reaction vessel and heat treated at 400°C and 1 kb total pressure for a period of over 20 days. During this period both mixtures reacted completely to form apatite. On microscopic examination no other phases were found.

The synthesized apatite was anhedral and had an average crystal dimension about 0.001 mm. Under the microscope the larger crystals, almost 0.003 mm, show faint birefringence. The carbon dioxide contents were determined by dissolving the samples in hydrochloric acid and collecting the liberated carbon dioxide in a weighing tube containing ascarite-magnesium perchlorate. By this method, the carbonate hydroxylapatite was found to contain 2.29 percent of carbon dioxide (by weight), and carbon dioxide was not detected in the carbonate-free hydroxylapatite. Apatite from Durango, Mexico, was analyzed and found to contain 0.05 percent carbon dioxide.

Analyses of the two samples and weight loss data are given in Table 1. The carbonate apatite is characterized by a deficiency in both phosphorus and calcium compared to hydroxylapatite. Substitution of the carbonate ions for phosphate ions coupled with the substitution of hydronium ions for calcium ions could easily explain these differences. The carbonate apatite lost several percent of volatile substances on heating to 1120°C; whereas the hydroxylapatite lost no weight. Heating to 1460°C results in a weight loss for both samples, although the *heated product is still apatite, and the heated carbonate apatite still effervesced in acid, indicating that some carbon dioxide is still contained in the material.* As a result, the analyses in Table 1 plus the total weight loss with heating to 1460°C do not and should not total 100 percent. Glass was not found by microscopic examination of the heated material.

Dimensions of the unit cell of the synthesized apatite was determined by x-ray powder diffraction. The average value was obtained from (300), (310), and (410) for $a_0$ and (002) was used for $c_0$ (see Table 2 where they are compared with apatite from Cerro de Mercado, Durango, Mexico).

There is no significant difference in $c_0$ between pure hydroxylapatite and a carbonate-bearing hydroxylapatite. The $a_0$ dimension, however, shows a slight increase for the substitution of carbonate containing hydroxylapatite. Such an increase, although slight, is opposite to that reported by McConnell (*2*) and by Altschuler *et al.* (*3*) for natural fluorapatite and carbonate fluorapatite. Possibly there are chemical differences other than the carbonate contents of the natural materials.

Omega index of the synthesized carbonate apatite is 1.637 ± .002, and that of the hydroxylapatite is 1.642 ± .002. Simpson (*4*) synthesized hydroxylapatite in the presence of other calcium phosphate phases and a large excess of water and found the omega index of the apatite to be about 1.652. The reason for the difference is unknown. Possibly the previously studied material was phosphorus-rich or the $H_4O_4^{-4}$ ion has a significant role in either or both materials.

Thus, a coupled substitution of carbonate and hydronium ions for phosphate and calcium ions, respectively, takes place in apatite. Substitution of 2.29 percent carbon dioxide very slightly increases the $a_0$ dimension and decreases the omega index of refraction. Neither the index nor the lattice dimension show sufficient change to be useful for establishing the carbonate content of apatite.

DALE R. SIMPSON
*Department of Geology, Lehigh University, Bethlehem, Pennsylvania*

### References and Notes

1. D. McConnell, *Naturwissenschaften* **47**, 227 (1960).
2. ———, *Bull. Soc. Franc. Mineral. Crist.* **75**, 428 (1952).
3. Z. S. Altschuler, E. A. Cisney, I. H. Barlow, in abstracts of International Geological Congress, *Compt. Rend.* **9**, section XI (1953).
4. D. Simpson, *Am. Mineralogist* **49**, 363 (1964).
5. R. Collins, *J. Am. Chem. Soc.* **81**, 5275 (1959).
6. W. G. Perdok, *Schweiz. Monatschr. Zahnkeilk.* **62**, 249 (1952).
7. O. R. Trautz, *Ann. N.Y. Acad. Sci.* **60**, 696 (1955).
8. D. McConnell, personal communication (1964).
9. ———, *Am. Mineralogist* **45**, 209 (1960).
10. Supported by NIH grant DE-01959.

