Reports

Lead Isotope Variation with Growth Zoning in a Galena Crystal

Abstract. *A large crystal of lead sulfide from Picher, Oklahoma, has significant differences in isotopic composition of lead in successive growth zones. Lead isotope ratios in the parent ore-fluid evidently changed with time during crystal growth. The growth history of this crystal, interpreted quantitatively, points to a tentative hypothesis of genesis of Mississippi Valley deposits of lead and zinc.*

Lead isotope variations detected in successive growth zones of a single crystal of galena are a fossil record of physical and chemical activity in the geologic environment when the crystal was growing. The data, even though superior in geologic control and analytical precision to previously published results, do not yield an unequivocal interpretation. The importance of the study, rather, is to show that the problem of the genesis of Mississippi Valley Pb-Zn deposits can be resolved by more elegant lead isotope studies.

Nier's first lead isotope analyses in 1938 (*1*) showed that lead from Joplin, Missouri, differed from ordinary leads and varied measurably in composition. This lead, abnormally rich in radiogenic Pb^{206}, Pb^{207}, and Pb^{208}, has come to be called "J-lead" (*J* for Joplin). This kind of lead is now recognized as distinctive of Mississippi Valley Pb-Zn ores, but its genetic significance is an unresolved mystery.

In an earlier article (*2*) we described a zoned galena crystal from "M" bed in the Picher (Oklahoma) field of the Tri-State mining region and reported preliminary lead isotope analyses that suggested variations in the relative abundances of the isotopes from one growth zone to another. The early measurements implied that radiogenic lead is present in increasing abundance in successively younger growth zones, concentrically arranged from a growth nucleus outward to the present crystal faces. Maximum differences reported were about 4 percent in abundance of Pb^{206}, and about 2 percent for Pb^{208}. Variations of Pb^{204} and Pb^{207} were within analytical error. New isotope analyses of higher precision (Table 1) now confirm the general nature of the early analyses and permit inquiry into geologic processes that might have caused the variations.

The sampling of the zoned crystal is of critical importance to this study and was described in the previous article, which was illustrated with photographs of the crystal (*2*, Fig. 199.1). The crystal was cut in half, and one sawed surface was etched to reveal growth structures within the crystal. The sampling of the growth zones is illustrated in figure 1*A* which shows the sites of sample I (approximate growth nucleus); samples F, G, and H (2 cube-faced samples and 1 octahedral-faced sample, all from the innermost growth zone observed); and samples E, D, K, C, and B from successively younger growth zones. Sample A, scraped from an exterior cube-face that had been previously cleaned with detergent, represents the outermost skin of the crystal (*3*).

The lead iodides were analyzed on a 12-inch radius solid-source mass spectrometer. The results on the crystal samples are reported in Table 1, together with five analyses of reference lead sample GS4 made during the investigation. The measurements were originally calculated as atom percent, but for convenience the data are presented in Table 1 as ratios to Pb^{204}. A reasonable statement of precision for the individual analyses of crystal samples is 0.5 percent for Pb^{204} and approximately 0.2 percent for the three major isotopes. This estimate is based on 32 analyses of the reference sample GS4 made during a longer period, 15 March 1962 to 15 January 1963 (*4*):

Atom %,	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
av. 32 runs	1.452	23.62	22.52	52.40
S.D.	$\pm 0.003_0$	$\pm 0.01_7$	$\pm 0.01_4$	$\pm 0.02_8$

The isotopic analyses (Table 1) indicate that the crystal has an inner core (samples I, F-G-H, and E)—about 10 percent of the crystal by volume—in which there are no variations greater than the analytical uncertainty. From sample E outward the isotopic composition varies progressively through growth zones D, K, C, and B. Outermost skin A deviates slightly from this sequence; it is intermediate in composition between samples B and C. The variations imply that several isotopes, especially Pb^{206} and Pb^{208}, have been added in increments that increase outward in successively younger growth layers.

