosphere because of anthropogenic activity. Nitrous oxide is produced by microbial nitrification and denitrification in soils, the ocean, and other aquatic environments, and it is a by-product in the manufacture of nylon. Thiemens and Trogler (1991) indicate that the release of artificial by-product nitrous oxide may account for 10 percent of the increase observed in atmospheric nitrous oxide concentrations. The δ^{18}O value of typical tropospheric nitrous oxide is ~ +44 ‰ (Wahlen and Yoshinari, 1985; Kim and Craig, 1993), whereas the various sources of nitrous oxide emissions have a wide range of δ^{18}O values as a result of isotope fractionation during its formation and degradation in marine and continental environments (Kim and Craig, 1993; Rahn and Wahlen, 2000). In suboxic sea water, denitrification progressively depletes ^{14}N and ^{16}O of nitrous oxide, enriching residual dissolved nitrous oxide in ^{15}N and ^{18}O. Yoshinari and others (1997) report δ^{18}O values as high +109 ‰ for residual nitrous oxide collected from a depth of about 400 m in the Arabian Sea. This is the highest δ^{18}O value for a material of natural terrestrial origin found in the literature; the mole fraction of ^{18}O in this sample is 0.002 218 and A_r(O) = 15.999 76.

Nitrate chemical reagents typically have δ^{18}O values relatively close to that of atmospheric O_2 (~ +24 ‰), which is commonly used in the manufacture of the nitrate. Reported δ^{18}O values of atmospheric nitrate range from about +14 ‰ to +76 ‰ (Durka and others, 1994; Kendall, 1998; Williard and others, 2001). In contrast, δ^{18}O values of dissolved nitrate in soils and ground waters range from about –2 ‰ to +22 ‰ (Amberger and Schmidt, 1987; Kendall, 1998; Williard and others, 2001). The relatively low values reflect incorporation of oxygen depleted in ^{18}O from local meteoric water into the nitrate during nitrification (microbial oxidation of ammonium to nitrate) in soils.

Other Oxides Yapp (1987b; 1993) has investigated the oxygen and hydrogen isotopic composition of goethite (FeOOH). At 25 ºC, goethite is enriched in ^{18}O by 6.1 ‰ relative to formation water (Yapp, 1990). Yapp finds a substantial variation in oxygen isotope fractionation between goethite and water, and proposes that mineral pairs, such as chert-goethite, might be suitable for determining temperatures of formation. The δ^{18}O values of goethite in Yapp's (1987b; 1993) studies range between –15.5 ‰ and +4.4 ‰.

Gibbsite [$Al(OH)_3$] is the most common aluminum-bearing mineral in lateritic bauxites and is formed in tropic and subtropical environments. Bird and others (1990) have shown that at 25 ºC gibbsite is enriched in ^{18}O by 16.0 ‰ relative to the water from which it formed. This enrichment is in contrast to an earlier study by Lawrence and Taylor (1972) whose results may have been affected by either partial dehydroxylation of the gibbsite during out gassing prior to extraction or by the presence of a goethite contaminant in the samples (Bird and others, 1989). The δ^{18}O of gibbsite in the studies of Bird and others (1989) and Bernard (1978) ranged from +5.6 ‰ to +12.0 ‰. Boehmite [γ-AlO(OH)] also is present in lateritic bauxites. Boehmite is enriched in ^{18}O relative to formation waters by 17.5 ‰, and δ^{18}O values range between +11.5 ‰ and +16 ‰ (Bird and others, 1989).

The lowest δ^{18}O in a chert (SiO_2) sample is +9.4 ‰ from the 3.4-billion-year-old Onverwacht Group, South Africa (Knauth and Lowe, 1978). The low ^{18}O content may result from silicification at elevated temperature during burial. Labeyrie and others (1986) find δ^{18}O values as high as +45 ‰ in chert from Antarctica, presumably caused by chert formation at low temperature.

Phosphates The apatite minerals in phosphorite deposits ranging in age from Archaean to Recent were analyzed for oxygen isotopic composition by Shemesh and others (1983). They found a range in δ^{18}O from +11.5 ‰ to +25.1 ‰. The oxygen in apatite virtually is inert to isotopic post-depositional exchange. Shemesh and others were able to attribute some of the change in δ^{18}O over time to differences in the δ^{18}O of sea water that precipitated the phosphorites, but they also attributed some of the change to phosphorite formation at higher temperatures in the past. The lowest δ^{18}O value in phosphates was measured on samples from Montana and Tennessee (Longinelli and Nuti, 1968), both with a value of +8.6 ‰.

Biogenic apatite acquires its isotopic composition through exchange between phosphate and water in enzyme-catalyzed reactions, such as the formation of bones and teeth, according to Shemesh and others (1983). Thus, the δ^{18}O value of phosphate in bones and teeth is closely linked to the δ^{18}O of ingested water because the temperature of mammals is relatively constant and because biogenic phosphate precipitates in oxygen isotopic equilibrium with body water (Longinelli, 1984). Cormie and others (1994) demonstrated a linear relation between the δ^{18}O of bone phosphate of North American deer and the δ^{18}O of precipitation. The relation improved when relative humidity was included because deer obtain most of their ingested water from leaves. In the literature, the lowest δ^{18}O in phosphate in skeletal parts is +6.0 ‰ from a fish from Lake Baikal, Russia, where Siberian weather gives rise to lake water with low ^{18}O content. The highest δ^{18}O in phosphate in skeletal parts is +26.7 ‰ for a fossil horse tooth from New York State (Bryant and others, 1994).

Silicates Many publications have been written on the oxygen isotopic composition of silicates (for example, Valley and others, 1986; Kyser, 1987). The most abundant igneous rock type in the Earth's crust are mid-ocean ridge basalts, which cover most of the ocean floor. The δ^{18}O of this material is +5.7 ± 0.5 ‰ (Kyser, 1986), which is a good representation of the bulk Earth and Moon. Thus, oxygen isotope ratios between mineral pairs commonly serve as geothermometers. Oxygen isotope studies help elucidate processes in weathering of rock, in fluid flow in hydrothermal systems, in formation of ore-forming fluids, and in metamorphism of rock, to name just a few. Excluding secondary alteration, the ^{18}O contents of minerals in igneous and metamorphic rocks are generally correlated with SiO_2 contents. Thus, ^{18}O content increases in the order magnetite, biotite, muscovite, feldspar, quartz or in the order magnetite, ilmenite, hornblende, pyroxene, feldspar (Taylor, 1968).

Blattner and others (1997) measured a δ^{18}O value of –16.2 ‰ for basaltic fragments from Marie Byrd Land at a longitude of 76 º S, which they attribute to alteration by ^{18}O depleted water. Böhlke and others (1984) measured a δ^{18}O value of +34.9 ‰ for phillipsite, which they attributed to formation at low temperature in isotopic equilibrium with modified sea water.

Sulfates Van Stempvoort and Krouse (1994) provide a comprehensive review of δ^{18}O in sulfate. Mizutani and Rafter (1969) measured δ^{18}O values of sulfate in precipitation as high as +14.1 ‰. Correcting for chloride and sulfate sea-spray addition, they calculate δ^{18}O values for the pure atmospheric component to be as high as +19.5 ‰. Norman and Krouse (1992) report δ^{18}O values of sulfate in air as low as –19 ‰ and attribute the low ^{18}O concentrations to incorporation of oxygen from ^{18}O depleted Canadian atmospheric water vapor in the sulfate.

The oxygen isotopic composition of sulfate in the modern ocean is essentially constant both vertically and horizontally. Longinelli (1989) reported a mean δ^{18}O value of +9.45 ± 0.15 ‰, but this value may be too positive if NBS 127 barium sulfate (table 16), which was produced from marine sulfate and has a δ^{18}O value of +8.7 ‰ using another analytical technique (Kornexl and others, 1999), was not fractionated in oxygen isotopes during preparation. Continental waters have a large range in oxygen isotopic composition. Hendry and others (1989) analyzed the δ^{18}O of dissolved sulfate in tills of southern Alberta, Canada, and found values as negative as –19.8 ‰. The δ^{18}O of water was similar or identical to that of dissolved sulfate. They attribute the low ^{18}O content of dissolved sulfate to oxidation of reduced sulfate in the presence of water similar in ^{18}O content. The highest δ^{18}O of dissolved sulfate is +23.2 ‰ found in Searles Lake brine (Longinelli and Craig, 1967).

Sulfate minerals show a wide variation in oxygen isotopic composition that reflects different origins. Yonge and Krouse (1987) analyzed the oxygen isotopic composition of sulfate minerals in Castleguard Cave, Columbia Icefields, Canada. A sample of mirabilite ($Na_2SO_4 \cdot 10H_2O$) yielded a δ^{18}O value of –10.0 ‰. The low ^{18}O content likely was inherited from the water in the cave, with a δ^{18}O as negative as –22 ‰. Cecile and others (1983) report

δ^{18}O values for barite nodules up to +31.2 ‰. Sakai (1971) reported a similar maximum in barite concretions in the Japan Sea.

Plants and animals The oxygen in organic matter is derived from three sources: (1) oxygen in atmospheric carbon dioxide (δ^{18}O = ~+41 ‰), (2) oxygen in water from the hydrologic cycle (δ^{18}O variation is –15 ‰ to +2 ‰), and (3) atmospheric oxygen (δ^{18}O = +23.8 ± 0.3 ‰; recalculated from Kroopnick and Craig, 1972, by correcting to a CO_2-H_2O isotope-fractionation factor of 1.0412; Friedman and O'Neil, 1977). The δ^{18}O of cellulose has been studied since the recognition by Libby and Pandolfi (1974) that the δ^{18}O of cellulose in tree rings is correlated to the δ^{18}O of leaf water. As a result of the summation of the isotope fractionation between carbon dioxide and water (+41 ‰), exchange of oxygen in cellulose with that in carbonyl, and direct introduction of water into organic intermediates, the δ^{18}O of cellulose is +27 ± 4 ‰ relative to that of leaf water (Sternberg, 1989; Schmidt and others, 2001). The range in δ^{18}O of naturally occurring carbohydrates and immediate descendents (cellulose, soluble sugars, and glycerol) is between +19 ‰ for cane sugar (Hillaire-Marcel, 1986) and +37.0 ‰ for cellulose from *Bouteloua hirsuta* (Sternberg and others, 1984). The data of Schmidt and others (2001) show that natural Furaneol® (δ^{18}O = +31.5 ± 1.5 ‰) can be distinguished easily from synthetic Furaneol® (δ^{18}O = +10 ± 2 ‰). Orange juice adulterated with beet sugar can be detected by stable hydrogen and oxygen isotopic composition of the sugar in orange juice (Donner and others, 1987).

Aliphatic acids, esters, carbonyl compounds, and alcohols have lower δ^{18}O values than carbohydrates because the former obtain oxygen from water or exchange oxygen by equilibration with water. Schmidt and others (2001) show that this group of compounds has δ^{18}O values that range from 0 ‰ in ergosterol (probably yeast) to +27 ± 2 ‰ in glycerol from plant fats (Rossmann and others, 1998). Synthetic ethanol (δ^{18}O = +3 ± 2 ‰ to +8.1 ‰; Misselhorn and others, 1983; Schmidt and others, 2001; Dunbar, 1982) can be easily distinguished from natural ethanol (δ^{18}O = +16.4 ‰ to +20 ± 2 ‰; Bricout, 1978; Misselhorn and Grafahrend, 1990). Once formed, natural esters no longer exchange oxygen with water in biological systems (Schmidt and others, 2001). Their δ^{18}O values range between +10 ‰ (Hillaire-Marcel, 1986) and +34.7 ‰ (Werner, 1998). The alcohols from natural esters range from +4 ‰ to +8 ‰ (Werner, 1998).

Aromatic compounds that obtain oxygen from atmospheric oxygen and exchange oxygen with water are depleted in ^{18}O relative to cellulose, attaining values of ~+12 ‰ (Gray and Thompson, 1977). However, Dunbar and Wilson (1982) find δ^{18}O values as low as –4.3 ‰ for caffeine from *Caffea arabicas* and *Camellia sinensis*.

Magnesium A_r(Mg) = 24.3050(6)

Magnesium is the seventh most abundant element in the cosmos behind hydrogen, helium, oxygen, carbon, neon, and nitrogen. Abundant supplies are found in the minerals dolomite [$CaMg(CO_3)_2$], magnesite ($MgCO_3$), and epsomite ($MgSO_4\cdot 7H_2O$). Magnesium can be produced by electrolysis of fused anhydrous $MgCl_2$ at 750°C or by the reaction of calcined dolomite with FeSi at 1150°C. Magnesium is important as a strong, light metal, having a density about two-thirds that of aluminum. It is used as the elemental metal and in alloys.

Reference materials and reporting of isotope ratios

Although both $n(^{25}\text{Mg})/n(^{24}\text{Mg})$ and $n(^{26}\text{Mg})/n(^{24}\text{Mg})$ isotope-abundance ratios can be measured, $n(^{26}\text{Mg})/n(^{24}\text{Mg})$ ratios generally are measured on terrestrial materials and reported as δ^{26}Mg values relative to NIST SRM 980 magnesium metal, which is assigned a δ^{26}Mg value of 0 ‰. The absolute isotope abundances of SRM 980 have been determined by Catanzaro and others (1966) and are listed in table 18.

Ranges in Isotopic Composition

In natural materials, the oxidation state of magnesium always is two, and, thus, it was expected that the range in isotopic variation of magnesium-bearing materials would be small. Daughtry and others (1962) measured the δ^{26}Mg values of carbonates where dolomitization had occurred and reported variations as large as 50 ‰. Shima (1964) measured the magnesium isotope abundances of standard rock samples G-1 and W-1, sea water, and reagent magnesium and found no isotopic variations. Catanzaro and Murphy (1966) measured 60 natural samples including carbonates, evaporites, hydroxides, silicates, oxides, biological matter, and sea water using thermal ionization mass spectrometry. Within their analytical uncertainty for δ^{26}Mg of ±2.2 ‰ (2-σ uncertainty), they observed no isotopic variation.

Table 18. *Isotopic composition of NIST SRM 980 magnesium metal*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{24}Mg	23.985 041 87(26)	0.789 92(25)
^{25}Mg	24.985 837 00(26)	0.100 03(9)
^{26}Mg	25.982 593 00(26)	0.110 05(19)

[A] From Audi and Wapstra (1993).
[B] Calculated from Catanzaro and others (1966) and Rosman and Taylor (1998).

Table 19. *Magnesium isotopic composition of selected magnesium-bearing materials*

[Values for δ^{26}Mg given in per mill relative to SRM 980 elemental magnesium]

	Minimum δ^{26}Mg Value		Maximum δ^{26}Mg Value	
Substance	δ^{26}Mg	Reference	δ^{26}Mg	Reference
MARINE SOURCES				
Sea water	+2.55±0.12	Chang and others, 2001b	+2.55±0.12	Chang and others, 2001b
Foraminifera	–1.95	Chang and others, 2001b	+0.85	Chang and others, 2001b
ELEMENTAL MAGNESIUM	–0.12	Chang and others, 2001b	+0.12	Chang and others, 2001b

They attributed the variations seen by Daughtry and others (1962) to the fact that "those workers apparently did not control their analyses as strictly as necessary." Using a multiple collector inductively coupled plasma mass spectrometer, Chang and others (2001b) analyzed sea water, foraminifera, and SRM 980 magnesium metal, and found δ^{26}Mg variations spanning 4.5 ‰ (table 19 and figure 7).

Marine sources Four sea-water samples analyzed by Chang and others (2001b) using multiple collector inductively coupled plasma mass spectrometry were indistinguishable (δ^{26}Mg = +2.55 ± 0.12 ‰) in isotopic composition and have the highest ^{26}Mg content found in the literature for a material of natural terrestrial origin. The mole fraction of ^{26}Mg in these samples is 0.1103 and A_r(Mg) = 24.3055. Marine foraminifera were depleted in ^{26}Mg by 1.7 ‰ to 4.5 ‰ relative to sea water, consistent with a kinetic isotope fractionation of 1.8 ‰ to 2.5 ‰ during calcite precipitation. The sample with the lowest ^{26}Mg value for a material of natural terrestrial origin is a foraminifer with a δ^{26}Mg value of –1.95 ‰ (Chang and others, 2001b). The mole fraction of ^{26}Mg in this sample is 0.1099 and A_r(Mg) = 24.3046. This value is consistent with the results of a cave study by Galy and others (2000), which indicates that calcite is depleted in ^{26}Mg relative to water from which it is precipitating.

Elemental magnesium The δ^{26}Mg of SRM 980 elemental magnesium has been analyzed by numerous workers. However, the analyses of Chang and others (2001b) yield the best reproducibility with a 2-σ standard deviation of ±0.12 ‰.

