Iodine-129: Its Occurrence in Nature and Its Utility as a Tracer

Abstract. Natural production rates of the 16 million-year iodine-129 from spontaneous fission and from cosmic-ray reactions are estimated to contribute a steady-state concentration of more than 10^{-14} gram of I^{129} per gram of I^{127} to the hydrosphere, the atmosphere, and the biosphere. These concentrations are expected to be detectable by neutron-activation analysis in natural materials that concentrate iodine. Substantial additional contributions have been made by fission-produced I^{129} in fallout, serving as an intrinsic tracer for natural iodine kinetics. Iodine-129 activation analysis has advantages as a tracer technique.

Iodine-129 occurs as a long-lived fission product of uranium, with a half-life of 1.6×10^7 years, in a (thermal neutron) fission yield of about 1 percent. This iodine isotope has found little use as a tracer because of its inherently low specific activity (0.16 μc/mg) and the low energy of its radiations (150 kev β^-, 38 kev γ). The low specific radioactivity results from the long lifetime (small decay constant, λ), a property which could make I^{129} particularly useful in many kinds of tracer experiments which require long periods of time to conduct. Further, the properties of low specific activity and low radiation energy are desirable from the standpoints of safe handling and effect on the environment (for example, on molecular species exposed to the radiations). The long lifetime not only permits experiments of essentially infinite duration but also permits long-term storage of labeled compounds and samples collected for assay.

The deficiencies of I^{129} as a tracer are successfully overcome if, instead of attempting to follow it by measuring its intrinsic radioactive decay processes as one customarily does with a radioactive tracer, one subjects matrices containing it to neutron-activation analysis. The isotopic capture cross-section for thermal neutrons has been set at between 27 and 35 barns (*1, 2*). The (n, γ) activation product is 12.6-h I^{130}, which has readily detectable β and γ radiations. Other thermal neutron reactions either on I^{129}, on the naturally occurring I^{127}, or on neighboring elements, do not present serious interferences.

Iodine-129 thus can be characterized quite uniquely as a nuclide occurring in nature only to the extent it exists in secular equilibrium with current formation processes, which may thus be added to a chemical, physical, or biological system in which its inherent concentration is virtually zero, to serve as a "nonradioactive" tracer (in the radiological hazard sense) for the element iodine in any of its forms or for solvents or other media (water, air, organic materials, and so forth) into which it is introduced physically or chemically.

As a fission product I^{129} is produced in current-day fission reactors in multikilogram quantities, readily separable from the bulk of the radiologically hazardous fission products.

After neutron activation of an iodine-containing sample to saturation with respect to the 12.6-h I^{130}, the saturation activity will be given by the production rate of I^{130} atoms, $N\sigma\phi$, where N is the number of I^{129} atoms in the sample, σ is the isotopic capture cross-section of I^{129} (30 barns), and ϕ is the thermal neutron flux per square centimeter per second. The improved measurement sensitivity for I^{129} thus achieved by measuring the activation product at $\phi = 10^{14}$ is

$$\sigma\phi/\lambda_{129} = 2.3 \times 10^6,$$

corresponding to an increase in specific activity from 0.16 *micro*curies to 350 *milli*curies per *milli*gram of I^{129}, or to a 3.5-picocurie sample of activation product from 10^{-14} g of I^{129}.

Other neutron-activation products following iodine chemistry are not expected to interfere with I^{130} measurement, except, of course, the 25-m I^{128}, which will be produced ($\phi = 10^{14}$, $\sigma = 6.3$ barns) at a rate of 3×10^{12} per second per gram of I^{127} (natural iodine), and which will thus be the dominant iodine activity in most samples immediately after irradiation.

The half-life disparity (25 min versus 756 min), however, will lead to a reduction factor of over 10^{12} for I^{128} in a 17-hour post-irradiation cooling period, during which time the I^{130} activity will be reduced by a factor of only 2.5. Such a reduction factor will bring the I^{128} activity produced in a gram of I^{127} to the same order of magnitude as the I^{130} activity produced in 10^{-13} g of I^{129}.

Detailed information on the radiation spectra in I^{130} and I^{128} decay is available from the usual sources (*3*). Both are negative β emitters (some β^+ in I^{128}) and each has a complex spectrum of γ-rays. However, the highest energy γ-ray in I^{128} is 0.99 Mev (0.3 percent intensity), while that in I^{130} is 1.15 Mev (40 percent intensity). The two nuclides could be distinguished on this basis alone with a scintillation detector-pulse height discriminator arrangement. Measurement of characteristic γ-γ coincidences could be employed in the presence of considerable contamination by foreign activation products.