The isotopic variations and their relation to crystal growth are represented in Fig. 2*A* which shows the Pb^{208}/Pb^{207} and Pb^{206}/Pb^{207} ratios for several growth zones expressed as permillage deviation from the isotopic composition of the growth nucleus I. The variations are plotted against the estimated number of lead atoms in the crystal as it grew, computed from the spacing of growth-zones sample. Isotopes Pb^{206} and Pb^{208} increase toward

Table 1. Lead isotope analyses of samples from galena crystal TSO-MK, and of reference sample GS4. Values are atom ratios.

No. and date (1962)	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
	Skin		
A* (10/18)	22.68	16.04	41.71
	Growth zones		
B* (10/ 9)	22.92	16.10	42.02
B* (10/22)	22.84	16.03	41.90
C* (10/15)	22.56	16.02	41.58
K† (10/ 8)	22.56	16.11	41.83
D* (10/23)	22.38	16.05	41.61
D‡ (12/11)	22.33	16.04	41.54
D† (12/10)	22.33	16.03	41.48
	Core		
E* (10/10)	21.95	16.00	41.31
E† (12/ 7)	21.91	15.99	41.17
F* (10/12)	22.00	16.04	41.41
G† (10/19)	22.01	16.06	41.38
H* (10/11)	21.96	16.01	41.22
I* (10/17)	21.97	16.05	41.30
	Reference sample GS4		
(10/ 5)	16.26	15.53	36.08
(10/16)	16.27	15.50	36.01
(10/24)	16.28	15.49	36.01
(12/ 6)	16.26	15.49	36.03
(12/14)	16.20	15.44	35.90

* Original PbI_2 preparation used in previous study (2), prepared by R. G. Milkey. †New galena sample and PbI_2 prepared by I. C. Frost or J. C. Antweiler. ‡ Original PbI_2 repurified and reprecipitated by J. C. Antweiler.

the exterior of the crystal. The variations evidently resulted from progressive changes in the isotopic composition of lead in the ore-forming fluid during the growth of the crystal.

Various working hypotheses can be invoked to account for the changes in composition of ore-lead as the crystal grew. Some hypotheses would involve the gradual evolution of lead by radioactive decay of U and Th within a closed geologic system. Such hypotheses have a built-in rate factor that would imply that this crystal grew during a long span of geologic time, of the order of 10^8 years. Other hypotheses would invoke simple mixing of two different leads, either two J-leads like samples I and B, or an ordinary lead with pure radiogenic lead. But if the variations in the crystal are a record of an episode in the growth of a Tri-State ore body, and in the genesis of Mississippi Valley J-leads in general, as seems likely, then the genetic process was one that progressively modified the composition of ordinary lead by adding increments of radiogenic lead.

The variations within the crystal give some basis for calculating the composition of the radiogenic increments and the kind of ordinary lead that may have been involved. The Pb^{208}/Pb^{206} ratio in the incremental lead is constant within analytical uncertainty (Fig. 2*B*). The role of Pb^{207} in the radiogenic increment is tested in Fig. 2*C*. The 45-degree solid line would represent no addition of Pb^{207}, whereas the actual measurements suggest that small increments of Pb^{207} are probably present, within the range from a Pb^{207}/Pb^{206} ratio of zero (no added Pb^{207}), through 0.046 (the present-day ratio), to 0.069 (the ratio in which lead was being produced by uranium decay 500 million years ago). The reported variations in Pb^{207}/Pb^{204} ratio (Table 1) are within the analytical uncertainty, and improvement in analytical precision of at least an order of magnitude will be needed to define these small variations. The uncertainty of the present data is indicated in Figs. 2*B* and 2*C* by the five replicate analyses of reference sample GS4, plotted as permillage deviations from the mean.

The progressive covariation of all three radiogenic isotopes is best seen on trilinear coordinates. Figures 1*B* and 1*C* show this covariation for the crystal data in relation to a curve representing the evolution of ordinary lead (*5*) as well as published data (*6*) on Mississippi Valley J-leads in general and J-leads of the Tri-State mining region in particular. The variations within this single crystal are similar to and about half as large as the total variations reported for galenas from several ore-bearing horizons and from a number of mines throughout the Tri-State district. The variations in the crystal data equal about one-fifth of the overall variation of Mississippi Valley J-leads and are more nearly linear than the variations in any other set of such data yet reported.