Silicon A_r(Si) = 28.0855(3)

Behind oxygen, silicon is the second most abundant element in the Earth's crust (Ding and others, 1996). Silicates are the most common silicon-

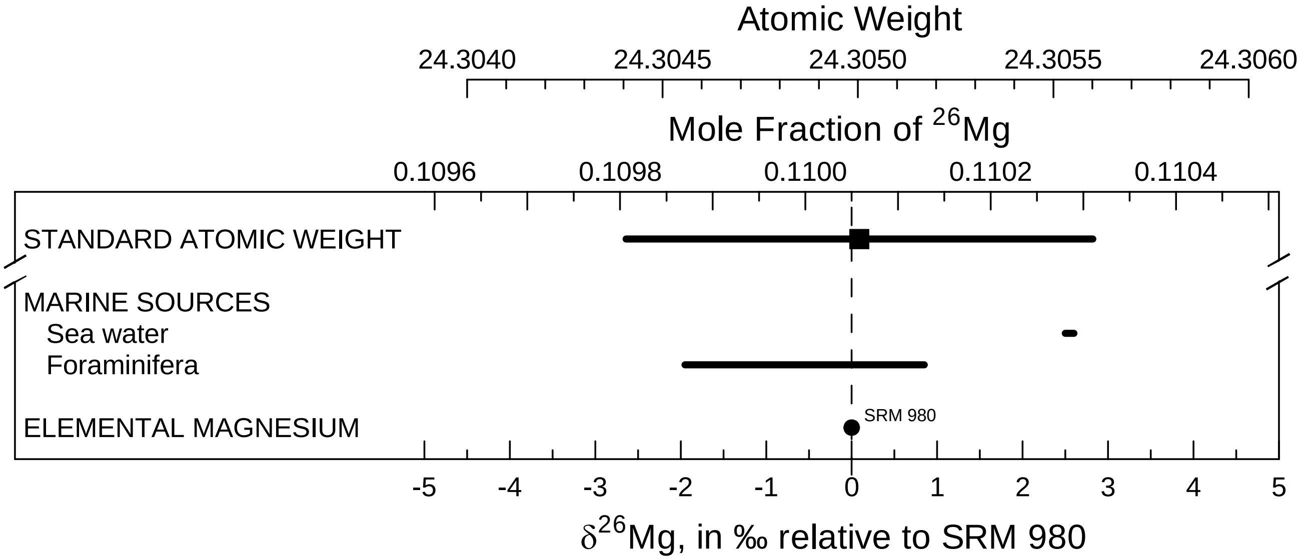

Figure 7. Magnesium isotopic composition and atomic weight of selected magnesium-bearing materials. The δ^{26}Mg scale and the ^{26}Mg mole-fraction scale were matched using the data in table 18; therefore, the uncertainty in placement of the atomic-weight scale and the ^{26}Mg mole-fraction scale relative to the δ^{26}Mg scale is equivalent to ±2.1 ‰.

bearing compounds, comprising 75 % of crustal rocks by weight. Silica, SiO_2, is the second most abundant silicon-bearing compound, comprising 12 % of crustal rocks. These two classes of minerals make up 87 % of the Earth's crust. Silicon is typically made by reduction of quartzite or sand with coke in an electric arc furnace. Silicon is used increasingly in semiconductors, in alloys, and in polymers.

Reference materials and reporting of isotope ratios

Although both $n(^{29}\mathrm{Si})/n(^{28}\mathrm{Si})$ and $n(^{30}\mathrm{Si})/n(^{28}\mathrm{Si})$ isotope-abundance ratios can be measured, $n(^{30}\mathrm{Si})/n(^{28}\mathrm{Si})$ ratios generally are measured on terrestrial materials and reported as δ^{30}Si values relative to NIST NBS 28 silica sand, which is assigned a δ^{30}Si value of 0 ‰. $n(^{30}\mathrm{Si})/n(^{28}\mathrm{Si})$ isotope-abundance ratios are determined on SiF_4 using electron impact ionization mass spectrometry and can be measured with a 1-σ standard deviation of ±0.1 ‰. The absolute isotope abundances of NBS 28 can be calculated (table 20) from the absolute isotope abundances of IRMM-017 elemental silicon (table 21), which have been determined by De Bièvre and others (1994), and from the δ^{30}Si measurement of IRMM-017 relative to NBS 28 (–1.3 ‰) determined by T. Ding (unpublished data).

Other isotopic reference materials (table 21) include: IRMM-017 elemental silicon, IRMM-018 SiO_2, NIST SRM 990 elemental silicon, and rose quartz (quartz from the Rose Quartz Pegmatite, a quartz and feldspar pegmatite in the Pala district near San Diego, California, and used as a reference material by the California Institute of Technology, Pasadena, California, USA) (Tilles, 1961; Molini-Velsko and others, 1986). The first three have been used primarily for absolute isotope-abundance measurements.

Ranges in Isotopic Composition

In natural materials, the valence state of silicon always is +4 and the relative mass difference between its isotopes is smaller than those of the elements with lower atomic weight. Thus, isotopic variation of silicon isotopes (table 22 and figure 8) is smaller (< 8 ‰) than that of most of the elements considered above (hydrogen through magnesium). An anomalous δ^{30}Si value of –11.2 ‰ for a kaolin sample (Ding and others, 1988) is not included in table 22 and figure 8. The most comprehensive document on silicon isotopic variations is that of Ding and others (1996). T hey present silicon isotope distribution graphs based on more than 1000 samples. Other compilations of silicon isotope-abundance variations and isotope-fractionation factors include Hoefs (1987) and Douthitt (1982).

Silicon isotopic equilibrium fractionations are present among silicon-bearing compounds. The ^{30}Si content of silicates varies with polymerization of the silicon-oxygen tetrahedra, increasing from nesosilicates (isolated SiO_4 tetrahedra, such as olivine), inosilicates (chains of SiO_4 tetrahedra, such as

Table 20. *Silicon isotopic composition of NBS 28 silica sand*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{28}Si	27.976 926 49(22)	0.922 223(9)
^{29}Si	28.976 494 68(22)	0.046 853(6)
^{30}Si	29.973 770 18(22)	0.030 924(7)

[A] From Audi and Wapstra (1993).

[B] Values are based on De Bièvre and others (1994) and a $\delta^{30}Si$ value for IRMM-017 SiO_2 of –1.3 ‰ relative to NBS 28 silica sand (T. Ding, unpublished data).

Table 21. *Silicon isotopic composition of selected silicon-bearing isotopic reference materials*

[Values given in per mill relative to NBS 28 silica sand]

Reference Material	Substance	$\delta^{29}Si$	$\delta^{30}Si$	Reference
SRM 990	elemental Si	+0.3	+0.5	T. Ding, unpublished data
IRMM-017	elemental Si	–0.7	–1.3	T. Ding, unpublished data
IRMM-018	SiO_2	0.0	0.0	T. Ding, unpublished data
California Institute of Technology rose quartz	SiO_2		–0.28	Molini-Velsko and others, 1986

enstatite), phyllosilicates (sheets of SiO_4 tetrahedra, such as talc), to tectosilicates (frameworks of SiO_4 tetrahedra, such as albite), the ^{30}Si content increases. However, the magnitude of the isotope fractionation is small—the largest is on the order of 1 ‰. Thus, silicon isotope-ratio measurements of minerals cannot be used for geothermometry because isotope-ratio measurements cannot be made sufficiently accurately. Additionally, no experimental determinations of equilibrium fractionation factors of silicon isotope ratios have been made.

Kinetic isotope fractionation is important in precipitation of SiO_2 from solution (Douthitt, 1982; Li and others, 1995). Because the lighter isotope, ^{28}Si, can move into the product more quickly than the heavier isotope, ^{30}Si, sponge spicules, opal sinter, and clay minerals are enriched in ^{28}Si relative to the solution.

Igneous rocks The great majority of silicon isotope ratios in igneous rocks are found in three studies (Douthitt, 1982; Ding and others, 1988; and Ding and others, 1996). Values of $\delta^{30}Si$ of basalts range from –1.0 ‰ to –0.3 ‰ (Ding and others, 1996). Values of basaltic andesites range from –0.7 ‰ to +0.2 ‰. The range for gabbros is larger, from –0.9 ‰ to +0.3 ‰, and may reflect assimilation of crustal rocks. Douthitt (1982) conducted a large investigation of granite rocks. Additional studies by Ding and others (1996) lead to the conclusions that granites are enriched in ^{30}Si relative to mafic igneous rocks and that $\delta^{30}Si$ values of granites range from –0.4 ‰ to +0.4 ‰, with a mean of about –0.1 ‰. Granites of different origins show no clear differences in their silicon isotope ratios (Ding and others, 1996). The igneous rock with the highest ^{30}Si content ($\delta^{30}Si$ = +0.4 ‰) is a monzonite from Dongping gold mine, Hebei, China (Lu and Wan, 1992).

Metamorphic rocks Because metamorphic rocks are a major reservoir of silicon and because relatively few silicon isotope ratios have been determined on these materials, Ding and others (1996) measured more than 90 rocks and minerals for silicon isotopic composition. These results indicate that during metamorphism to slates and schists silicon isotope abundances are preserved. The $\delta^{30}Si$ of slates and schists range from –1.1 ‰ to

Table 22. *Silicon isotopic composition of selected silicon-bearing materials*

[Values for δ^{30}Si given in per mill relative to NBS 28 silica sand]

	Minimum δ^{30}Si Value		Maximum δ^{30}Si Value	
Substance	δ^{30}Si	Reference	δ^{30}Si	Reference
IGNEOUS ROCKS	–1.0	Douthitt, 1982	+0.4	Lu and Wan, 1992
METAMORPHIC ROCKS	–1.1	Ding and others, 1996	+1.1	Huang and others, 1991
VEIN QUARTZ AND SILICIFIED ROCKS	–1.5	Ding and others, 1996	+1.1	Huang and others, 1991
SEDIMENTARY ROCKS				
Quartz sandstones	–0.2	Ding and others, 1996	+0.2	Ding and others, 1996
Clay minerals	–2.6	Douthitt, 1982	+1.5	Douthitt, 1982
Sinter	–3.4	Douthitt, 1982	+0.2	Douthitt, 1982
Sea-floor hydrothermal siliceous precipitates	–3.1	Wu, 1991	0.0	Ding and others, 1996
Other siliceous rocks	–0.8	Ding and others, 1996	+3.4	Ding and others, 1988
DISSOLVED SILICA	–0.4	Douthitt, 1982	+3.4	Ding and others, 1998
BIOGENIC SILICA	–3.7	Douthitt, 1982	+2.5	Douthitt, 1982
ELEMENTAL SILICON	–1.3	T. Ding, unpublished data	+0.5	T. Ding, unpublished data

+0.4 ‰. The δ^{30}Si of plagioclase amphibolites, granulites, leucogranulites, gneisses, migmatites, and hornfels range from –0.6 ‰ to +0.3 ‰ (Jiang and others, 1992; Ding and others, 1996), reflecting the isotopic compositions of their protoliths.

Vein quartz and silicified rocks Although not large in mass, quartz veins are widespread and are closely related to mineralization. Their δ^{30}Si values range from –1.5 ‰ to +0.7 ‰; however, the majority of values are in the range –0.9 ‰ to +0.7 ‰ (Ding and others, 1988; Ding and others, 1996). This relatively wide range in isotopic composition suggested to Ding and others (1996) that silicon in vein quartz has multiple sources or may be isotopically fractionated during precipitation. That the mean δ^{30}Si of vein quartz is near –0.2 ‰ suggests that the majority of vein quartz occurrences are related to granite, sandstone, and felsic metamorphic rocks (Ding and others, 1996). A number of silicified rocks have been analyzed for silicon isotope abundances. Huang and others (1991) analyzed silicified limestone and found values as low as –0.3 ‰ and as high as +1.1 ‰ (ore-bearing silicified limestone). The wide variation in isotopic composition suggests multiple sources of silicon.

Sedimentary rocks The range of silicon isotopic composition of quartz sandstones is small (–0.2 ‰ to +0.2 ‰), in accord with the conclusion that they are formed from residual quartz derived from weathering of granites (Ding and others, 1996).

Douthitt (1982) analyzed 14 clay mineral samples and Ding and others (1988) report on more than a dozen clay minerals samples. Depending upon their origin, clay minerals show a wide range in silicon isotopic composition (–2.6 ‰ to +1.5 ‰). However, the majority of δ^{30}Si values lie between

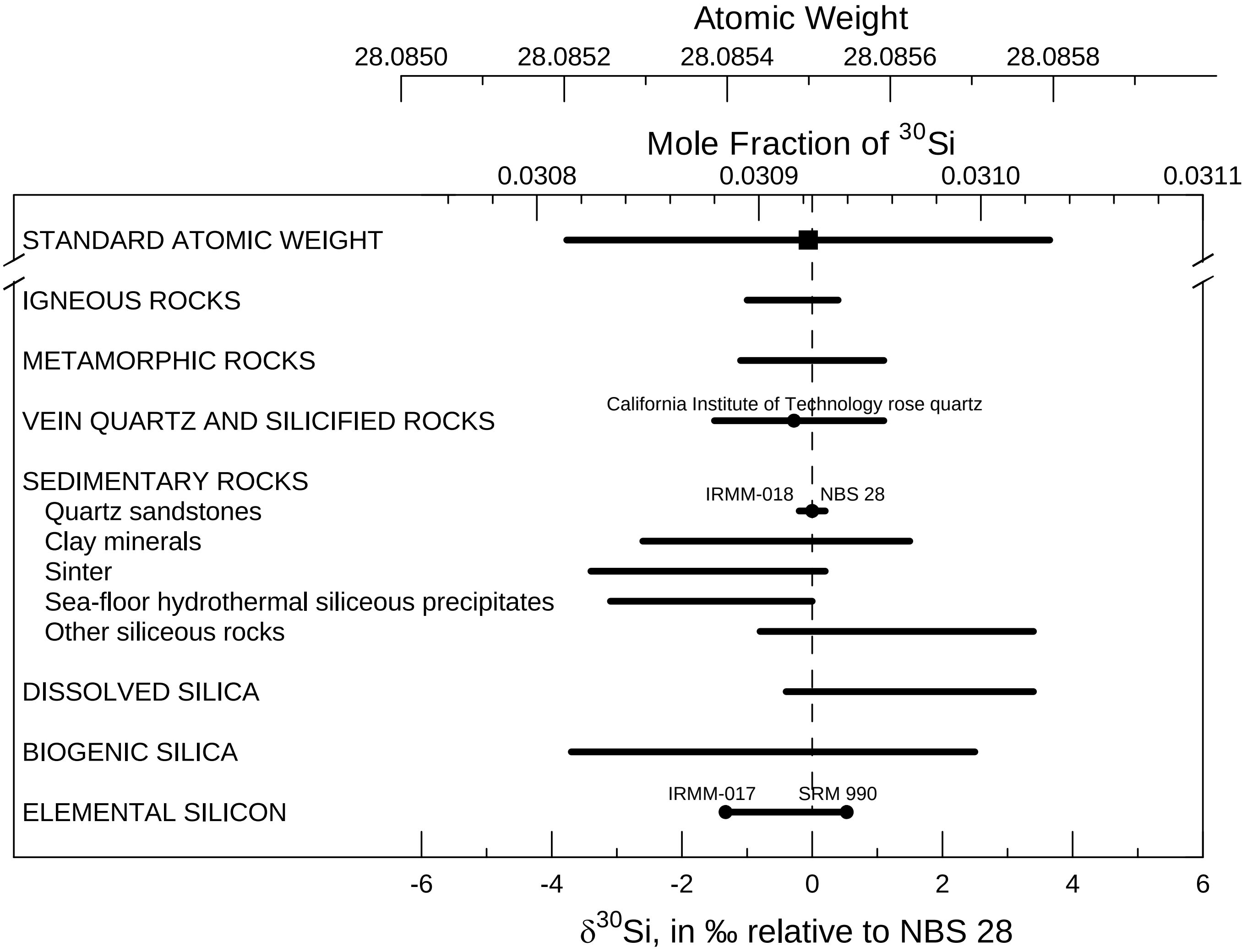

Figure 8. Silicon isotopic composition and atomic weight of selected silicon-bearing materials. The δ^{30}Si scale and ^{30}Si mole-fraction scale were matched using the data in table 20; therefore, the uncertainty in placement of the atomic-weight scale and the ^{30}Si mole-fraction scale relative to the δ^{30}Si scale is equivalent to ±0.23 ‰.

–1 ‰ and 0 ‰, indicating that little isotope fractionation accompanies formation of clays in weathering of silicates. The clay sample with the lowest ^{30}Si content is a poorly ordered kaolinite. The sedimentary rock with the highest ^{30}Si content also is a kaolinite, but no X-ray diffraction information is available. Douthitt (1982) concludes that although little or no isotope fractionation occurs during clay formation, substantial isotope fractionation can occur under as yet poorly understood conditions.

Silica sinters are siliceous precipitates, composed primarily of opal, that are formed by hot springs at their vent sites. The δ^{30}Si varies greatly (–3.4 ‰ to +0.2 ‰) and large variation occurs within the same geothermal field. For example, sinter from Steamboat Springs, Nevada ranges from –1.2 ‰ to 0.1 ‰ (Douthitt, 1982). The δ^{30}Si values of sinters typically are negative because ^{28}Si is enriched preferentially in sinter by kinetic isotope fractionation.

Sea-floor hydrothermal siliceous precipitates are found on mid-ocean ridges and back-arc basins. Precipitates from the Okinawa trench and the Mariana trench range from –3.1 ‰ to 0.0 ‰ (Wu, 1991; Ding and others, 1996). Black siliceous precipitates forming at temperatures above 100 °C fall in the range –0.6 ‰ to –0.4 ‰. Those precipitating at cooler temperatures show more variability in isotopic composition (–3.1 ‰ to –0.6 ‰).

A wide variety of sedimentary siliceous rocks are present, including banded siliceous rocks, ore-bearing siliceous rocks, and massive siliceous rock. Silica is present in carbonate rocks as trace amounts, thin siliceous laminae, and chert concretions. Depending upon the source of the silicon, the δ^{30}Si in these rocks can range from –0.8 ‰ to +3.4 ‰ (Ding and others, 1996), the latter being the sample (a silicified mid-Proterozoic spheroidal stromatolite from North China) with the highest ^{30}Si content found in the literature for a material of natural terrestrial origin. The mole fraction of ^{30}Si in this sample is 0.031 023 and A_r(Si) = 28.085 78.