Levels in Nature

Prior to the nuclear age I^{129} will have been introduced into the atmosphere, lithosphere, and hydrosphere, presumably in a radioactive secular equilibrium situation, from cosmic-ray production and natural fission processes. If samples of suitable size or isotopic concentration, or both, are available, it will be possible to ascertain these equilibrium levels within the limits of sensitivity described above.

Using neutron-activation analysis, Purkayastha and Martin (*1*) measured the I^{129} content of pitchblende (from natural fission), and established a limit of $<10^{-8}$ atom of I^{129} per atom of I^{127}

in a "natural" iodine sample, source unspecified. It should be possible now to explore readily the region between this value and $I^{129}/I^{127} = 10^{-14}$. While it is not possible to predict with confidence the levels that existed before the nuclear age, it would indeed be surprising if they lie below this limit in equilibrium samples which have concentrated iodine in recent geologic times.

The principal earth-level processes contributing fission-product elements to the lithosphere and hydrosphere in modern geologic times are the spontaneous fission processes in uranium and thorium. Neutron-induced natural fission contributes relatively little additional (*1*), and this only in uranium-rich minerals.

Pre-fallout iodine obtained from marine plants and animals should be representative of natural I^{129} levels, since their environment represents a relatively homogeneous equilibrium. The uranium concentration in sea water is reported as 3 μg/liter (*4*). The yield of I^{129} in spontaneous fission of U^{238} is unknown, but may be assumed from the recent work of Kuroda *et al.* to be of the order of 0.1 percent (*5*). At a U^{238} spontaneous fission rate of 4×10^{-3} g^{-1} sec^{-1}, the steady-state I^{129} concentration would be 2.1×10^{-18} g/liter of sea water. Since the total iodine concentration in sea water is 6×10^{-5} g/liter (*4*), the I^{129}/I^{127} ratio is predicted to be about 3.5×10^{-14}, near the lower limit of the range of detectability for a 1-g iodine sample, easily detectable in a 10-g sample of marine iodine. Weathering processes will contribute approximately an equal quantity of the spontaneous fission product to the marine environment.

Contributions from spontaneous fission of U^{235} might be of equal or greater magnitude as a result of a shift in the mass-yield curve.

Production of I^{129} in the upper atmosphere obviously has occurred in pre-1945 processes whose contribution can be estimated in terms of reasonably assumed parameters. Assuming sufficiently energetic neutrons, protons, and γ-rays, reactions producing I^{129} will occur in Xe^{129}, Xe^{130}, Xe^{131}, and Xe^{132}.

If it is assumed that the atmospheric atom fraction for Xe is 10^{-8} and that the effective elemental cross-section for production of I^{129} is 10 mbarn, the steady-state surface density of the activation product will be about 10^{6} atoms per square centimeter of the earth's surface. If the atmospheric and lithospheric residence times are short relative to the lifetime of I^{129}, this source will contribute an additional concentration of about 10^{-14} g of I^{129} per gram of I^{127} to the oceans.

The experimental evalution of I^{129} levels arising from these reactions will be significant in developing the entire geophysical and biospheric history of I^{129}, and perhaps in highly significant dating measurements in the several-million-year age range.

The occurrence of I^{129} as a fission-product provides a "built-in" tracer for the fate of fission iodine through the atmosphere, the hydrosphere, and the biosphere. Based on cumulative levels of Sr^{90} in soil prior to the recent tests (about 3×10^{18} atom/mi^{2}) (*6*), I^{129} deposition from nuclear tests, integrated to mid-1960, should approximate 10^{18} atoms per square mile (1 percent fission yield), or about 10^{7} atoms per square centimeter of the earth's surface.

If reasonable biological concentration factors are assumed, this material should now appear in selected biological samples in easily detectable quantities. The absolute sensitivity of this detection is greater by a factor of 3 for fission iodine inventories than for fission Sr^{90} inventories.

Since 1945, I^{129} has been added to the upper atmosphere in several substantial increments as a result of nuclear explosions. If lithospheric and hydrospheric entry are similar to those observed for Sr^{90}, this source will have added substantially to the pre-nuclear age base line described above. Its contribution of I^{129} to the oceans as a whole will have undoubtedly exceeded that of the natural processes by a large factor, and individual samples of marine iodine will show quite high I^{129}/I^{127} ratios as a result of incomplete mixing.

Analysis of biological samples dating back to 1945 should show these increments, and, when interpreted in terms of atmospheric inventories and fallout rates, should provide valuable information on the rates of entry of I^{129} into the biosphere.