2 December 1964

■

# Lead Isotopes in Gasoline and Aerosols of Los Angeles Basin, California

Abstract. *The isotopic composition of lead isolated from antiknock gasolines and the aerosols of the Los Angeles basin was determined. The lead isotopic composition of the aerosols was similar to that of rural snow. The high concentration of lead in water of precipitation and that of the surface of the sea can be attributed to automobile exhausts.*

The lead content of rural snow, sampled at Lassen Volcanic National Park, California, is about 1.6 μg/kg (*1*). This high concentration of lead could not be accounted for by soil dust, and the contamination was attributed to industrial pollutants. The source of the lead contaminants can be identified by their isotopic composition because each lead ore has its characteristic isotopic composition (*2*). We now report on the isotopic composition of leads in antiknock gasoline and in the aerosols of the Los Angeles basin, California. The aerosols were collected from an electrostatic air filter at the Geochemistry Laboratory of the California Institute of Technology (Pasadena) during the spring of 1964. The sooty deposits consisted of about 5 percent ash, which contained about 50,000 parts of lead per million. Gasoline samples were purchased from service stations in the San Diego area in May 1964, and the aerosols were gathered during the same period. The lead content (mean) of antiknock gasoline is 2.1 g per gallon (*3*). The lead in the gasoline and in the air filtrate was extracted by refluxing with concentrated hydrochloric acid for several hours. This lead was then isolated and purified by dithizone extraction (*4*). Mass spectrometric analyses were performed at the California Insti-

Table 1. Isotopic composition of leads in gasoline and aerosols.

| Sources | Ratio of $Pb^{206}$ to | | |
|---|---|---|---|
| | $Pb^{204}$ | $Pb^{207}$ | $Pb^{208}$ |
| | *Gasolines* | | |
| Wilshire D | 18.14 | 1.160 | 0.4771 |
| Wilshire Regular | 18.10 | 1.156 | .4751 |
| Douglas | 18.05 | 1.152 | .4745 |
| Standard Oil Regular | 17.92 | 1.142 | .4724 |
| Shell Oil Regular | 17.38 | 1.115 | .4650 |
| Average | 17.92 | 1.145 | .4728 |
| | *Other sources* | | |
| Los Angeles aerosols | 18.04 | 1.154 | 0.4746 |
| Lassen Volcanic Park snow (*1*) | 18.01 | 1.144 | .4690 |
| 1947 Tetraethyl lead (*6*) | 18.69 | 1.204 | .4880 |
| Pacific sediment lead (*5*) | 18.73 | 1.197 | .4836 |

tute of Technology with an instrument having a 30-cm radius and solid source (Table 1).

The first four gasoline samples (Table 1) showed a uniform lead isotopic composition within analytical error. Lead composition of the Shell regular gasoline differed slightly from the average, but this lead alkyl may have been manufactured by another chemical plant. Comparison of the isotopic composition of lead in the Los Angeles basin aerosols with that of the average gasoline lead indicates that these two kinds of lead are indentical within the limits of measurement error. The isotopic composition of such lead represents a typical "tertiary" age lead which is less radiogenic than that of the common "modern" lead. The average isotopic composition of the Pacific sediment lead which represents a "quaternary" age (*5*) is also listed in Table 1 for comparison.

The isotopic composition of lead in the 1963 winter rural snow (*1*) is also similar to that of the Los Angeles basin aerosols. The difference between the rural snow and the aerosols with respect to the ratio of $Pb^{206}$ to $Pb^{207}$ was about 0.8 percent. This could be due to the measurement error or to lead alkyls of slightly different lead isotopic composition.

The isotopic composition of lead in the tetraethyl lead manufactured by the Ethyl Corporation in 1947 is given in Table 1. This analysis was performed by Diebler and Mohler (*6*) on a gas source instrument with errors of about ± 1 percent for $Pb^{206}$, $Pb^{207}$, and $Pb^{208}$, and of about ± 5 percent for $Pb^{204}$. This antiknock additive which was manufactured 17 years ago had more radiogenic isotopes of lead than some present-day lead alkyls have; this suggests that the isotopic composition of the mixed pool of feed lead has changed slightly with time.

The average annual production of lead alkyls in the northern hemisphere is equivalent to about $2.7 \times 10^{11}$ g of lead for recent years (*7*). If one assumes that this quantity of lead alkyls was combusted and uniformly distributed on the surface of the northern hemisphere, it would amount to an average of 1.1 mg of lead per square meter. The average precipitation at Lassen Volcanic National Park is about 1 m per annum (*8*). Thus, the lead contamination from the leaded gasoline alone at Lassen Park is calculated to be 1.1 $\mu$g per kilogram of precipitation. A slightly high value for contamination will be obtained because Lassen Park is situated near industrialized regions.

Since the advent of antiknock gasoline in 1923, more than $2.6 \times 10^{12}$ g of lead in the form of lead alkyls have been marketed and combusted (*7*). Thus, the average cumulative contamination from industrial lead on the surface of the northern hemisphere is about 10 mg of lead per square meter from gasoline-burning alone. Within highly industrialized and motorized areas, such as the Los Angeles basin, the content of lead in the air should be several hundredfold higher than this average. Part of this lead has been discharging, directly or through runoff, into the oceans; and as pointed out by Tatsumoto and Patterson (*1*), only a short time span is required for the abnormal amount of lead now present in the surface sea water of the northern hemisphere to accumulate. Part of this contaminant has undoubtedly been incorporated into plants and animals (*7*). Because of the well-known toxicity of lead, the overall effect of lead pollutants in the air and on the ground cannot be ignored.