Dissolved silica Ding and others (1998) report values from +0.7 ‰ to +3.4 ‰ for dissolved silica from the Yangtzi River, China. De La Rocha and others (2000) analyzed silicon isotope ratios in rivers from Africa, South America, and North America and they find a much smaller range (+0.5 ‰ to +1.2 ‰). Dissolved silica is enriched in ^{30}Si relative to igneous rocks because during weathering ^{28}Si is preferentially concentrated in clay minerals. Douthitt (1982) analyzed the δ^{30}Si of hot springs in Yellowstone National Park, Wyoming and Mammoth, California (USA), and found a range of –0.4 ‰ to +0.1 ‰.

The δ^{30}Si of dissolved silicon from several ocean basins is +1.1 ± 0.3 ‰, and the deep Pacific Ocean is depleted in ^{30}Si relative to the Atlantic Ocean by about 0.4 ‰ (De La Rocha and others, 2000). The more positive δ^{30}Si values are found in surface waters, because of preferential incorporation of ^{28}Si in biogenic opal formation by diatoms.

Biogenic silica Almost all organisms contain some silicon. Sometimes silicon appears as opal in major skeletal structures. Silica-rich organisms include tracheophyta, rice husk, bamboo, diatoms, sponges, and radiolaria. The isotopic composition varies greatly from species to species (–3.7 ‰ to +2.5 ‰). The lowest δ^{30}Si value found in the literature (–3.7 ‰) for a material of natural terrestrial origin is from biogenic sponge spicules from the Gulf of California, Mexico (Douthitt, 1982). The mole fraction of ^{30}Si in this sample is 0.030 816 and A_r(Si) = 28.085 22. In the literature, the highest ^{30}Si content of biogenic silica is found in a horsetail plant (*Equisetum*) from California (USA) (Douthitt, 1982). Ding and others (1996) analyzed the silicon isotope abundances in 5 bamboo samples from Beijing, Qingdao (Shandon province), and Ningbo (Zhejiang province), and found values between –2.2 ‰ and +1.8 ‰. The δ^{30}Si values differed from place to place and also within a single bamboo plant. The ^{30}Si concentration increases from the main stem to the leaves. Rice plants from Hunan and Jiangsu provinces had δ^{30}Si values between –1.0 ‰ and +1.8 ‰ (Ding and others, 1996).

De La Rocha and others (1998) found that δ^{30}Si of diatoms varied by about 1 ‰ in the Southern Ocean over the last glacial cycle. They attribute the observed δ^{30}Si variations to greater production of opal by diatoms during the interglacials resulting in an increase in the ^{30}Si content of the thus further depleted finite-sized pool of dissolved silica in surface waters of the Southern Ocean. De La Rocha and others (1997) demonstrated that the δ^{30}Si variations in the diatoms were not caused by variation in temperature of formation.

Elemental silicon Three elemental silicon samples were analyzed for isotopic composition for this report. They included NIST SRM 990, IRMM-017, and a high purity silicon disk donated by Dominion Semiconductor, Manassas, Virginia; the δ^{30}Si were –1.3 ‰, +0.5 ‰, and –0.6 ‰, respectively (T. Ding, unpublished data).

Sulfur A_r(S) = 32.065(5)

The average concentration of sulfur in the Earth's crust is 340 mg/kg (Greenwood and Earnshaw, 1997); it is the sixteenth element in order of crustal abundance. Important commercial sources of sulfur include elemental sulfur in salt domes in the United States and Mexico, evaporite deposits in southeastern Poland, H_2S in natural gas and crude oil, and pyrite (FeS_2) and other metal-sulfide ores (Greenwood and Earnshaw, 1997). Sulfur commonly is converted into sulfuric acid and then into numerous other compounds for commercial use.

Reference materials and reporting of isotope ratios

Although sulfur has 4 stable isotopes (table 23) ranging from ^{32}S to ^{36}S, the $n(^{34}\mathrm{S})/n(^{32}\mathrm{S})$ isotope-abundance ratios typically are measured in relative isotope-ratio work because these are the 2 most abundant isotopes. The historical reference material for relative isotope-ratio measurements of sulfur isotopes, CDT troilite (FeS) from the Cañon Diablo meteorite, varies in δ^{34}S by as much as 0.4 ‰ (Beaudoin and others, 1994). Consequently, an advisory committee of the IAEA recommended in 1993 that the Ag_2S reference material IAEA-S-1 (previously known as NZ-1) be assigned a δ^{34}S value of –0.3 ‰ exactly, thereby establishing a VCDT scale (Vienna CDT, the new primary reference for sulfur isotope ratios having a δ^{34}S value of 0 ‰). This recommendation was adopted by IUPAC in 1995 (Krouse and Coplen, 1997). The absolute sulfur

Table 23. *Sulfur isotopic composition of a material with $\delta^{34}S$ = 0 relative to VCDT*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{32}S	31.972 070 73(15)	0.950 3957(90)
^{33}S	32.971 458 54(15)	0.007 4865(12)
^{34}S	33.967 866 87(14)	0.041 9719(87)
^{36}S	35.967 080 88(25)	0.000 1459(21)

[A] From Audi and Wapstra (1993).

[B] From Ding and others (2001).

Table 24. *Sulfur isotopic composition of selected sulfur-bearing isotopic reference materials*

[Values for $\delta^{34}S$ given in per mill relative to VCDT (Krouse and Coplen, 1997)]

Reference Material	Substance	$\delta^{34}S$	Reference
IAEA-S-1 (NZ1)	Ag_2S	–0.3 (exactly)	Gonfiantini and others, 1995
IAEA-S-2 (NZ2)	Ag_2S	+22.67 ± 0.15	T. Ding, unpublished data
IAEA-S-3	Ag_2S	–32.55 ± 0.12	T. Ding, unpublished data
Soufre de Lacq	S	+16.90 ± 0.15	H.P. Qi, U.S. Geological Survey, written communication, 2002
NBS 123	ZnS (sphalerite)	+17.44	Zhang and Ding, 1989
NBS 127	$BaSO_4$	+21.1	T. B. Coplen, unpublished data
IAEA-SO-5	$BaSO_4$	+0.49 ± 0.11	T. Ding, unpublished data
IAEA-SO-6	$BaSO_4$	–34.05 ± 0.08	T. Ding, unpublished data

isotope abundances of IAEA-S-1 and VCDT have been determined (Ding and others, 2001) and the abundances of VCDT are listed in table 23.

Table 24 lists three silver sulfides, an elemental sulfur, a zinc sulfide, and three barium sulfates used as reference materials. These internationally distributed secondary sulfur-bearing reference materials are distributed by IAEA and (or) NIST for environmental and hydrological studies. Some of the values in table 24 are new values measured during this study by T. Ding (unpublished data), T. B. Coplen (unpublished data), and H.P. Qi (U.S. Geological Survey, written communication, 2001).

Of the elements on which numerous isotopic measurements have been completed (hydrogen, carbon, nitrogen, oxygen, and sulfur), sulfur is perhaps the most analytically challenging. Sulfur isotope ratios usually are determined on SO_2 using electron impact ionization mass spectrometry and commonly are measured with a 1-σ standard deviation of ±0.2 ‰. However, measurements of sulfur isotopic reference materials by different laboratories, typically analyzing SO_2 gas, display unacceptably wide variation. Some of this difficulty may be caused by memory effects in sample preparation and in isotope-ratio analysis, or by incorrectly accounting for the oxygen isotopic composition of the SO_2 analyzed. To minimize these effects, T. Ding has analyzed sulfur isotopic reference materials (table 24) by converting sulfur into SF_6 instead of SO_2, following the strategy of Rees (1978). Results indicate that the SF_6 sulfur isotope scale is expanded. For example, whereas NBS 127 $BaSO_4$ was reported by Hut (1987) to have a $\delta^{34}S$ value of +20.32 ‰, T. B. Coplen (unpublished data) finds a value of +21.1 ‰. On a scale in which IAEA-S-1 is assigned $\delta^{34}S$ = –0.3 ‰ and IAEA-S-2 has $\delta^{34}S$ = +22.67 ‰, the value of Soufre de Lacq elemental sulfur measured by continuous flow isotope-ratio mass spectrometry is +16.90 ± 0.15 ‰ (H. P. Qi, U.S. Geological Survey, written communication, 2002), more positive than the value of +16.2 ‰ reported by Carmody and Seal (1999).

Ranges in Isotopic Composition

The valence of sulfur is –2 to +6 in naturally occurring materials. Inorganic sulfur compounds with intermediate valence states (sulfite, thiosulfate, polythionates, and others) tend to be found in nature as transitory intermediates during redox reactions and are thus not readily recoverable. These intermediate species, such as SO_3^-, tend to have low concentrations and short lifetimes in natural low temperature geological and hydrologic systems. In springs in Western Canada, Smejkal and others (1971) found an intermediate believed to be SO_3^{2-} with $\delta^{34}S$ values lower by 7 ‰ to 12 ‰ than coexisting SO_4^{2-} (~+20 ‰). The $\delta^{34}S$ value of HS^- was typically at least 30 ‰ lower than that of SO_4^{2-} in the same springs. In manufactured compounds, different sulfur moieties (for example, central and ligand sulfur in thiosulfate) may have different $\delta^{34}S$ values.

Farquhar and others (2000) reported mass-independent fractionation effects for $\delta^{32}S$, $\delta^{34}S$, and $\delta^{36}S$ from sulfide and sulfate in rocks older than 2450 Ma, which they attributed to gas-phase atmospheric reactions involving low oxygen partial pressures before 2.450 Ga. Rumble and others (2002) have extended the magnitude of sulfur isotope mass-independent anomalies, and they report values for $\delta^{33}S$ of between –2 ‰ and +7 ‰ in excess of mass-dependent values for black shale with an age of 2.5 Ga.

Sulfates The dissolved sulfate of sea water composes a substantial sulfur reservoir. This dissolved sulfate is uniform both vertically and horizontally with a mean reported $\delta^{34}S$ value of +20.0 ± 0.25 ‰ (Rees and others, 1978; Thode and others, 1961). Given recent comparisons between sulfur dioxide and sulfur hexafluoride as the gas introduced into the isotope-ratio mass spectrometry, this value probably should be about 1 ‰ more positive. It would then agree with the value of +21.1 ‰ for NBS 127 in table 24, which was prepared from dissolved sulfate of sea water. Evidently, either memory effects with sulfur dioxide or inadequate correction for oxygen isotopic composition yields $\delta^{34}S$ values that are closer to zero, effectively "shrinking" the $\delta^{34}S$ scale when sulfur dioxide is analyzed, which is most of the time because sulfur hexafluoride is more difficult to produce.

The dominant mechanism of terrestrial sulfur isotope fractionation is low temperature bacterial sulfate reduction whereby $^{32}SO_4^{2-}$ may react up to 1.07 times faster than $^{34}SO_4^{2-}$ (Weyer and others, 1979). As reduction proceeds, unreacted sulfate and product sulfide that does not mix with earlier produced sulfide can acquire highly positive $\delta^{34}S$ values. Thus, values up to +110 ‰ were found for remnant dissolved sulfate in anaerobic bottom water (trapped sea water) in ice covered stratified lakes in the Canadian Arctic (Jeffries and Krouse, 1984) and in barite concretions (Sakai, 1971; Goldberg and others, 1969), and near +70 ‰ for pyrite in Upper Silesia (Gehlen and Nielsen, 1969) and Paleozoic sedimentary rocks at Ozhezkazgan (Bogdanov and others, 1972). Atmospheric sulfate $\delta^{34}S$ values as low as –32 ‰ are reported by van Everdingen and others (1982) for airborne H_2SO_4, resulting from oxidation of biogenic sulfide. In the literature the highest value found for a material of natural terrestrial origin is +135 ‰ from dissolved sulfate in pore fluids in deep ocean sediments undergoing bacterial reduction off the coast of Washington State, U.S.A. (Rudnicki and others, 2001). The mole fraction of ^{34}S in this sample is 0.0473 and $A_r(S)$ = 32.075. In contrast, secondary sulfate produced by bacterial and chemical oxidation of sulfides, elemental sulfur, and organic sulfur have $\delta^{34}S$ values close to those of the reactant substrates.

In a set of more than 13,000 natural samples, the bulk of the samples containing the oxidized sulfur were found to have $\delta^{34}S$ values between +5 ‰ and +25 ‰, whereas the corresponding range for reduced sulfur was –5 ‰ to +15 ‰ (Nielsen, 1991). Although the total variation in terrestrial $\delta^{34}S$ values extends from –55 ‰ to +135 ‰, most commercial sulfur comes ultimately from 2 reservoirs: lower crustal sulfide (mean = ~+2 ‰) and oceanic sulfate (variable over geological time from +10 ‰ to +25 ‰). Some 40 laboratory reagents were found to have $\delta^{34}S$ values ranging from –4 ‰ to +26 ‰, with a peak in the distribution near 0 ‰ (H. R. Krouse, unpublished data). Unfortunately, a working list with manufacturer and catalog number could prove misleading because barium sulfate from the same manufacturer and catalog number was found to have $\delta^{34}S$ values of –2.7 ‰ and +11.5 ‰ when purchased

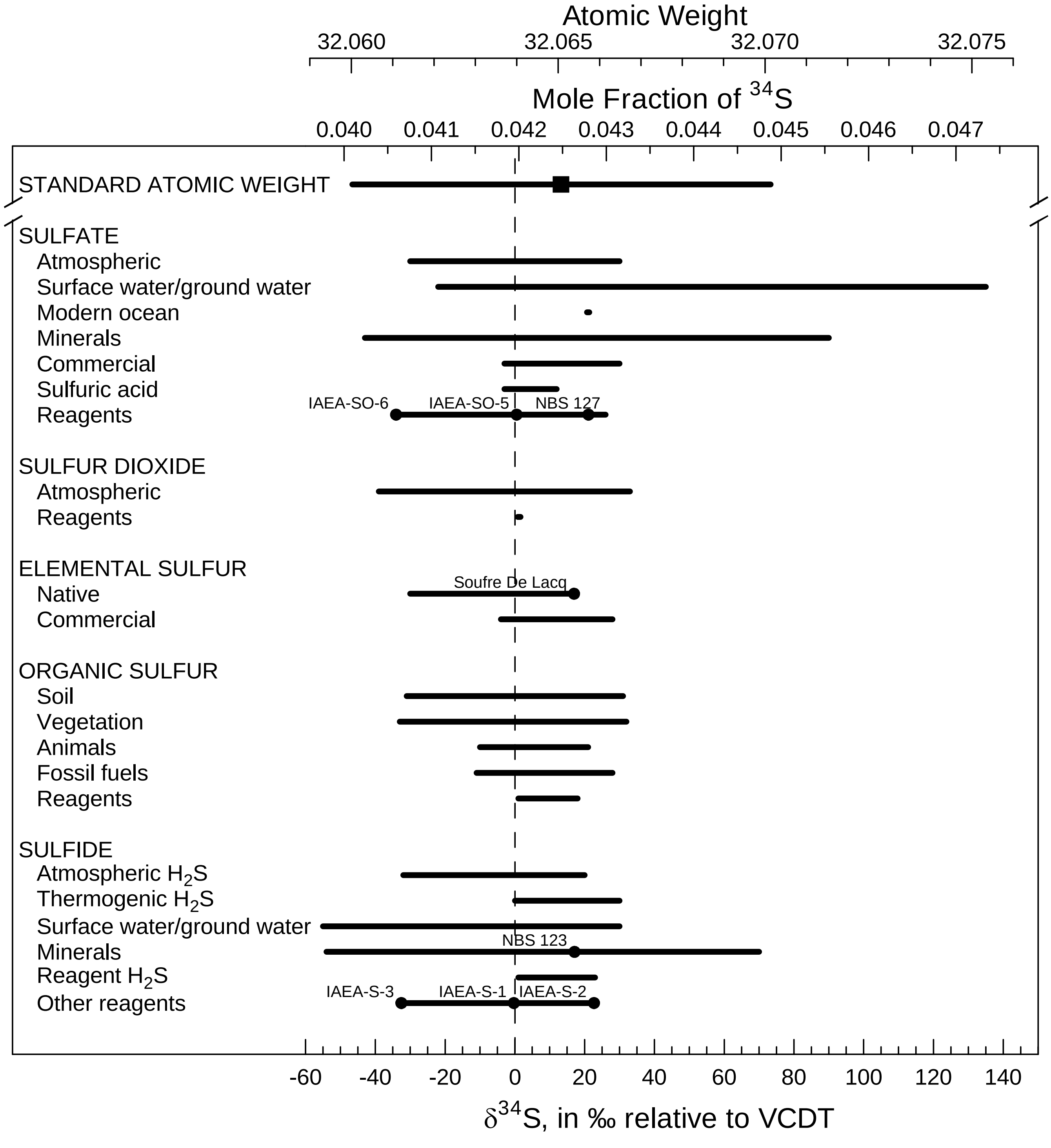

Figure 9. Sulfur isotopic composition and atomic weight of selected sulfur-bearing materials. The δ^{34}S scale and ^{34}S mole-fraction scale were matched using the data in table 23; therefore, the uncertainty in placement of the atomic-weight scale and the ^{34}S mole-fraction scale relative to the δ^{34}S scale is equivalent to ±0.2 ‰.

in 1973 and 1985, respectively.

Sulfur dioxide Sulfur dioxide produced from sour (H_2S rich) gas processing is relatively enriched in ^{34}S (Krouse and Grinenko, 1991). Monitoring of the δ^{34}S of atmospheric sulfur dioxide near a sour gas (H_2S) plant in Crossfield, Alberta, yielded values from +4 ‰ to +28 ‰ (Krouse, 1980), the former corresponding to natural background and the latter downwind of emissions. However, sulfur dioxide from oxidation of biogenic hydrogen sulfide also can be extremely depleted in ^{34}S. Van Everdingen and others (1982) report $\delta^{34}S$ values of –38.5 ‰ to –26.5 ‰ for sulfur dioxide from oxidation of biogenic hydrogen sulfide in Northwest Territories, Canada.