If the analytical sensitivities described above are correct, analysis of iodine-rich specimens for I^{129} should provide a convenient measure of ages in the Cenozoic range. Petroleum brines and marine sediments should provide interesting samples.

The weapon-produced material provides a built-in long-term tracer for atmospheric transport and a soluble element for measuring fresh-water flow and oceanographic mixing rates. Its occurrence in fallout provides an intrinsic tracer for the cycling of iodine through the atmosphere and the oceans and for determining the contribution of fission processes to the total atmospheric iodine concentrations (*7*, *8*).

The ultrasensitive analytical method for I^{129} also presents an opportunity for its measurement in meteorites, in which it will have been formed by cosmic-ray spallation reactions on cesium, barium, and rare earth elements. It thus can serve as an additional monitor of the radiation history of meteorites, in a range of time periods between that of Be^{10} (2.7×10^{6} years) and that of K^{40} (1.3×10^{9} years).

Tracer Applications

As a deliberately added tracer, I^{129} opens many new vistas for tracer work, particularly as it relates to the tracing of iodine in any of its chemical forms, but also as it relates to atmospheric and hydrologic tracer studies.

The advantages of the I^{129} radiotracer-activation approach to tracer studies over conventional tracing techniques are:

1) The long half-life of I^{129} (1.6×10^{7} years) permits tracer studies of essentially infinite duration.

2) The long lifetime and low radiation energy of the nuclide result in virtual elimination of the radiological health hazard associated with the use of conventional radioactive tracers.

3) Problems encountered from radiation effects on the system under study and on labeled compounds are virtually eliminated; its applicability as a second label in I^{131}- or I^{125}-labeled compounds is obvious.

4) While I^{129} can be used in a very limited range of studies as a conventional radiotracer, utilizing direct measurement of its radiations, the radiotracer-activation approach increases the measurement sensitivity by factors greater than 10^{6}, so that quantities less than 10^{-13} g may be detected.

5) The radiotracer-activation method is superior to stable isotope tracing, inasmuch as the tracer nuclide does not occur in nature in abundances even remotely comparable with those of stable nuclides, or with quantities of the long-lived tracer which may be added to the system under study.

Viewed in combination, the advantages just listed and the detection sensitivity for I^{129} have implications for many different kinds of tracer studies. When introduced into any system, I^{129} behaves essentially as a nonradioactive substance insofar as environmental effects and nuclear stability are concerned. Samples of the system or of any of its parts may be taken at any time following introduction of the tracer, and subjected at will to neutron-activation analysis. The net result of the sensitivity is that a single gram of I^{129} may be traced through processes which result in dilution factors up to 10^{13}. This is an equivalent dilution sensitivity to that attainable with about 350 curies of any radionuclide.

For full realization of the potentialities of the tracer applications described here for I^{129}, the base-level values (natural and artificial) described above should be established experimentally. Work is now in progress in our laboratories to obtain these values in pre-1945 and current biospheric, atmospheric, and hydrospheric iodine samples (*9*). Simple demonstration experiments of tracer applications of I^{129} in chemical systems (solubility of lead iodide), and in biological systems (with I^{125} as a parallel tracer) (*10*) have been performed successfully (*11, 12*).

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8. Since Br^{79} is "shielded" in fission by the 7×10^4 –yr Se^{79}, perturbations in the natural Br^{79}/Br^{81} ratios in upper atmospheric bromine might also be anticipated.
9. This work is supported in part by the U.S. Atomic Energy Commission.
10. R. L. Bogner, R. C. Koch, I. Gruverman, unpublished work.
11. Since preparing this manuscript, I have seen a prepublication copy of a paper from Argonne National Laboratory presenting a detailed analytical procedure for I^{129} (M. H. Studier, C. Postmus, Jr., J. Mech, R. R. Walters, and E. N. Sloth, *J. Inorg. Nucl. Chem.*, in press).
12. I acknowledge with pleasure stimulating discussions on this subject with R. A. Brightsen and other colleagues at NSEC, and with Professors Truman P. Kohman of Carnegie Tech. and Paul K. Kuroda of the University of Arkansas.

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Unit-Cell Dimensions of Natural and Synthetic Scapolites

Abstract. In natural scapolites the cell dimension *a* shows a regular increase from marialite to meionite composition, while *c* remains constant. Both *a* and *c* of synthetic meionite are larger than the corresponding dimensions of synthetic marialite. The cell volume of both natural and synthetic scapolites is a nearly linear function of composition. Variations in cell dimensions of scapolites may be caused by differences in structural state similar to those in plagioclase feldspars.