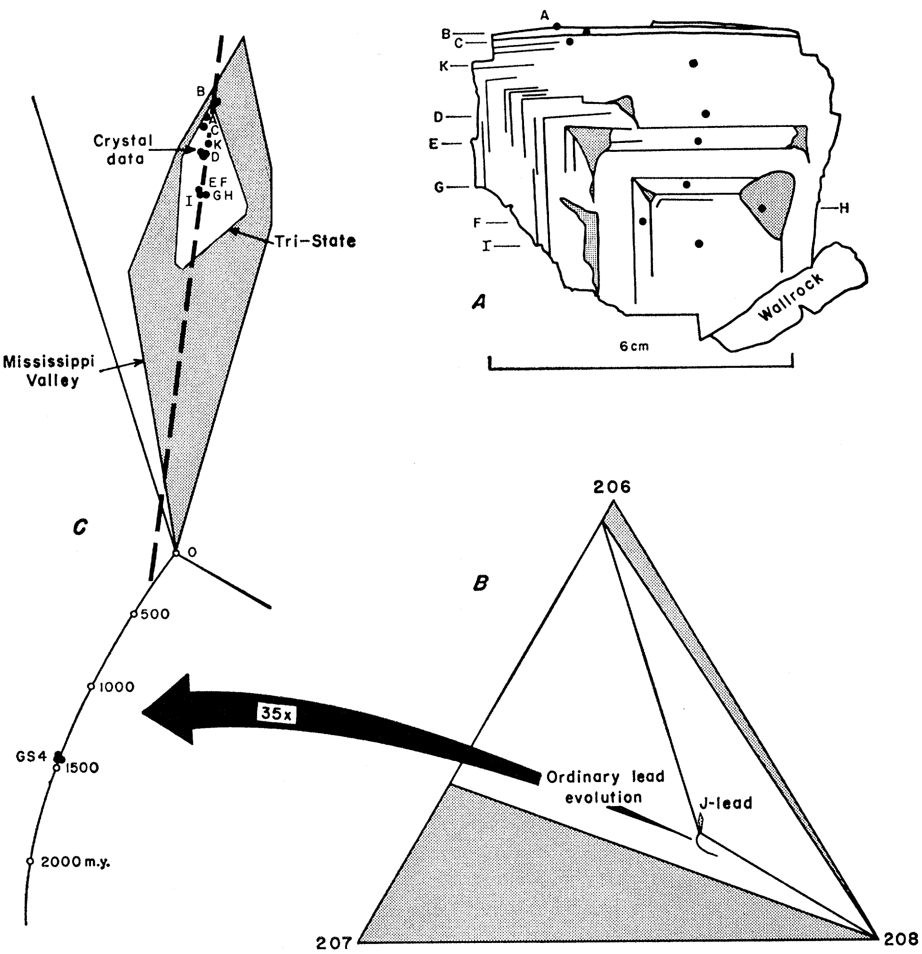

Fig. 1. Sampling and isotopic variation of growth zones of cross-sectioned galena crystal TSO-MK. (*A*) Sample sites. (*B*) J-leads and ordinary lead evolution on three-component diagram. (*C*) Detail of *B* (×35), showing trend (dashed line) of crystal data (dots) in relation to Tri-State (white area) and Mississippi Valley (stippled area) J-leads, and evolution of ordinary lead (curve).