Elemental sulfur Elemental sulfur and many chemical compounds produced from sour gas are relatively enriched in ^{34}S (Krouse and Grinenko, 1991). Elemental sulfur produced by bacterial oxidation tends to have nearly the same sulfur isotopic composition as reactant sulfide. Thode and others (1960) found $\delta^{34}S$ values of elemental sulfur in northeast Venezuela ranging between –0.3 ‰ and +17.9 ‰. In New Zealand geothermal areas, Rafter and others (1960) found $\delta^{34}S$ values of elemental sulfur between –12 ‰ and +3 ‰.

Organic sulfur Assimilation of sulfate by bacteria and plants produces organic sulfur with $\delta^{34}S$ values similar to the sulfate nutrient (Krouse and Grinenko, 1991), and variation in sulfur isotopic composition can be large. For example, natural allyl isothiocyanate (mustard oil) ranges in $\delta^{34}S$ between –17.1 ‰ and +12.4 ‰ (Remaud and others, 1997). Different forms of sulfur produced by thermochemical reactions of sulfur compounds, particularly S^0 with organic matter, can differ by several per mill in $\delta^{34}S$ (Krouse and others, 1987b).

Sulfides Very negative $\delta^{34}S$ values were reported for biogenic hydrogen sulfide and metal sulfides in environments where the fraction of sulfate reduction was small, for example –50 ‰ for biogenic bisulfide in spring waters and boreholes (Weyer and others, 1979), pyrite in some Deep Sea Drilling Project sediment cores (Krouse and others, 1977), pyrite concretions in sedimentary rocks (Bogdanov and others, 1972), and hydrotroilite in river sediments (Veselovsky and others, 1969). The most negative $\delta^{34}S$ value (–55 ‰) of a naturally occurring terrestrial material was measured on dissolved bisulfide from under ice cover in a sewage treatment lagoon by H.R. Krouse (unpublished data). The mole fraction of ^{34}S in this sample is 0.0398 and $A_r(S) = 32.059$. Thermogenic H_2S in sour gas fields tends to have $\delta^{34}S$ values ranging from +15 ‰ to +30 ‰ because of its derivation from marine evaporitic sulfate.

Chlorine $A_r(Cl) = 35.453(2)$

Chlorine is the twentieth most abundant element in the Earth's crust. The chloride in ocean water is an immense chlorine reserve. Large evaporite deposits of halite (NaCl) and other chlorides can be found. The primary uses of chlorine are in reagents including organic compounds (vinyl chloride and propylene oxide), bleaches, and numerous inorganic compounds (HCl, and others).

Reference materials and reporting of isotope ratios

Most relative abundance measurements of Cl isotopes have been expressed relative to sea water chloride (SMOC or Standard Mean Ocean Chloride), which was thought to be homogeneous in $\delta^{37}Cl$ to within approximately ±0.15 ‰ (Kaufmann and others, 1988). One chorine isotopic reference material, NIST SRM 975 sodium chloride, is the basis of the absolute isotope-abundance determination of chlorine (Shields and others, 1962). Using a $\delta^{37}Cl$ value of +0.43 ‰ for SRM 975 relative to sea water chloride (Xiao and others, 2002b), one can calculate the absolute isotope abundances of sea water chloride (table 25). Because the supply of SRM 975 is exhausted, it has been replaced by SRM 975a (NIST, 2001), which is depleted in ^{37}Cl relative to SRM 975 by 0.23 ‰ (table 25).

Xiao and others (2002a) report $\delta^{37}Cl$ values as high as +0.94 ‰ for sea water from the Central Indian Ridge. Their results indicate that SMOC should be defined in terms of an internationally distributed homogeneous chlorine isotopic reference material and not random samples of sea water. Xiao and others (2002b) have purified a large sample of sodium chloride from sea water for distribution as a new chlorine isotopic reference material, named ISL 354 (table 26). It has a $\delta^{37}Cl$ value of $+0.05 \pm 0.02$ ‰ relative to sea water chloride (Xiao and others, 2002b) and has been sent to IAEA for international distribution.

Ranges in Isotopic Composition

Cl has a single oxidation state in most naturally occurring materials and a relatively small mass difference between its isotopes as compared to hydrogen, carbon, nitrogen, and oxygen. Thus, the range in $\delta^{37}Cl$ in natural materials is about 12 ‰ (table 27 and figure 10), much smaller than the isotopic variation of nitrogen or sulfur. Discussions of chlorine isotopic variations and isotope-fractionation mechanisms include Fuge (1974), Desaulniers and others (1986), Kaufmann and others (1993), and Eggenkamp (1994). The data reported by Vengosh and others (1989) are not used in this report because many of the values are anomalous. Vengosh and others used negative thermal ionization mass spectrometry without prior chemical preparation of the samples.

Table 25. *Chlorine isotopic composition of a material with $\delta^{37}Cl = 0$ relative to SMOC*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{35}Cl	34.968 852 71(4)	0.757 79(46)
^{37}Cl	36.965 902 60(5)	0.242 21(46)

[A] From Audi and Wapstra (1993).

[B] Calculated from Xiao and others (2002b), Shields and others (1962), and Rosman and Taylor (1998).

Table 26. *Chlorine isotopic composition of selected chlorine-bearing isotopic reference materials*

[Values given in per mill relative to SMOC]

Reference Material	Substance	$\delta^{37}Cl$	Reference
SRM 975	NaCl	+0.43 ± 0.04	Xiao and others, 2002b
SRM 975a	NaCl	+0.2 ± 1.5	NIST, 2001
ISL 354	NaCl	+0.05 ± 0.02	Xiao and others, 2002b

Chlorides Until recently, it was thought that ocean water was homogeneous in chlorine isotopic composition. The maximum range in δ^{37}Cl was –0.15 ‰ to +0.11 ‰ (Kaufmann and others, 1988). However, as pointed out above, Xiao and others (2002a) find that some sea water is substantially enriched in ^{37}Cl. They report δ^{37}Cl values of +0.59 ‰, +0.82 ‰, and +0.94 ‰ for sea water from three locations at the Central Indian Ridge.

Evaporites, such as halite (NaCl), kainite [$K_4Mg_4Cl_4(SO_4)_4{\cdot}4H_2O$], carnallite ($KMgCl_3{\cdot}H_2O$), and bischofite ($MgCl_2{\cdot}6H_2O$) are derived from evaporating ocean water and are slightly enriched in ^{37}Cl relative to ocean water from which they precipitated (Kaufmann and others, 1984; Eggenkamp and others, 1995). The δ^{37}Cl of hydrothermal ore deposit fluids is near 0 ‰; Eastoe and others (1989) found δ^{37}Cl of fluid inclusions from Mississippi Valley-type deposits in Tennessee to range between –1.1 ‰ and +0.8 ‰, and attributed isotope fractionation in hydrothermal fluids to high temperature equilibrium isotope exchange.

The chlorine content of oceanic crustal rocks is low, but chlorine isotopic composition has been measured in Costa Rica Rift ocean drill holes using positive thermal ionization mass spectrometry (Magenheim and others, 1995). Glasses range in δ^{37}Cl from +0.2 ‰ to +7.2 ‰, amphibole-bearing whole rocks range from +0.4 ‰ to +3.4 ‰, and smectite veins range from +4.0 ‰ to +7.5 ‰. The value of +7.5 ‰ is the most positive found in the literature for a material of natural terrestrial origin. For this sample the mole fraction of ^{37}Cl is 0.243 56 and A_r(Cl) = 35.4553. Magenheim and others (1995) conclude that Cl isotopes of smectite and amphibole samples are fractionated when sea water ^{37}Cl is preferentially incorporated into altered oceanic crust because of the stronger bond of ^{37}Cl. They conclude that the δ^{37}Cl of the source of chlorine in crustal rocks ranges between +3.0 ‰ and +7.2 ‰.

Chloride in ground waters is derived from a variety of sources including upwelling of brines from lower formations, road salt, and weathering of rock. Desaulniers and others (1986) point out that at low temperatures dissolved chloride in ground water usually is not affected by geochemical reactions with sediments or by biological processes. Thus, diffusion of chloride waters, which should affect the ^{37}Cl and ^{35}Cl distribution when ground-water flow is slow (because the diffusion coefficient of ^{37}Cl is smaller

Table 27. *Chlorine isotopic composition of selected chlorine-bearing materials*

[Values for δ^{37}Cl given in per mill relative to SMOC (Standard Mean Ocean Chloride)]

	Minimum δ^{37}Cl Value		Maximum δ^{37}Cl Value	
Substance	**δ^{37}Cl**	**Reference**	**δ^{37}Cl**	**Reference**
CHLORIDES				
Sea water	–0.15	Kaufmann and others, 1988	+0.94	Xiao and others, 2002a
Ground, surface, pore, and oil formation waters	–7.7	Ransom and others, 1995	+2.94	Liu and others, 1997
Hydrothermal fluid-inclusion water	–1.1	Kaufmann and Arnórsson, 1986	+0.8	Kaufmann and Arnórsson, 1986
NaCl (halite)	–0.2	Long and others, 1993	+0.7	Kaufmann and others, 1984
KCl (sylvite)	–0.5	Hoering and Parker, 1961	+0.3	Hoering and Parker, 1961
Rock or sediments	+0.2	Magenheim and others, 1995	+7.5	Magenheim and others, 1995
ORGANIC SOLVENTS				
CH_3Cl	–6.0	Tanaka and Rye, 1991	+4.0	Jendrzejewski and others, 2001
Other (trichloroethylene, and others)	–2.5	Aravena and others, 1996	+4.4	Aravena and others, 1996

than that of ^{35}Cl), should be measurable. In a study of ground waters in Quaternary glacial deposits of southwestern Ontario, Canada, samples from 2 sites ranged in δ^{37}Cl from –0.8 ‰ to +2.2 ‰ and correlated with chloride concentration. Desaulniers and others (1986) concluded that the isotopic enrichment in ^{35}Cl down gradient resulted from upward diffusion of saline formation waters over a period of about 15,000 years. Although Canadian Shield ground waters vary in δ^{37}Cl value between –0.51 ‰ and +0.17 ‰ (Frape and others, 1995), the range of Fennoscandian ground waters is much greater, –0.61 ‰ to +1.97 ‰ (Frape and others, 1995). The highest δ^{37}Cl value (+2.94 ‰) is reported for a hot-spring water (oil-field water) from Daqaidam in the Qaidam Basin, China (Liu and others, 1997). Large δ^{37}Cl variations (–4.3 ‰ to –1.2 ‰) are observed in oil formation waters from the North Sea Forties Field (Eggenkamp and Coleman, 1993; Eggenkamp, 1994). The concentrated brine of the basin center probably was overpressured and its very negative δ^{37}Cl values resulted either from ultrafiltration or diffusion during cross-formational flow (Eggenkamp, 1994). Pore water from the Nankai subduction zone has the lowest δ^{37}Cl value (–7.7 ‰) found in the literature for a material of natural terrestrial origin (Ransom and others, 1995). The mole fraction of ^{37}Cl in this sample is 0.240 77 and A_r(Cl) = 35.4497. This low value is attributed to formation of clays that preferentially incorporate ^{37}Cl into their structure, enriching pore water in ^{35}Cl.

Organic solvents Aravena and others (1996) and van Warmerdam and others (1995) analyzed chlorinated solvents including perchloroethylene (PCE), trichloroethylene (TCE), and 1,1,1 trichloroethane (TCA), supplied by different manufacturers and found a range in δ^{37}Cl of –2.5 ‰ to +4.4 ‰. Both noted that ^{37}Cl content was dependent upon manufacturing process. Each solvent analyzed had a δ^{37}Cl value that differed

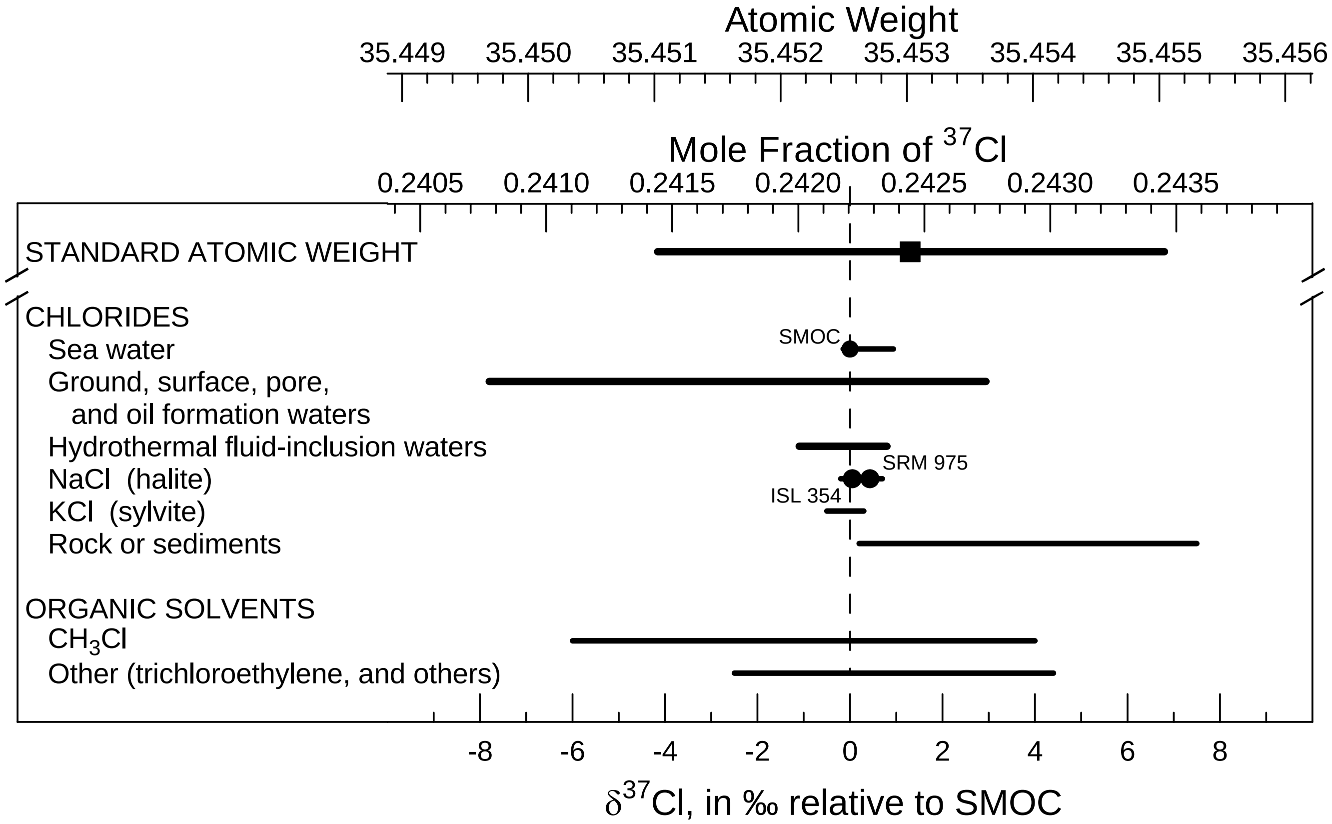

Figure 10. Chlorine isotopic composition and atomic weight of selected chlorine-bearing materials. The δ^{37}Cl scale and the ^{37}Cl mole-fraction scale were matched using the data in table 25; therefore, the uncertainty in placement of the atomic-weight scale and the ^{37}Cl mole-fraction scale relative to the δ^{37}Cl scale is equivalent to ±2.5 ‰.

between manufacturers. Differences were found in the δ^{13}C values of the solvents. Therefore, it was concluded that δ^{13}C and δ^{37}Cl measurements might be useful for identifying sources of chlorinated solvent plumes in ground water. In 1999, Beneteau and others analyzed PCE, TCE, and TCA from a new solvent batch from PPG Industries and Dow Chemicals to compare δ^{13}C and δ^{37}Cl values with those previously measured. Results indicate that the δ^{13}C and the δ^{37}Cl of TCA do not remain consistent from batch to batch (Beneteau and others, 1999). However, there is a consistent and substantial δ^{37}Cl difference between PCE from PPG Industries and DOW Chemicals that could allow the use of δ^{13}C data in conjunction with δ^{37}Cl values for fingerprinting applications. Jendrzejewski and others (2001) analyzed chlorinated hydrocarbons for carbon and chlorine isotopic content and came to the same conclusion. Chlorinated solvents increasingly are being found in ground waters and it should not be surprising if the extreme values in table 27 are exceeded in the future. The δ^{37}Cl of commercial methyl chloride ranges from –6.0 ‰ (Tanaka and Rye, 1991) to +4.0 ‰ (Jendrzejewski and others, 2001).

Calcium A_r(Ca) = 40.078(4)

Calcium is the fifth most abundant element in the Earth's crust. Pure calcium is prepared by electrolysis of fused $CaCl_2$. Elemental calcium is used in alloys, especially with aluminum, and it is used in the purification of chromium, zirconium, thorium, uranium, and rare earth elements. Calcium is used as a chemical scavenger in the steel industry to remove oxygen, sulfur, and phosphorus.