Scapolites are important constituents of certain marbles, skarns, volcanic rocks, and altered gneisses and igneous rocks. Most natural scapolites belong to a solid-solution series consisting primarily of the ideal end members marialite ($3NaAlSi_3O_8 \cdot NaCl$) and meionite ($3CaAl_2Si_2O_6 \cdot CaCO_3$). Scapolites are tetragonal, with the most probable space group *I4/m* (*1, 2*). Synthesis of pure marialite was recently achieved (*3*). The meionite synthesis reported earlier by Eitel (*4*) has also been substantiated.

Published values for the cell dimensions *a* and *c* of a variety of natural scapolites show no systematic relationships when plotted against each other or against composition. Recently Shaw (*5*), in an extensive review of the geochemistry of scapolites, presented six new analyses. Burley, Freeman, and Shaw (*6*) found a reasonably good correlation between $[2\theta(400) - 2\theta(112)]$ and composition for these analyses. However, their determination of the space group appears to be in error, as it differs from that reported by Pauling (*1*) and Gibbs and Bloss (*2*) from single-crystal data.

Shaw kindly supplied us with samples of the analyzed scapolites. Values of 2θ of the (130), (301), (112), (321), (400), (141), and (312) reflections were carefully measured in duplicate with a Norelco x-ray spectrometer, with quartz ($a = 4.9131$ A, $c = 5.4046$ A at 18°C) as internal standard. Precise cell dimensions were then calculated on a digital computer, with a least-squares refinement procedure. The results are plotted in Fig. 1, with the compositions given as calculated from the analyses by Shaw (*5*). Also plotted are the cell dimensions, calculated in the same way, of six samples of synthetic marialite synthesized at 1 atm, in 80 to 450 hours, at temperatures between 770° and 850°C; and of five samples of synthetic meionite synthesized at CO_2 pressures between 1 and 4 bars, in 70 to 340 hours, at temperatures between 850° and 975°C (see also *3*). The cell dimensions of two scapolites published by Gibbs and Bloss are also included in Fig. 1.

No systematic relationships were noted between the conditions of synthesis of marialite and meionite and the cell dimensions. The mean values of the cell dimensions, together with standard errors of the cell dimensions estimated from the range of values obtained from different samples, are as follows: synthetic marialite, $a = 12.064$ A ± 0.008 A, $c = 7.514$ A ± 0.004 A, cell volume = 1093.5 A^3 ± 1.1 A^3; for synthetic meionite, $a = 12.174$ A ± 0.008A; $c = 7.652$ A ± 0.015 A, cell volume = 1134.1 A^3 ± 1.3 A^3.

Values of *a* of natural scapolites increase regularly with increasing meionite content (Fig. 1*a*), while the value of *c* is apparently independent of composition (Fig. 1*b*). In synthetic scapolite,

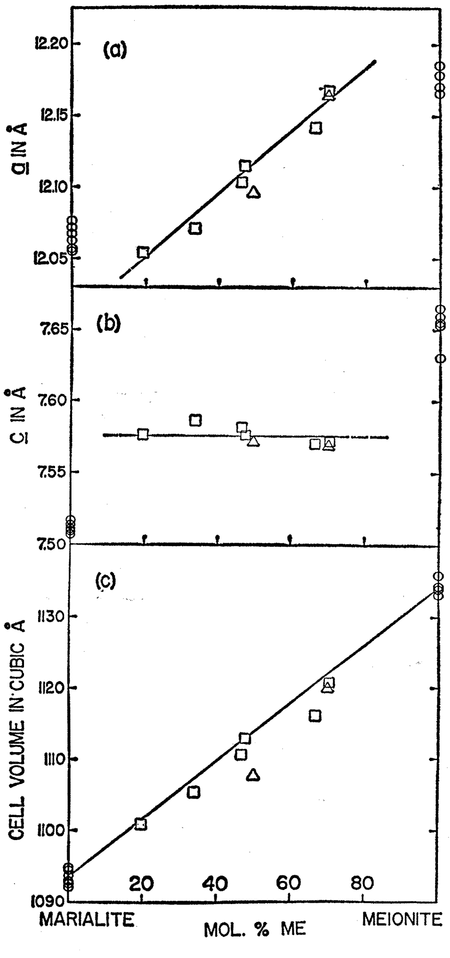

Fig. 1. Cell dimensions and cell volume of natural and synthetic scapolites, plotted as a function of mole percentage of meionite. Circles, synthetic scapolites; squares, natural scapolites of Shaw (*5*); triangles, natural scapolites of Gibbs and Bloss (*2*).