TSAIHWA J. CHOW
M. S. JOHNSTONE
*Scripps Institution of Oceanography, La Jolla, California*

### References and Notes

1. M. Tatsumoto and C. C. Patterson, *Nature* **199**, 350 (1963).
2. A comprehensive résumé of the isotopic composition of the major lead deposits was compiled by J. S. Brown, *Econ. Geol.* **57**, 673 (1962); and that of geochronologic important mineral lead was given by R. D. Russell and R. M. Farquhar, *Lead Isotopes in Geology* (Interscience, New York, 1960).
3. Private communication (1964) with J. Kozikowski of the Ethyl Corporation, Ferndale, Michigan. He stated, "Our records of March 1964 show that the national weighted average of tetraethyl lead content in premium gasoline was 2.49 ml TEL per gallon, and in regular grade gasoline, 1.82 ml TEL per gallon. One ml of TEL is equivalent to 1.057 grams of metallic lead. The ratio of premium-to-regular gasoline sales in the U.S. is about 30 to 70"; (TEL, tetraethyl lead). O. C. Blade [*U.S. Bur. Mines, Rept. Invest.* No. 4702 (1950)] gave the average content of 2.02 ml TEL per gallon of premium gasoline and 1.53 ml per gallon of regular gasoline, respectively. The averages were based on the analyses of 3659 samples from 135 companies. Evidently the lead alkyl content of gasoline has increased in recent years.
4. T. J. Chow and C. R. McKinney, *Anal. Chem.* **30**, 1499 (1958).
5. T. J. Chow and C. C. Patterson, *Geochim. Cosmochim. Acta* **26**, 263 (1962).
6. V. H. Diebler and F. L. Mohler, *J. Res. Natl. Bur. Stds.* **47**, 337 (1951).
7. C. C. Patterson, *J. Am. Med. Assoc.*, in press. We thank Dr. Patterson for making the statistical data available and also for his suggestions.
8. Based on the data of Manzanita Lake Weather Station, California, *U.S. Weather Bureau Climatological Data*, Washington, D.C. (1963).
9. Supported by the NSF and the ONR.

7 December 1964

## Thermal Neutron Activation: Measurement of Cross Section for Manganese-53

Abstract. *The product of the thermal neutron activation cross section and half-life for manganese-53 is* (350 ± 100) × $10^6$ *barn-years. If a value of* $2 \times 10^6$ *years is assumed for the half-life of manganese-53, then the cross section is 170 barns. This large cross section affords much greater sensitivity for the determination of manganese-53.*

The presence of $Mn^{53}$, produced by cosmic rays, in iron meteorites was predicted by Sheline and Hooper (*1*) and demonstrated by Honda *et al.* (*2*). It has since been measured in many iron and stone meteorites (*3*). Although the half-life of $Mn^{53}$ has not been determined directly by combining counting data with mass-spectrometric data, Kaye and Cressy (*4*) have estimated it to be $(1.9 \pm 0.5) \times 10^6$ years on the basis of measurements made on an iron meteorite of old terrestrial age and a stone meteorite of short cosmic-ray exposure age. Goel (*5*) found a half-life of $3 \times 10^6$ years by similar measurements on a meteorite whose exposure to cosmic rays had been relatively short. At present these values are the best estimates of the $Mn^{53}$ half-life.

Measurement of $Mn^{53}$ in meteorites requires hundred-gram samples and low-level counting systems equipped with heavy shielding and anti-coincidence guard counters. Since $Mn^{53}$ decays by pure orbital electron capture, only a soft x-ray is emitted, and the sample must be spread as thinly as possible to minimize self-absorption. If thermal neutrons are used to convert $Mn^{53}$ to 300-day $Mn^{54}$ according to the reaction $Mn^{53}(n,\gamma)Mn^{54}$, then the more easily measured 0.835-Mev $Mn^{54}$ $\gamma$-ray is made available. The purpose of the present work is the determination of the cross section for this neutron reaction.

The fast neutron reactions $Mn^{55}(n,2n)Mn^{54}$ and $Fe^{54}(n,p)Mn^{54}$ also produce $Mn^{54}$. Interference from the second reaction can be minimized by purifying the manganese sample prior to irradiation; interference from the first reaction can be reduced only by using a well-thermalized neutron flux.

The $Mn^{53}$ sample used for the irradiation was separated from the Odessa iron meteorite by Honda *et al.* (*2*). Their counting data for $Mn^{53}$ were used to calculate the $Mn^{53}$ activity in the