Reference materials and reporting of isotope ratios

Because the two isotopes ^{40}Ca and ^{44}Ca are the most abundant of calcium's six isotopes (table 28), $n(^{44}\text{Ca})/n(^{40}\text{Ca})$ isotope-abundance ratios have been measured and expressed as δ^{44}Ca values relative to a

Table 28. *Calcium isotopic composition of NIST SRM 915a calcium carbonate*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{40}Ca	39.962 5912(3)	0.969 41(6)
^{42}Ca	41.958 6183(4)	0.006 47(3)
^{43}Ca	42.958 7668(5)	0.001 35(2)
^{44}Ca	43.955 4811(9)	0.020 86(4)
^{46}Ca	45.953 6927(25)	0.000 04(1)
^{48}Ca	47.952 533(4)	0.001 87(1)

[A] From Audi and Wapstra (1993).

[B] Calculated from Moore and Machlan (1972) and the determination by D. J. DePaolo (University of California, Berkeley, California, written communication, 2001) that NBS 915a is depleted in ^{44}Ca relative to NBS 915 by 0.17 ‰.

variety of materials, depending upon the author. The Berkeley Center for Isotope Geochemistry (Berkeley, California) reports δ^{44}Ca values relative to a high purity calcium carbonate laboratory reference material (Skulan and others, 1997). Scripps Institution of Oceanography (San Diego, California) reports δ^{44}Ca values relative to sea water (Zhu and Macdougall, 1998). The University of Oxford expresses δ^{44}Ca values relative to NBS 915a calcium carbonate (Halicz and others, 1999). Russell and others (1978) reported $n(^{40}\mathrm{Ca})/n(^{44}\mathrm{Ca})$ isotope-ratio measurements relative to reagent calcium fluoride. $n(^{44}\mathrm{Ca})/n(^{40}\mathrm{Ca})$ isotope-ratio measurements can be performed using positive ion thermal ionization mass spectrometry. $n(^{44}\mathrm{Ca})/n(^{42}\mathrm{Ca})$ isotope ratios have been determined with multiple collector inductively coupled plasma mass spectrometry (Halicz and others, 1999) and isotope ratios can be determined with a 1-σ standard deviation of ±0.1 ‰.

The absolute isotope abundances of SRM 915 calcium carbonate were determined by Moore and Machlan (1972). Although SRM 915 is no longer distributed by NIST, D. J. DePaolo (University of California, Berkeley, California, written communication, 2001) has measured the δ^{44}Ca of SRM 915 and of SRM 915a, which has replaced it. Based on 2 mass spectrometric analyses, the δ^{44}Ca of SRM 915 is –0.80 ± 0.23 ‰ relative to the Berkeley calcium carbonate. The value for SRM 915a is –0.97 ± 0.20 ‰ also based on 2 analyses. Values of δ^{44}Ca are expressed relative to SRM 915a in this report because SRM 915a is an internationally distributed reference material. The absolute calcium isotope abundances of SRM 915a are given in table 28.

Ranges in Isotopic Composition

Calcium is found in naturally occurring materials only in the +2 valence state. Consequently, the range in calcium isotopic composition found in the literature is less than 5 ‰ (table 29 and figure 11). Whereas laboratories have expressed their calcium isotope ratios relative to different materials, δ^{44}Ca values are reported relative to the NIST SRM 915a scale in this report. The Berkeley δ^{44}Ca data are adjusted in this report by adding +0.97 ‰. The Scripps data are adjusted in this report by adding +1.89 ‰ because the δ^{44}Ca of Scripps sea water, which is used as their reference zero value, is +0.92 ‰ relative to the Berkeley calcium carbonate reference material (Skulan and others, 1997). It is not completely clear how to adjust the $n(^{40}\mathrm{Ca})/n(^{44}\mathrm{Ca})$ isotope-ratio measurements of Russell and others (1978) because their measurement of sea water suggests an adjustment of between 0.77 ‰ and 1 ‰, whereas their analysis of an Atlantic Ridge tholeiite suggests an adjustment of 0.67 ‰. We have compromised and adjusted their values upward by 0.8 ‰.

Igneous rocks The δ^{44}Ca values of igneous rocks fall in a small range (+0.7 ‰ to +1.35 ‰) based on measurements by Skulan and others (1997), who analyzed basalts, dacites, and a rhyolite, and based on measurements by Zhu and Macdougall

Table 29. *Calcium isotopic composition of selected calcium-bearing materials*

[Values for δ^{44}Ca given in per mill relative to SRM 915a calcium carbonate]

	Minimum δ^{44}Ca Value		Maximum δ^{44}Ca Value	
Substance	**δ^{44}Ca**	**Reference**	**δ^{44}Ca**	**Reference**
IGNEOUS ROCKS	+0.70	Skulan and others, 1997	+1.35	Zhu and Macdougall, 1998
DISSOLVED CALCIUM				
Sea water	+1.7	Russell and others, 1978	+2.00	De La Rocha and DePaolo, 2000
Rivers	–0.18	Zhu and Macdougall, 1998	+1.26	Zhu and Macdougall, 1998
CARBONATES				
Foraminifera, marine ooze, and calcium carbonate	–0.75	Zhu and Macdougall, 1998	+2.7	Russell and others, 1978
Reagent calcium carbonate	–12	Russell and others, 1978	+0.97	Skulan and others, 1997
PLANTS AND ANIMALS	–2.17	Skulan and DePaolo, 1999	+2.76	Skulan and DePaolo, 1999
ELEMENTAL CALCIUM	–6.0	Russell and others, 1978	–6.0	Russell and others, 1978

(1998) of three mid-ocean ridge basalt (MORB) samples. This range may be too large because of analytical difficulties as other evidence indicates that igneous rocks should be relatively homogeneous in calcium isotopic composition (Zhu and Macdougall, 1998). The δ^{44}Ca values of three MORB samples ranged between +1.20 ‰ and +1.35 ‰ (Zhu and Macdougall, 1998).

Carbonates Based on calcium isotope-ratio measurements by Russell and others (1978), Zhu and Macdougall (1998), De La Rocha and DePaolo (2000), and D. J. DePaolo (University of California, Berkeley, California, written communication, 2001), the δ^{44}Ca of dissolved carbonate in sea water is relatively uniform and ranges from +1.77 ‰ to +2.00 ‰. Biologically induced calcium isotope fractionation in the fixation of calcium affects the distribution of calcium isotopes in the terrestrial calcium cycle. As dissolved calcium in sea water is incorporated into foraminifera, ^{40}Ca is preferentially fixed, increasing the δ^{44}Ca of sea water. Thus, the δ^{44}Ca of most biological samples is lower than that of sea water. Nägler and others (2000) grew the foraminifera species *G. sacculifer* in sea water at constant temperature and determined a variation in δ^{44}Ca with temperature of 0.24 ± 0.02 ‰ per ºC; thus, calcium isotope-abundance variation is potentially a new tool for determining past sea surface temperatures. The highest ^{44}Ca content (δ^{44}Ca = +2.7 ‰) found in calcium carbonate is found in thinolite (Russell and others, 1978), a calcium carbonate tufa deposit in northwest Nevada.

Russell and others (1978) analyzed the calcium isotopic composition of reagent carbonates and found a range from –12 ‰ to +1.5 ‰. The sample with a δ^{44}Ca value of –12 ‰ was prepared from elemental calcium metal, which involves an evaporation-distillation process.

Plants and animals In a survey of numerous materials, Skulan and DePaolo (1999) found that calcium from bone and shell is depleted in ^{44}Ca relative to calcium of soft tissue from the same organism and relative to source (dietary) calcium. Platzner and Degani (1990) found that the δ^{44}Ca

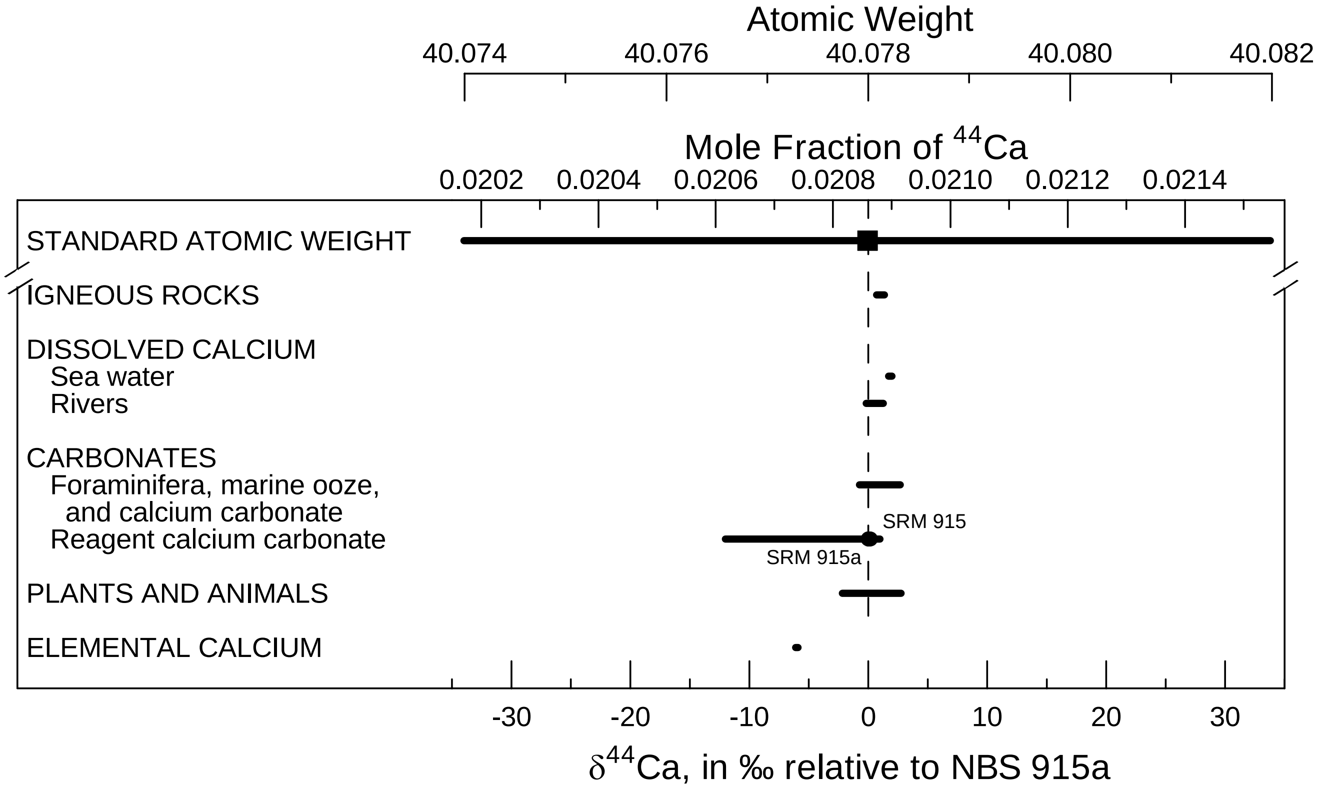

Figure 11. Calcium isotopic composition and atomic weight of selected calcium-bearing materials. The δ^{44}Ca scale and the ^{44}Ca mole-fraction scale were matched using the data in table 28; therefore, the uncertainty in placement of the atomic-weight scale and the ^{44}Ca mole-fraction scale relative to the δ^{44}Ca scale is equivalent to ±2 ‰.

values of pollen and seeds of date palm trees were about 0.6 ‰ more negative than those of leaves and pulp of these trees. Bullen (U.S. Geological Survey, written communication, 2002) finds that δ^{44}Ca values of spruce tree samples range between –1.0 ‰ and +1.36 ‰. The lowest δ^{44}Ca value of a naturally occurring terrestrial material (–2.17 ‰) is found in cougar bone (Skulan and DePaolo, 1999). The mole fraction of ^{44}Ca in this sample is 0.020 82 and A_{r}(Ca) = 40.0778. The highest δ^{44}Ca value (+2.76 ‰) in a material of natural terrestrial origin is found in egg white (Skulan and DePaolo, 1999). The mole fraction of ^{44}Ca in this sample is 0.020 92 and A_{r}(Ca) = 40.0784.

Elemental calcium Russell and others (1978) report a δ^{44}Ca value of –6.0 ‰ for a sample of elemental calcium metal. They point out that one method for the preparation of elemental calcium involves an evaporation-distillation process, which causes substantial fractionation of calcium isotopes.

Chromium A_{r}(Cr) = 51.9961(6)

The average concentration of chromium in the Earth's crust is 122 mg/kg (Greenwood and Earnshaw, 1997). The primary ore of chromium is chromite ($FeCr_2O_4$). The principal uses of chromium are in the production of non-ferrous alloys and anti-corrosion chromium plating.

Reference materials and reporting of isotope ratios

Because the isotopes ^{52}Cr and ^{53}Cr are the most abundant chromium isotopes (table 30), $n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$ ratios usually are measured and expressed as δ^{53}Cr values relative to NIST SRM 979 chromium nitrate. $n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$ isotope-ratio measurements can be performed using positive ion thermal ionization mass spectrometry, and isotope ratios can be determined with a 1-σ standard deviation of approximately ±0.1 ‰. The absolute isotope abundances of chromium in SRM 979 chromium nitrate was measured by Shields and others (1966) and is listed in table 30.

Table 30. *Chromium isotopic composition of NIST SRM 979 chromium nitrate*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{50}Cr	49.946 0495(14)	0.043 452(85)
^{52}Cr	51.940 5115(15)	0.837 895(117)
^{53}Cr	52.940 6534(15)	0.095 006(110)
^{54}Cr	53.938 8846(15)	0.023 647(48)

[A] From Audi and Wapstra (1993).
[B] From Rosman and Taylor (1998) and Shields and others (1966).

Table 31. *Chromium isotopic composition of selected chromium-bearing materials*

[Values for δ^{53}Cr given in per mill relative to SRM 979 chromium nitrate]

	Minimum δ^{53}Cr Value		Maximum δ^{53}Cr Value	
Substance	δ^{53}Cr	Reference	δ^{53}Cr	Reference
CHROMIUM (VI)				
$K_2Cr_2O_7$	+0.16	Ellis and others, 2002	+0.56	Ellis and others, 2002
Ground water	+1.1	Ellis and others, 2002	+5.8	Ellis and others, 2002
CHROMIUM (III)				
$Cr(NO_3)_3$	0.0 ± 0.2	Ellis and others, 2002	0.0 ± 0.2	Ellis and others, 2002

Ranges in Isotopic Composition

Chromium is expected to show isotope fractionation because there is substantial relative mass difference between its four isotopes (table 30) and because it is found in both +6 and +3 oxidation states in the lithosphere. Relatively few chromium isotopic measurements have been performed. Previous work by Ball (1996) is not included in this report because there may have been analytical problems during isotopic measurements (T. Bullen, U.S. Geological Survey, oral communication, 2001). For example, Ball found that the $n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$ isotope-abundance ratio of SRM 979 chromium nitrate changed by 3.3 ‰ by application of his purification methods, suggesting that the sample preparation may not have been quantitative. Other investigators have not observed problems with SRM 979.

The observed isotopic variation of chromium extends outside the limits of the uncertainty of its atomic weight (table 31 and figure 12). In future meetings, CAWIA may want to consider expanding its atomic-weight uncertainty or consider adding a footnote *g* to chromium in the Table of Standard Atomic Weights (Coplen, 2001) to indicate that "geological specimens are known in which the element has an isotopic composition outside the limits for normal material." It is not now assigned a footnote *g*.

Chromium (VI) Reagent $K_2Cr_2O_7$, chromium (VI) plating solution, and chromium (VI) in ground water have been analyzed (Ellis and others, 2002). The δ^{53}Cr of reagent $K_2Cr_2O_7$ and plating solution is near 0 ‰. However, chromium (VI)-contaminated ground water shows a large variation in δ^{53}Cr value (+1.1 ‰ to +5.8 ‰). This large variation is attributed to preferential reaction of ^{52}Cr during chromate reduction with an isotope-fractionation factor of about 3.5 ‰, based on experimental studies (Ellis and others, 2002). Laboratory experiments with autoclaved sediments showed the same reduction rates. Ellis and others

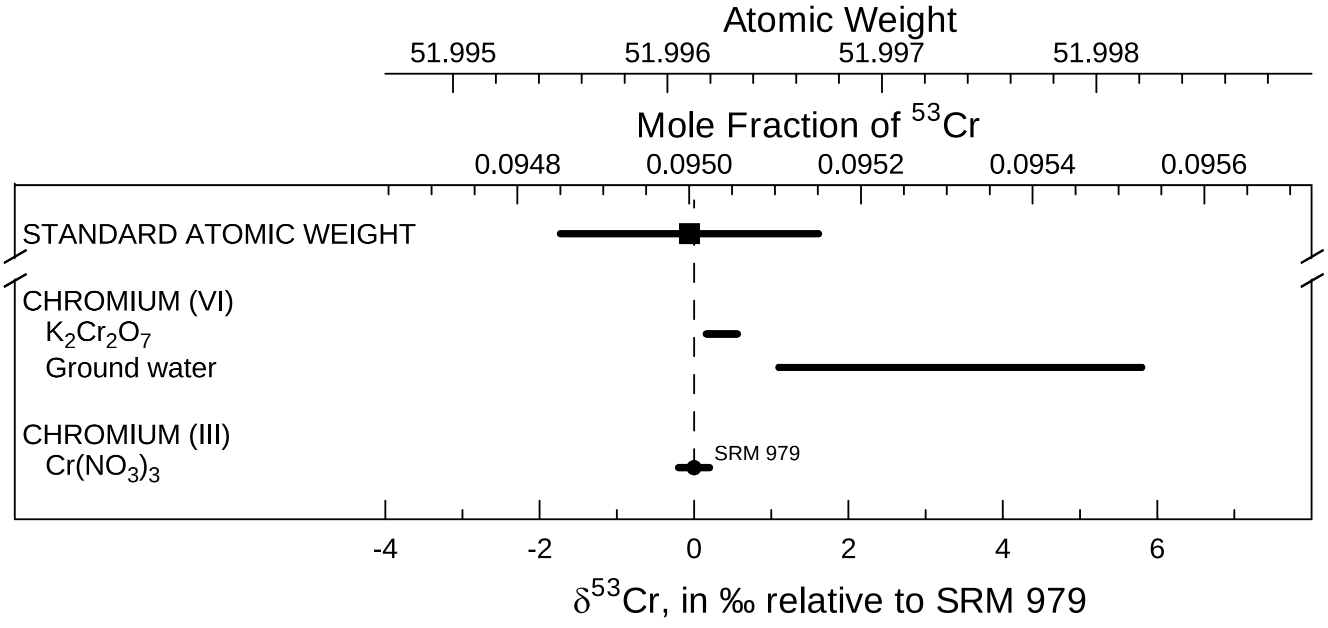

Figure 12. Chromium isotopic composition and atomic weight of selected chromium-bearing materials. The δ^{53}Cr scale and the ^{53}Cr mole-fraction scale were matched using the data in table 30; therefore, the uncertainty in placement of the atomic-weight scale and the ^{53}Cr mole-fraction scale relative to the δ^{53}Cr scale is equivalent to ±1.2 ‰.

(2002) accordingly concluded that abiotic reduction dominates over microbial reduction in their experiments. Rayleigh kinetic fractionation results in δ^{53}Cr values as high as +5.8 ‰ in residual chromium (VI), which represent the naturally occurring terrestrial sample with the highest ^{53}Cr content found in the literature. For this sample the mole fraction of ^{53}Cr is 0.095 53 and A_r(Cr) = 51.9982.

Chromium (III) Numerous analyses of SRM 979 chromium nitrate have been performed (Ellis and others, 2002) using thermal ionization mass spectrometry and a separation procedure that is effective at separating chromium from isobaric interference with iron, vanadium, and titanium. The variation in δ^{53}Cr of SRM 979 is within analytical error (±0.2 ‰), and SRM 979 has the lowest ^{53}Cr content found in the literature. The mole fraction of ^{53}Cr in SRM 979 (δ^{53}Cr = 0 ‰) is 0.095 01 and A_r(Cr) = 51.9961.

Iron (Ferrum) A_r(Fe) = 55.845(2)

After oxygen, silicon, and aluminum, iron is the fourth most abundant element in crustal rocks. The major ores of iron include hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($2Fe_2O_3 \cdot 3H_2O$), and siderite ($FeCO_3$). Its primary use is in steel (with up to 1.7 % carbon) and in stainless steel (with nickel and other metals).

Reference materials and reporting of isotope ratios

Relative iron isotope ratios commonly are based on $n(^{56}\text{Fe})/n(^{54}\text{Fe})$ measurements and can be expressed relative to IRMM-014 elemental iron, which is assigned a δ^{56}Fe value of 0 ‰. $n(^{56}\text{Fe})/n(^{54}\text{Fe})$ isotope-ratio measurements have been performed using thermal ionization mass spectrometry and using multiple collector inductively coupled plasma mass spectrometry; isotope ratios can be determined with a 1-σ standard deviation of ±0.15 ‰. The absolute isotope abundances of IRMM-014 elemental iron are shown in table 32.

Ranges in Isotopic Composition

Iron can act as an electron acceptor under anaerobic conditions and as an electron donor under both anaerobic and aerobic conditions. Thus, there is the potential for kinetic fractionation of iron isotopes during metabolic reactions. A recent summary of isotope abundance variations of iron in natural materials and a discussion of iron isotope fractionation is given in Anbar (2001). Theoretical equilibrium $n(^{56}\text{Fe})/n(^{54}\text{Fe})$ fractionations at 25 °C among iron-

Table 32. *Isotopic composition of IRMM-014 elemental iron*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{54}Fe	53.939 6147(14)	0.058 45(23)
^{56}Fe	55.934 9418(15)	0.917 54(24)
^{57}Fe	56.935 3983(15)	0.021 191(65)
^{58}Fe	57.933 2801(15)	0.002 819(27)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Taylor and others (1992).

Table 33. *Iron isotopic composition of selected iron-bearing materials*

[Values for δ^{56}Fe given in per mill relative to IRMM-014 elemental iron]

	Minimum δ^{56}Fe Value		Maximum δ^{56}Fe Value	
Substance	δ^{56}**Fe**	**Reference**	δ^{56}**Fe**	**Reference**
IGNEOUS ROCKS	–0.8	Berger and von Blanckenburg (2001	+0.15	Beard and Johnson, 1999
SEDIMENTARY ROCKS				
Fe-Mn oxides	–1.62	Beard and others, 1999	+0.17	Beard and Johnson, 1999
Banded iron formations	–0.34	Beard and Johnson, 1999	+1.36	Beard and Johnson, 1999
Fe in dolomite	–2.54	Bau and others, 2001	–0.87	Bau and others, 2001
Fe oxyhydroxide	–2.02	Bullen and others, 2001	+0.11	Bullen and others, 2001
NON-MARINE SOURCES				
Ground water	–2.20	Bullen and others, 2001	–0.74	Bullen and others, 2001
PLANTS AND ANIMALS	–2.9	Walczyk, 2001	–2.5	Walczyk, 2001
ELEMENTAL IRON	–0.04	Zhu and others, 2000b	+0.04	Zhu and others, 2000b

bearing aqueous complexes are as large as 14 ‰ (Schauble and others, 2001).

The variation in isotopic composition of iron-bearing materials is shown in table 33 and figure 13. For comparative purposes, the high purity J-M iron used as a reference material by Beard and Johnson (1999) and Beard and others (1999) is assumed to be identical in isotopic composition to the high purity

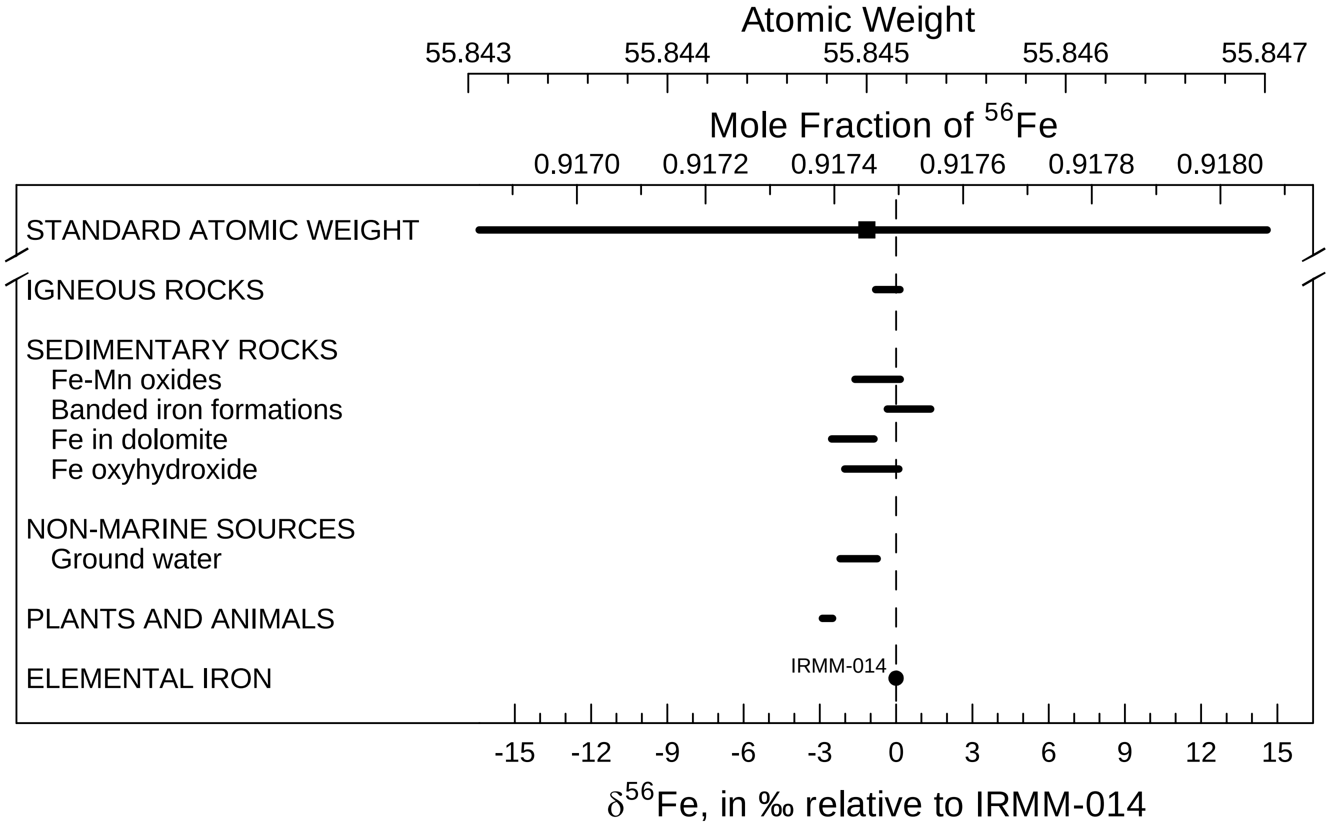

Figure 13. Iron isotopic composition and atomic weight of selected iron-bearing materials. The δ^{56}Fe scale and the ^{56}Fe mole-fraction scale were matched using the data in table 32; therefore, the uncertainty in placement of the atomic-weight scale and the ^{56}Fe mole-fraction scale relative to the δ^{56}Fe scale is equivalent to ±4.3 ‰.

elemental iron reference material IRMM-014 used by other workers; this assumption also was made by Anbar (2001). No isotopic results of Dixon and others (1992) are included in this report because they contain internal inconsistencies among the isotope ratios according to Beard and Johnson (1999).

The *n*(^{57}Fe)/*n*(^{56}Fe) isotope-abundance ratio of ground water from a toxic waste site in South Carolina (USA) (JP-4 fuel spill) in a microbially mediated anaerobic zone was about 0.5 percent greater than *n*(^{57}Fe)/*n*(^{56}Fe) of 0.5N HCl leachates of aquifer sediment and was substantially greater than *n*(^{57}Fe)/*n*(^{56}Fe) of ground water from the upgradient aerobic zone (Bullen and McMahon, 1997). Brantley and others (2001) have shown that iron isotopes are fractionated by as much as 1 ‰ during leaching of hornblende by *Anthrobacter* or *Streptomyces*. Nonbiological fractionation of iron isotopes can also be large. Anbar and others (2000) observed a maximum isotope fractionation of 6 ‰ during elution of iron in HCl media from anion exchange columns. Anbar and others (2000) proposed that this isotope fractionation is an equilibrium isotope fractionation between dissolved $FeCl_4^-$, which is a tetrahedral complex, and Fe chloro-aquo complexes (for example, $FeCl_2(H_2O)_4^+$, which is an octahedral complex). Therefore, differences in bonding energy may explain isotope fractionations.

Igneous rocks Beard and Johnson (1999) and Beard and others (1999) conclude that the iron isotopic variation of igneous rocks is relatively small (δ^{56}Fe < 0.3 ‰). Zhu and others (2001) find that *n*(^{56}Fe)/*n*(^{54}Fe) is lower in olivine than that in coexisting pyroxene by 0.24 ‰. However, Berger and von Blanckenburg (2001) determined that *n*(^{57}Fe)/*n*(^{54}Fe) is lower in magnetite that that in sheet silicates (biotite and chlorite) by as much as 1.2 ‰ in greenschist and upper amphibolite facies rocks.

Sedimentary rocks Zhu and others (2000b) determined the iron isotopic composition of a ferromanganese crust in North Atlantic Deep Water deposited over the past 6 million years and found δ^{56}Fe values between –0.77 ‰ and –0.13 ‰. They found an excellent correlation with lead isotope abundances and concluded that δ^{56}Fe variations reflect changes in iron input from terrigenous sources; they attributed none of the variation to biologically induced mass fractionation. The δ^{56}Fe of oceanic Fe-Mn nodules analyzed by Beard and others (1999) ranged from –1.62 ‰ to –0.96 ‰; those analyzed by Beard and Johnson (1999) ranged between –1.36 ‰ and –0.81 ‰. A freshwater nodule from Green Bay Lake, Michigan was enriched in ^{56}Fe with a δ^{56}Fe value of +0.17 ‰ (Beard and Johnson, 1999). Polizzotto and others (2000) report δ^{56}Fe values of between –1.2 ‰ and –0.7 ‰ for hydrothermal fluids from several locations along the Juan de Fuca Ridge. They propose that iron in basalts is isotopically fractionated during leaching of iron and (or) during precipitation of sulfide minerals, and that this iron may be a source of iron depleted in ^{56}Fe to deep-sea sediments.

Banded iron formations may reflect biogeochemical processes, and they are variable in iron isotopic composition. The δ^{56}Fe of samples from a Proterozoic formation range from –0.34 ‰ for a dark layer to +1.36 ‰ for a light layer (Beard and others, 1999). The sample with a δ^{56}Fe value of +1.36 ‰ has the highest ^{56}Fe content found in the literature for a naturally occurring terrestrial substance. The mole fraction of ^{56}Fe in this sample is 0.917 60 and A_r(Fe) = 55.845 32. An Archean banded iron formation had a much smaller range of δ^{56}Fe values (0 ‰ for a black layer to +0.35 ‰ for a red layer). The iron in dolomite associated with the banded iron formation in the Hamersley Group, Western Australia, is substantially depleted in ^{56}Fe and δ^{56}Fe ranges from –2.54 ‰ to –0.87 ‰ (Bau and others, 2001).

Field (Mount Ruapehu in Tongariro National Park, New Zealand) and laboratory studies by Bullen and others (2001) indicate that the mineral ferrihydrite, formed as a result of abiotic oxidation of aqueous ferrous iron, contains ferric iron that is enriched in ^{56}Fe relative to coexisting aqueous iron. As iron in solution is consumed and the δ^{56}Fe of dissolved iron increases, the δ^{56}Fe of ferrihydrite increases from –2.02 ‰ to +0.11 ‰ because the formation of ferrihydrite at pH > 5 is essentially irreversible.

Non-marine sources Dissolved iron in ground water from Mount Ruapehu in Tongariro National Park, New Zealand, has δ^{56}Fe values between –2.20 ‰ and –0.74 ‰ (Bullen and others, 2001). This range occurs because of formation of ferrihydrite enriched in ^{56}Fe relative to that in aqueous iron. This process (Rayleigh isotope fractionation) enriches the remaining dissolved iron in ^{56}Fe as ferrihydrite forms.

Plants and animals Using multiple collector inductively coupled plasma mass spectrometry, Walczyk (2001) found iron in human blood to be depleted in ^{56}Fe relative to iron in non-biologic sources. The δ^{56}Fe of blood from 10 human males ranged from –2.9 ‰ to –2.5 ‰. The sample with a δ^{56}Fe value of –2.9 ‰ has the lowest ^{56}Fe content found in the literature for a naturally occurring terrestrial substance. The mole fraction of ^{56}Fe in this sample is 0. 917 42 and A_r(Fe) = 55.844 77.

Elemental iron IRMM-014 has been analyzed by Zhu and others (2000b) and based on their analytical reproducibility is homogeneous to better than ±0.04 ‰.

Copper (Cuprum) A_r(Cu) = 63.546(3)

The average concentration of copper in the Earth's crust is 68 mg/kg (Greenwood and Earnshaw, 1997). Copper is mined primarily from sulfide, oxide, and carbonate deposits. The primary commercial source of copper is $CuFeS_2$ (chalcopyrite). The primary use of copper is in electrical wires, but coinage and copper alloys, such as brass, are important copper-bearing products.

Reference materials and reporting of isotope ratios

Copper isotope ratios, $n(^{65}Cu)/n(^{63}Cu)$, are reported relative to the primary reference NIST SRM 976 elemental copper, with an assigned δ^{65}Cu value of 0 ‰. Copper isotope-ratio measurements have been performed by positive ion thermal ionization mass spectrometry and by multiple collector inductively coupled plasma mass spectrometry; isotope ratios, using the latter, can be determined with a 1-σ standard deviation of better than ±0.05 ‰. The absolute isotope abundances of SRM 976 elemental copper have been determined by Shields and others (1964) and are listed in table 34.

Ranges in Isotopic Composition

The first survey of copper isotopic variation in natural materials was that of Walker and others (1958), who found a range of more than 12 ‰ (table 35 and figure 14). These observations were confirmed by Shields and others (1965) in a study on 106 samples of carbonates, oxides, sulfides, and native copper. Both of these studies used thermal ionization mass spectrometry. Development of multiple collector plasma source mass spectrometry (Walder and Freedman, 1992) has made isotopic analysis of copper much easier and improved analytical precision significantly (Maréchal and others, 1999; Zhu and others, 2000a).

Table 34. *Isotopic composition of SRM 976 elemental copper*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{63}Cu	62.929 6007(15)	0.691 74(20)
^{65}Cu	64.927 7938(19)	0.308 26(20)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Shields and others (1964).

Table 35. *Copper isotopic composition of selected copper-bearing materials*

[Values for δ^{65}Cu given in per mill relative to NIST SRM 976 elemental copper]

	Minimum δ^{65}Cu Value		Maximum δ^{65}Cu Value	
Substance	δ^{65}Cu	Reference	δ^{65}Cu	Reference
CARBONATES	–1	Shields and others, 1965	+9	Shields and others, 1965
CHLORIDES	–7.65	Gale and others, 1999	–1.6	Shields and others, 1965
OXIDES	–0.7	Shields and others, 1965	+5	Shields and others, 1965
SULFATES	–0.7	Shields and others, 1965	+3.6	Shields and others, 1965
SULFIDES				
$CuFeS_2$ (chalcopyrite)	–1.4	Shields and others, 1965	+5.74	Maréchal and others, 1999
Cu_5FeS_4 (bornite)	–3.2	Shields and others, 1965	+2.4	Shields and others, 1965
Cu_2S (chalcocite)	–3.3	Shields and others, 1965	+6	Shields and others, 1965
Other	–4.5	Walker and others, 1958	+2.7	Walker and others, 1958
NATIVE COPPER	–3.03	Maréchal and others, 1999	+2	Shields and others, 1965
ARCHAEOLOGICAL COPPER INGOTS	–4.30	Gale and others, 1999	–0.22	Gale and others, 1999
PLANTS AND ANIMALS	+0.08	Maréchal and others, 1999	+1.8	Walker and others, 1958

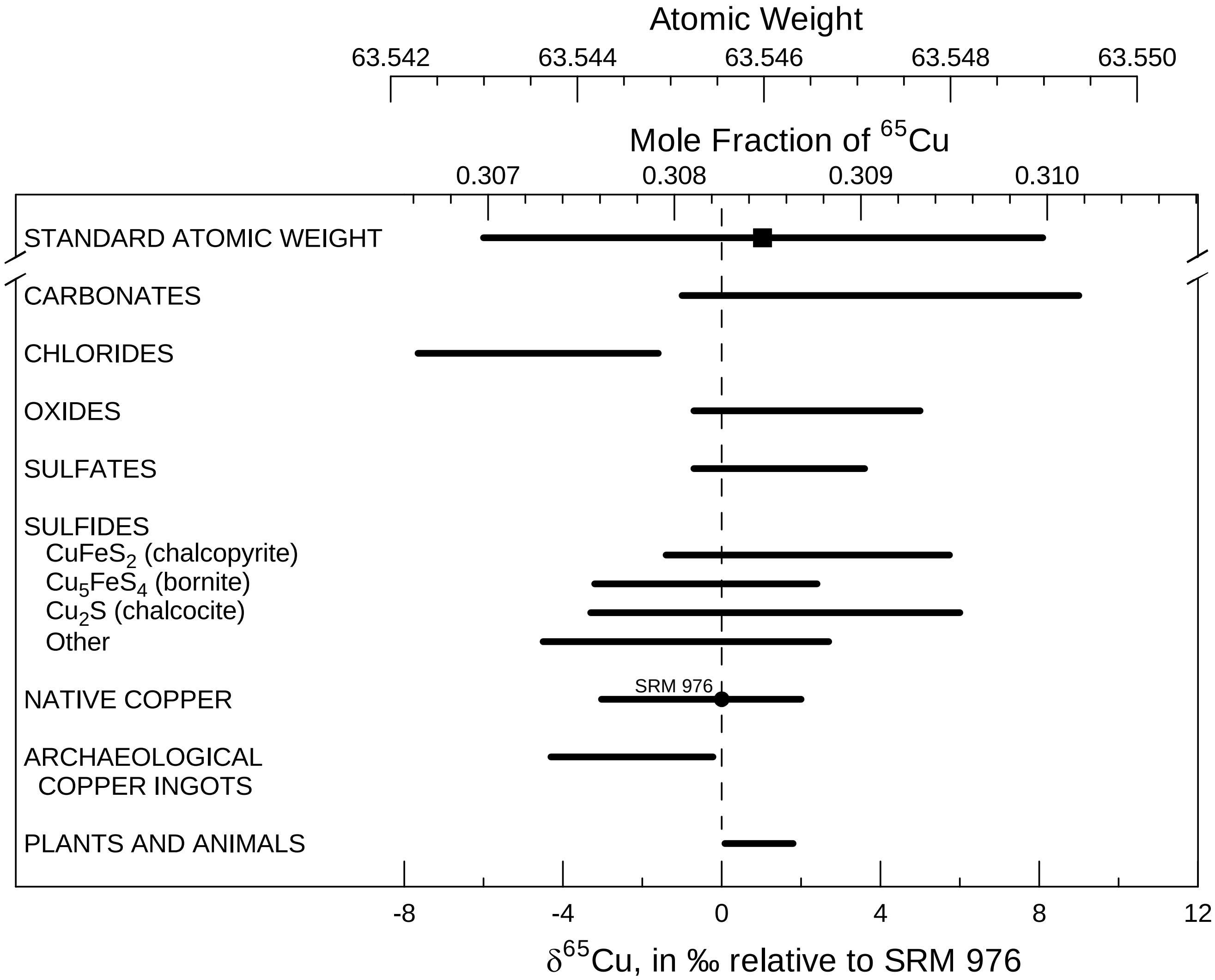

Figure 14. Copper isotopic composition and atomic weight of selected copper-bearing materials. The δ^{65}Cu scale and the ^{65}Cu mole-fraction scale were matched using the data in table 34; therefore, uncertainty in placement of the atomic-weight scale and the ^{65}Cu mole-fraction scale relative to the δ^{65}Cu scale is equivalent to ±0.9 ‰.

Carbonates Shields and others (1965) analyzed a dozen carbonates for copper isotopic composition. They ranged in δ^{65}Cu from –1 ‰ for malachite [$CuCO_3{\cdot}Cu(OH)_2$] from Kyshtymsk, USSR to +9 ‰ for aurichalcite [$2(Zn, Cu)\ CO_3{\cdot}3(Zn, Cu)(OH)_2$] from Globe, Arizona (USA). The aurichalcite has the highest ^{65}Cu content found in the literature for a material of natural terrestrial origin. This sample and value need to be scrutinized in light of developing technology. For this sample, the mole fraction of ^{65}Cu is 0.3102 and A_r(Cu) = 63.549.

Chlorides Specimens of atacamite [$CuCl_2{\cdot}3Cu(OH)_2$] from Atacama, Chile, have been analyzed by 2 groups (table 35). Shields and others (1965) determined a δ^{65}Cu value of –1.65 ‰, whereas Gale and others (1999) reported –7.65 ‰ for their specimen. Such discrepancies make it evident that these samples and values need to be scrutinized in light of developing technology. For the value of –7.65 ‰, the lowest ^{65}Cu content found in the literature for a material of natural terrestrial origin, the mole fraction of ^{65}Cu is 0.3066 and A_r(Cu) = 63.542.

Oxides Shields and others (1965) analyzed 15 copper oxides. They ranged in δ^{65}Cu from –0.7 ‰ for cuprite (CuO) from Bisbee, Arizona (USA), to –5.0 ‰ for cuprite from Demidoff, Ukraine (table 35 and figure 14).

Sulfates Shields and others (1965) analyzed 7 sulfates for copper isotopic composition. The δ^{65}Cu of these samples ranged from –0.7 ‰ for brochantite [$CuSO_4 \cdot 3Cu(OH)_2$] from Chuquicamata, Chile, to +3.6 ‰ for brochantite from Morenci, Arizona (USA) (table 35 and figure 14).

Sulfides Shields and others (1965) analyzed 17 chalcopyrite ($CuFeS_2$), 9 bornite (Cu_5FeS_4), 20 chalcocite (Cu_2S), and a few other copper sulfide samples. Maréchal and others (1999) analyzed 3 chalcopyrite samples by multiple collector plasma source mass spectrometry. Zhu and others (2000a) analyzed the copper isotopic composition of chalcopyrite from marine black smoker sulfide deposits (hydrothermal systems) and found δ^{65}Cu values ranging from –0.45 ‰ to +1.17 ‰. They concluded that δ^{65}Cu values reflect mass fractionation at low temperature rather than heterogeneity in the source. The ranges in δ^{65}Cu in sulfides are shown in table 35 and figure 14.

Native copper More than 15 isotope-ratio analyses of native copper are reported in the literature (Walker and others, 1958; Shields and others, 1965; Maréchal and others, 1999; Zhu and others, 2000a). The δ^{65}Cu values of native copper range from –3.03 ‰ from Ray, Arizona (USA) (Maréchal and others, 1999) to +2 ‰ from Pima, Arizona (USA) (Shields and others, 1965).

Archaeological copper ingots Gale and others (1999) showed that fire refining does not alter the isotopic composition of copper. They analyzed 8 Late-Bronze Age copper oxhide ingots from sites in Cyprus, Crete, and Sardinia, and found a range in δ^{65}Cu from –4.30 ‰ to –0.22 ‰. They concluded that copper isotope ratios can make a contribution to identifying provenance of archaeological objects made of copper based alloys. Three ingots from Crete differ in δ^{65}Cu by 2.8 ‰ and do not match the isotopic composition of any copper deposits so far analyzed in the Mediterranean region, including Cyprus and Turkey.

Plants and animals Walker and others (1958) analyzed marine seaweed (+1.8 ‰), organic concentrate from shale (0 ‰), and oak tree leaves (+0.9 ‰). Two marine sediments analyzed by Walker and others (1958) differed greatly in δ^{65}Cu, +0.5 ‰ and +8.1 ‰; these values are not shown in table 35 or figure 14 because the specific compound analyzed by Walker is not listed. Maréchal and others (1999) analyzed mussel (+0.08 ‰) and human blood (+0.30 ‰). These ranges are shown in table 35 and figure 14.

Zinc A_r(Zn) = 65.409(4)

The average concentration of zinc in the Earth's crust (76 mg/kg) is slightly greater than that of copper (Greenwood and Earnshaw, 1997). The major ores of zinc are ZnS (known as zinc blende in Europe and sphalerite in the United States) and $ZnCO_3$ (known as calamine in Europe and smithsonite in the United States). The primary use of zinc is in anti-corrosion coatings. The standard atomic weight of zinc was changed by CAWIA from 65.39(2) to 65.409(4) in July 2001, based on the calibrated measurement by Chang and others (2001a).

Reference materials and reporting of isotope ratios

There are no internationally distributed isotopic reference materials for zinc. In their survey of zinc isotope ratios, Maréchal and others (1999) reported $n(^{66}Zn)/n(^{64}Zn)$ ratios and expressed their results as δ^{66}Zn values expressed in per mill relative to JMC (Johnson Matthey) 3-0749 L solution. Zinc isotope-ratio measurements have been performed using positive ion thermal ionization mass spectrometry and multiple collector inductively coupled plasma mass spectrometry. Using the latter technique, isotope ratios can be determined with a 1-σ standard deviation of better than ±0.05 ‰. The absolute isotope abundances of zinc have been determined by Rosman (1972) and are reported in table 36.

Ranges in Isotopic Composition

The advent of multiple collector plasma source mass spectrometry (Walder and Freedman, 1992) has improved the analytical precision of the isotopic analysis of zinc (Maréchal and others, 1999). The full range in naturally occurring materials is about 1 ‰ (Maréchal and others, 1999). The material with the lowest ^{66}Zn content is ZnS from the Lau Basin, Pacific Ocean, with a δ^{66}Zn value of –0.19 ‰ (Maréchal and others, 1999). The material with the highest reported ^{66}Zn content is a mussel with a δ^{66}Zn value of +0.82 ‰ (Maréchal and others, 1999). The observed range of Zn isotopic compositions is within the uncertainty of the standard atomic weight of zinc, even after its reduction in July 2001 to 0.004.

Table 36. *Isotopic composition of a naturally occurring sample of zinc*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{64}Zn	63.929 1461(18)	0.4863(20)
^{66}Zn	65.926 0364(17)	0.2790(9)
^{67}Zn	66.927 1305(17)	0.0410(4)
^{68}Zn	67.924 8473(17)	0.1875(17)
^{70}Zn	69.925 325(4)	0.0062(1)

[A] From Audi and Wapstra (1993).
[B] From Rosman and Taylor (1998) and Rosman (1972).

Selenium A_r(Se) = 78.96(3)

Selenium is not abundant on Earth as it is sixty-sixth in order of crustal abundance. The primary commercial source of selenium is the anode slime deposited during electrolytic refining of copper. The largest use in the United States (Greenwood and Earnshaw, 1997) is as a decolorizer of glass (0.01–0.15 g/kg). Higher concentrations produce pink and brilliant red glasses. Selenium also is used in semiconductor diodes, photocells, shampoos, and medicinal injections particularly in the livestock industry to combat muscle disease.

Few measurements of variations in the isotopic composition of terrestrial selenium have been made. The earliest data were obtained using SeF_6 in a gas source isotope-ratio mass spectrometer (Krouse and Thode, 1962) with a 1-σ standard deviation of ±0.5 ‰ in the $n(^{80}\mathrm{Se})/n(^{76}\mathrm{Se})$ isotope-abundance ratio. Johnson and others (1999) have developed a double-spike method that requires less than 500 nanograms of selenium per analysis. Solutions containing ~1 mg/kg selenium have been successfully analyzed by inductively coupled plasma isotope-ratio mass spectrometry (Wulff and others, 1999). The reproducibility is dependent upon the choice of isotopes because of interfering ions. Selenium isotope-ratio measurements have been performed using negative ion thermal ionization mass spectrometry, and $n(^{80}\mathrm{Se})/n(^{76}\mathrm{Se})$ ratios can be determined with a 1-σ standard deviation of ±0.2 ‰ (Johnson and others, 1999). Although absolute

Table 37. *Selenium isotopic composition of a naturally occurring material*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{74}Se	73.922 4767(16)	0.008 89(3)
^{76}Se	75.919 2143(16)	0.093 66(18)
^{77}Se	76.919 9148(16)	0.076 35(10)
^{78}Se	77.917 3097(16)	0.237 72(20)
^{80}Se	79.916 5221(20)	0.496 07(17)
^{82}Se	81.916 7003(22)	0.087 31(10)

[A] From Audi and Wapstra (1993).
[B] From Rosman and Taylor (1998) and Wachsmann and Heumann (1989).

isotope-abundance determinations have been made on naturally occurring samples (see table 37; Wachsmann and Heumann, 1989), absolute isotope-abundance determinations have not been made for any specimen used in relative abundance investigations.

The published maximum range of δ^{82}Se values (based on $n(^{82}\mathrm{Se})/n(^{76}\mathrm{Se})$ isotope-abundance ratios) in naturally occurring materials is 16 ‰ (Krouse and Thode, 1962). Selenium is analogous to sulfur in that bacterial redox reactions have been identified in nature and substantial kinetic isotope effects have been realized during laboratory chemical and bacterial $\mathrm{SeO_4^{2-}}$ and $\mathrm{SeO_3^{2-}}$ reductions (Krouse and Thode, 1962; Rees and Thode, 1966; Rashid, 1978; Rashid and Krouse, 1985; Johnson and others, 1999; Wulff and others, 1999; Herbel and others, 2000). If a k_{76}/k_{82} value of 1.018 (average for laboratory studies) existed during reduction of $\mathrm{SeO_3^{2-}}$ containing selenium with $A_r(\mathrm{Se}) = 78.963$, the initial $\mathrm{Se^0}$ product would have an $A_r(\mathrm{Se}) = 78.948$. However, in a study of selenium in surface water, oil refinery wastewater, and sediments from the San Francisco Bay Estuary, Johnson and others (2000) find that $n(^{80}\mathrm{Se})/n(^{76}\mathrm{Se})$ isotope-abundance ratios are lower by about 2 ‰ in total sediment extracts relative to that of the local bay water. The magnitude of this isotope fractionation is smaller than that expected for reduction of Se(VI) or Se(IV) to Se(0), and this suggests that reduction of soluble selenium in overlying waters is not the primary process by which selenium is incorporated into sediments. In addition, variable isotopic differences between riverine and refinery inputs were observed; thus, tracing of refinery inputs with selenium isotope ratios is not possible in this particular system (Johnson and others, 2000).

Molybdenum $A_r(\mathrm{Mo}) = 95.94(2)$

The average concentration of molybdenum in the Earth's lithosphere is about 1 mg/kg. Molybdenum is refined from molybdenite ($\mathrm{MoS_2}$), the largest ore deposit of which is found in Colorado, and is obtained as a byproduct from copper production. The primary use of molybdenum is in stainless steel and high-speed steel tools. The standard atomic weight of molybdenum was changed by CAWIA from 95.94(1) to 95.94(2) in July, 2001, based on data from Wieser and de Laeter (2000), which lead to an increase in uncertainty as required by guidelines used by CAWIA.

Reference materials and reporting of isotope ratios

Siebert and others (2001a) have measured the isotopic composition of a number of samples using multiple collector magnetic sector inductively coupled plasma mass spectrometry (MC-ICP-MS) using a molybdenum double spike. Isotope fractionations are determined on 4 molybdenum isotopes, providing an internal consistency check. The 2-σ external reproducibility on $n(^{98}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ isotope-abundance ratios is 0.06 ‰. Anbar and others (2001) using (MC-ICP-MS) and either a zirconium or ruthenium spike are able to analyze samples as small as 1 µg of molybdenum, giving a 2-σ precision in $n(^{97}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ of 0.2 ‰. Although there are no internationally distributed isotopic reference materials for molybdenum, Siebert and others (2001b) determined that ocean water is constant in $n(^{98}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ within ±0.1 ‰ and they recommend expressing $n(^{98}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ isotope-abundance ratios relative to molybdenum dissolved in ocean water, which is assigned a δ^{98}Mo value of 0 ‰. Although absolute isotope-abundance determinations have been made on naturally occurring molybdenum ore concentrates (see table 38; Moore and others, 1974), absolute isotope-abundance determinations have not been made for any specimen used in relative abundance investigations.

Ranges in Isotopic Composition

The advent of multiple collector plasma source mass spectrometry (Walder and Freedman, 1992) has improved the analytical precision of the isotopic analysis of molybdenum (Siebert and others, 2001a, 2001b; Anbar and others, 2001). Anbar and others (2001) observe a range in $n(^{97}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ during ion-exchange chromatography in the laboratory of ~3 ‰. They note a variation in $n(^{97}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ of ~0.6 ‰ between a natural sample of $\mathrm{MoS_2}$ and a laboratory reference material, which is a variation in $A_r(\mathrm{Mo})$ of 0.002, substantially less than the uncertainty in the standard atomic weight of molybdenum of 0.01. Smaller isotopic variations were observed by Siebert and others (2001a), who measured $n(^{98}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ differences of –0.3 ‰ and +0.1 ‰ for fine-grained sediments relative to their reference; they found a –0.3 ‰ $n(^{98}\mathrm{Mo})/n(^{95}\mathrm{Mo})$ difference between a hydrothermal molybdenite and their reference. In contrast to the preceding studies, no isotopic variability within a precision of 0.01 ‰ to 0.1 ‰ could be seen in terrestrial materials by Dauphas and

Table 38. *Molybdenum isotopic composition of SRM 333 molybdenum ore concentrate*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{92}Mo	91.906 810(4)	0.148 362(148)
^{94}Mo	93.905 0867(20)	0.092 466(92)
^{95}Mo	94.905 8406(20)	0.159 201(159)
^{96}Mo	95.904 6780(20)	0.166 756(167)
^{97}Mo	96.906 0201(20)	0.095 551(96)
^{98}Mo	97.905 4069(20)	0.241 329(241)
^{100}Mo	99.907 476(6)	0.096 335(96)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Moore and others (1974).

others (2001) who used multiple collector inductively coupled plasma hexapole mass spectrometry.

Siebert and others (2001b) analyzed Atlantic, Pacific, and Indian ocean water and found no δ^{98}Mo variation within analytical uncertainty (±0.1 ‰). Their range in δ^{98}Mo for sediments is –2.7 ‰ to –2.0 ‰. Their range for crusts of ferromanganese deep-sea nodules is –3.1 ‰ to –2.7 ‰.

Palladium A_r(Pd) = 106.42(1)

Palladium is relatively scarce in the Earth's crust; its concentration is about 0.15 mg/kg (Greenwood and Earnshaw, 1997). Native palladium is found in placer deposits or in sulfides or arsenides of copper and nickel sulfide ores. The largest single use of palladium is in electronic components, but large amounts are also used in dehydrogenation catalysis and dentistry (Greenwood and Earnshaw, 1997).

Shima and others (1978) analyzed samples from Sudbury, Ontario, Canada (containing 0.25 mg/kg Pd) and from the western Bushveld Igneous Complex in South Africa at Lonrho (containing 7.7 mg/kg Pd) for palladium isotopic composition (table 39) using positive ion thermal ionization mass spectrometry. Although Shima and others found no variation in isotopic composition in these terrestrial samples, Mermelengas and others (1981) reported evidence of isotope fractionation in a precious metal concentrate from the Atok mine in South Africa. A concentrate from a second mine, also from the Bushveld Complex, was not fractionated. Rosman and others (1989) reanalyzed these samples together with another 4 mineral concentrates and 1 highly refined sample of palladium metal. Their results are shown in table 40.

Rosman and others (1989) confirmed that palladium samples with relatively high atomic weights are present in the Atok mine, which is located in the eastern part of the Bushveld complex. No heavy-isotope enrichment was found in samples from the western part of the Bushveld Complex. Rosman and others concluded that isotope fractionation in the Atok-mine sample was produced by natural geochemical processes rather than by industrial processing or purification.

Tellurium A_r(Te) = 127.60(3)

Tellurium is also relatively scarce (seventy-third in order of crustal abundance). The principal commercial source of tellurium is the anode slime deposited during electrolytic refining of copper. The United States, Japan, and Canada dominate production. Tellurium is used in iron and steel production, in non-ferrous metal production, and in catalysts.

Tellurium has been analyzed for isotopic composition using both negative ion thermal ionization mass spectrometry (Smithers and Krouse, 1968) and positive ion thermal ionization mass

Table 39. *Palladium isotopic composition of a sample from Sudbury, Ontario, Canada*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{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)

[A] From Audi and Wapstra (1993).
[B] From Rosman and Taylor (1998) and Shima and others (1978).

Table 40. *Isotope fractionation of naturally occurring palladium-bearing samples*

[Pd concentration given in weight percent; isotope fractionation given in ‰/mass unit relative to reagent Pd[A]]

Location	Pd concentration	Isotope fractionation: Mermelengas and others, 1981	Isotope fractionation: Rosman and others, 1989
Atok mine	13.3	+3.8 ± 0.3[B]	+3.6 ± 0.2[B]
Merensky Reef	3–4	–0.2 ± 0.3[B]	+0.1 ± 0.2
Union Section	0.6	- -	+0.1 ± 0.2
Amandelbult Section	2.4	- -	+0.2 ± 0.2
Rustenburg Section, code R	3	- -	+0.2 ± 0.3
Rustenburg Section, code C	20	- -	+0.1 ± 0.1
Code 84/85, unknown section[C]	99.99	- -	+0.1 ± 0.2

[A] Same reagent used in both studies.
[B] Average of 2 measurements.
[C] Probably South Africa.

spectrometry (Wachsmann and Heumann, 1992). Although tellurium has 8 stable isotopes (table 41), few determinations of tellurium isotope abundance variation have been performed (Smithers and Krouse, 1968; Smith and others, 1978). Absolute isotope-abundance measurements have not been conducted on a specimen used in relative isotope-ratio investigations. The reported maximum range of δ^{130}Te values (based on the ^{130}Te/^{122}Te abundance ratio) is 4 ‰, the ranges being similar for natural telluride minerals, native Te, and commercial K_2TeO_3 (Smithers and Krouse, 1968). A kinetic isotope effect k_{122}/k_{130}, as high as 1.008, has been obtained during TeO_3^{2-} reduction. If tellurite (TeO_3^{2-}) with A_r(Te) = 127.603 were reduced with this k_{122}/k_{130} value, the initial Te^0 product would have A_r(Te) = 127.58. By analogy with sulfur and selenium, the natural variation in tellurium isotope

Table 41. *Tellurium isotopic composition of a naturally occurring material*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{120}Te	119.904 026(11)	0.000 96(1)
^{122}Te	121.903 0558(29)	0.026 03(1)
^{123}Te	122.904 2711(20)	0.009 08(1)
^{124}Te	123.902 8188(16)	0.048 16(2)
^{125}Te	124.904 4241(20)	0.071 39(2)
^{126}Te	125.903 3049(20)	0.189 52(4)
^{128}Te	127.904 4615(19)	0.316 87(4)
^{130}Te	129.906 2229(21)	0.337 99(3)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Smith and others (1978).

abundances because of mass fractionation probably is higher than reported here.

In contrast to mass fractionation effects, highly anomalous tellurium isotope abundances have been found near the Oklo natural fission reactor found in Gabon (Loss and others, 1988; Loss and others, 1989). Thus, A_r(Te) at Oklo is highly variable and this variability is dependent upon many factors, such as the amount of fissiogenic tellurium present, neutron capture reactions involving tellurium nuclei, and the migration (retention) of precursor nuclei. For example, the range reported for the ratio n(fission product ^{125,128,130}Te)/n(primordial Te) for Zone 9 at Oklo was 81 to 190 (Loss and others, 1989). The maximum corresponds to a molar concentration of ^{130}Te of about 80 percent as compared to 34 percent found for the "normal" abundance. Fission product tellurium isotopes increase A_r(Te), so that A_r(Te) is greater than 129.

Thallium A_r(Tl) = 204.3833(2)

The average concentration of thallium in the Earth's crust is 0.7 mg/kg (Greenwood and Earnshaw, 1997). Thallium is recovered from the smelting of zinc-lead ores and from flue dust emitted during sulfide roasting for the manufacture of sulfuric acid. There are no major commercial uses of thallium.

Reference materials and reporting of isotope ratios

Thallium isotope ratios are reported relative to the primary reference NIST SRM 997 elemental thallium metal, with an assigned δ^{205}Tl value of 0 ‰. Thallium isotope-ratio measurements have been performed by thermal ionization mass spectrometry and by multiple collector inductively coupled plasma mass spectrometry. Using the latter technique, isotope ratios can be determined with a 1-σ standard deviation of better than ±0.05 ‰ (Rehkämper and Halliday, 1999). The absolute isotope abundances of SRM 997 elemental thallium have been determined by Dunstan and others (1980) and are listed in table 42.

Ranges in Isotopic Composition

The first survey of thallium isotopic fractionation of natural materials was that of Dunstan and others (1980). Using thermal ionization mass spectrometry, they found no isotopic variability within analytical uncertainty. Rehkämper and Halliday (1999) found isotopic variation among reagents, igneous rocks, and crusts of ferromanganese deep-sea nodules (table 43 and figure 15). Rehkämper and others (2001) confirmed isotopic variation in ferromanganese crusts. The observed isotopic variation of thallium extends outside the limits of the uncertainty of its atomic weight (figure 15). In future meetings, CAWIA may consider expanding the atomic-weight uncertainty of

Table 42. *Isotopic composition of SRM 997 elemental thallium*

[Atomic mass given in unified atomic mass units, u]

Isotope	Atomic Mass[A]	Mole Fraction[B]
^{203}Tl	202.972 329(3)	0.295 24(9)
^{205}Tl	204.974 412(3)	0.704 76(9)

[A] From Audi and Wapstra (1993).

[B] From Rosman and Taylor (1998) and Dunstan and others (1980).

Table 43. *Thallium isotopic composition of selected thallium-bearing materials*

[Values for δ^{205}Tl given in per mill relative to NIST SRM 997 elemental thallium]

	Minimum δ^{205}Tl Value		Maximum δ^{205}Tl Value	
Substance	δ^{205}Tl	Reference	δ^{205}Tl	Reference
IGNEOUS ROCKS	–0.18	Rehkämper and Halliday, 1999	+0.35	Rehkämper and Halliday, 1999
SEDIMENTARY ROCKS	+0.33	Rehkämper and others, 2001	+1.43	Rehkämper and others, 2001
REAGENTS	–0.14	Rehkämper and Halliday, 1999	+0.02	Rehkämper and Halliday, 1999

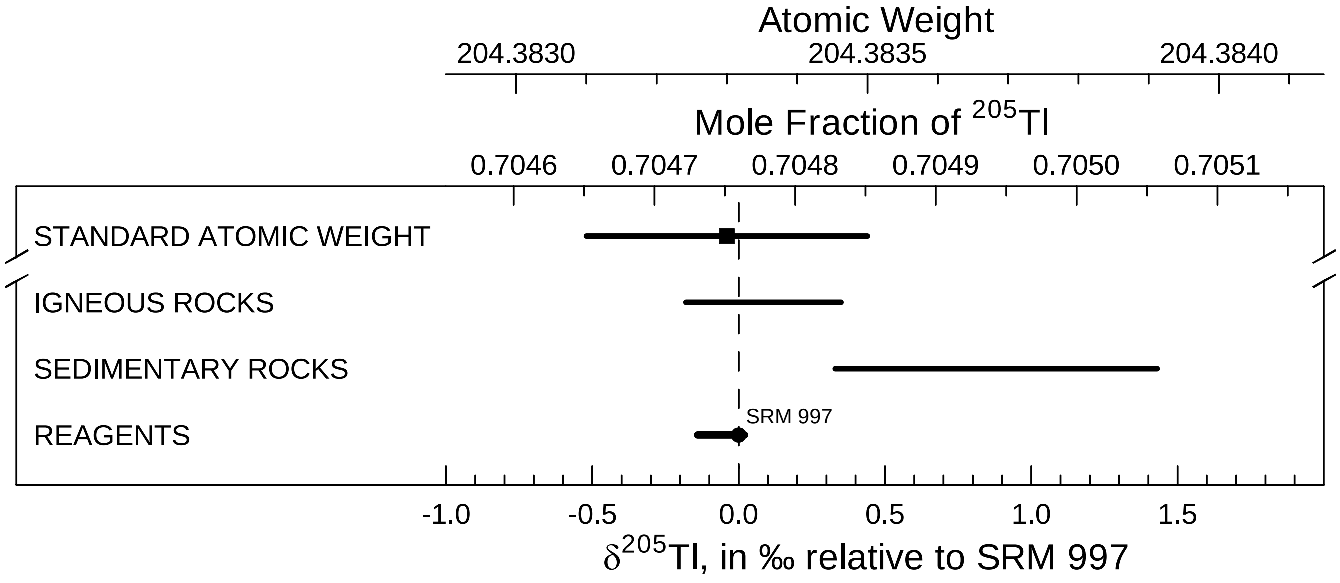

Figure 15. Thallium isotopic composition and atomic weight of selected thallium-bearing materials. The δ^{205}Tl scale and the ^{205}Tl mole-fraction scale were matched using the data in table 42; therefore, uncertainty in placement of the atomic-weight scale and the ^{205}Tl mole-fraction scale relative to the δ^{205}Tl scale is equivalent to ±0.4 ‰.

thallium or consider adding a footnote *g* to thallium in the Table of Standard Atomic Weights (Coplen, 2001) to indicate that "geological specimens are known in which the element has an isotopic composition outside the limits for normal material." It is not now assigned a footnote *g*.

Igneous rocks The δ^{205}Tl of igneous rocks ranges from –0.18 ‰ to +0.35 ‰, based on analysis of seven terrestrial samples Rehkämper and Halliday (1999). The lowest ^{205}Tl content in the literature of a material of natural terrestrial origin (δ^{205}Tl = –0.18 ‰) is found in a volcanic rhyolite in the East Rift Zone of Iceland. For this sample the mole fraction of ^{205}Tl is 0.704 72 and A_r(Tl) = 204.383 24.

Sedimentary rocks The δ^{205}Tl of crusts of ferromanganese deep-sea nodules ranges from +0.33 ‰ to +1.43 ‰ (Rehkämper and others, 2001; Rehkämper and Halliday, 1999). High δ^{205}Tl values (+1.31 ‰ to +1.43 ‰) were found in ferromanganese crusts of samples collected from the Southern Atlantic Ocean, the Indian Ocean, and the central Pacific Ocean (Rehkämper and others, 2001). For the sample of a material of natural terrestrial origin with the highest ^{205}Tl content in the literature (δ^{205}Tl = +1.43 ‰), the mole fraction of ^{205}Tl is 0.705 06 and A_r(Tl) = 204.383 91 (Rehkämper and others, 2001).

Reagents The δ^{205}Tl of thallium-bearing laboratory reagents ranges from –0.14 ‰ to +0.02 ‰ (Rehkämper and Halliday, 1999).

Summary and Conclusions

The standard atomic weights and their uncertainties tabulated by the Commission on Atomic Weights and Isotopic Abundances of the International Union of Pure and Applied Chemistry are intended to apply to most normal terrestrial materials and laboratory reagents. The Subcommittee on Natural Isotopic Fractionation was formed to investigate the effects of isotope abundance variations of elements upon their atomic weights and atomic-weight uncertainties. The aims of the subcommittee are (1) to identify elements for which the uncertainties of the standard atomic weights are significantly larger than measurement uncertainties because of isotope abundance variations caused by fractionation processes (excluding variations caused by radioactivity) and (2) to provide information about the range of atomic-weight variations in specific chemical compounds of each of these elements. The following elements were found to meet these criteria: hydrogen, lithium, boron, carbon, nitrogen, oxygen, silicon, sulfur, chlorine, copper, and selenium. The chemical elements magnesium, calcium, iron, zinc, molybdenum, palladium, and tellurium have isotopic variations in materials of natural terrestrial origin, but these variations do not require expansion of the uncertainty of the atomic weights of these elements. Two chemical elements, chromium and thallium, have isotope-abundance variations in materials of natural terrestrial origin that may exceed atomic-weight uncertainties.

With the proliferation of microprobe techniques for isotope measurements, large variations in isotopic composition have been found in source materials over distances of the order of 1 to 1000 µm (McKibben and Eldridge, 1994). Such data are excluded from this compilation, as are data from extraterrestrial materials and elements exhibiting isotope-abundance variation caused by radioactivity.

There are no internationally distributed isotopic reference materials for the elements zinc, selenium, molybdenum, palladium, and tellurium. Preparation of such materials will help to make isotope-ratio measurements among laboratories comparable.

Many laboratories are not reporting isotope abundance variations relative to current internationally distributed isotopic reference materials. For example, some laboratories are not reporting δ^{56}Fe values relative to IRMM-014 elemental iron. Some laboratories are not reporting δ^{44}Ca values relative to SRM 915a calcium carbonate. The International Union of Pure and Applied Chemistry may consider preparation of guidelines discussing the advantages of reporting delta values relative to present iron and calcium isotopic reference materials.

This report should not be considered as a comprehensive compilation of stable isotope ratios in the literature. Rather, this report is intended to illustrate ranges of isotope-abundance variations that may be encountered in natural and anthropogenic compounds, and in reagents and naturally occurring terrestrial materials.

The minimum and maximum concentrations of a selected isotope in materials of natural terrestrial origin of selected chemical elements discussed in this report are given below:

Isotope	Minimum, mole fraction	Maximum, mole fraction
^{2}H	0.000 0255	0.000 1838
^{7}Li	0.9227	0.9278
^{11}B	0.7961	0.8107
^{13}C	0.009 629	0.011 466
^{15}N	0.003 462	0.004 210
^{18}O	0.001 875	0.002 218
^{26}Mg	0.1099	0.1103
^{30}Si	0.030 816	0.031 023
^{34}S	0.0398	0.0473
^{37}Cl	0.240 77	0.243 56
^{44}Ca	0.020 82	0.020 92
^{53}Cr	0.095 01	0.095 53
^{56}Fe	0.917 42	0.917 60
^{65}Cu	0.3066	0.3102
^{205}Tl	0.704 72	0.705 06

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