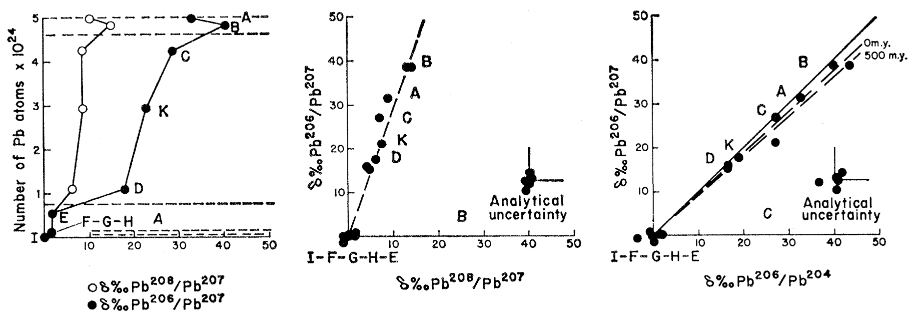

Fig. 2. Variations in lead isotope ratios. (*A*) Pb^{208}/Pb^{207} and Pb^{206}/Pb^{207} variations versus cumulative number of lead atoms, as measured from growth nucleus I. Dashed lines represent growth zones. (*B*) Pb^{208}/Pb^{207} versus Pb^{206}/Pb^{207}, as variations from the core E-F-G-H-I. Dashed line represents mean ratio in which Pb^{208} and Pb^{206} were added. (*C*) Pb^{206}/Pb^{204} versus Pb^{206}/Pb^{207}. Solid line represents no additions of Pb^{207}; dashed lines show amounts of Pb^{207} in lead being generated by uranium-decay now, and 500 million years ago.

Note that the Mississippi Valley leads (Fig. 1*C*) vary in composition from ordinary lead to J-leads even more radiogenic than the outer growth zones of the crystal. The data for the crystal, when extrapolated (dashed line) in the direction of ordinary lead, intersect our lead evolution curve (*5*) at about 300 million years. It is therefore permissible to interpret the crystal as a product of simple mixing of such ordinary lead, having model age of 300 million years, with radiogenic lead. The data for the crystal, extrapolated in the opposite direction, give a solution for radiogenic lead composed of Pb^{206}, Pb^{207}, and Pb^{208} in the ratio 1.0:0.055:0.75. Radiogenic lead of this composition would have been forming in an environment with Th/U about 2.2, at a time about 200 million years ago. The radiogenic component would account for about 9 percent of the mixture in the core of the crystal, and about 11 percent in outer growth layers.

Translated into terms of geologic process, these isotopic variations seem to imply progressive leaching of lead, probably during a protracted period of time, from rocks with appropriate content of lead, uranium, and thorium. The data seem to imply source rocks younger than Precambrian, presumably some of the Paleozoic sedimentary rocks within which the Tri-State ores were deposited. Growth of the zoned crystal would seem to have occurred intermittently, during part or all of a period some 300 to 100 million years ago, equivalent to late Paleozoic and Mesozoic time on the Holmes timescale.

With the help of appropriate geologic sampling and more precise isotopic measurements, further studies of isotopic variations of this kind will ultimately show whether this simple hypothesis, or some other, best explains the genesis of Mississippi Valley J-leads.

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References and Notes

1. A. O. Nier, *J. Am. Chem. Soc.* **60**, 1571 (1938).
2. R. S. Cannon, Jr., K. L. Buck, A. P. Pierce, U.S. Geol. Survey Profess. Paper 450-E, in *Geological Survey Res. 1962* (1963), art. 199, pp. E73–77.
3. Sampling of the crystal was done by Cannon; chemical treatment by J. C. Antweiler, I. C. Frost, or R. G. Milkey; isotopic analysis by Delevaux; and mathematical study by Pierce and Cannon. Further details are reported elsewhere (*2*). The lead iodides prepared of samples A, B, C, D, E, F, H, and I for the original study were again used for isotopic analysis. Iodide B was split and analyzed in duplicate. Iodide D also was split: one half was used "as is," and the other half was repurified and reprecipitated as iodide. In addition, new galena samples were cut from the crystal from new positions G and K and from old positions D and E, purified, and precipitated as PbI_2.
4. M. H. Delevaux, U.S. Geol. Survey Profess. Paper 475-B, in *Geological Survey Research 1963* (1963), art. 42, pp. B160–61.
5. The curves on Figs. 1B and 1C represent our empirical solution for the isotopic evolution of ordinary lead during the past 4.55×10^9 yr: R. S. Cannon, Jr., A. P. Pierce, J. C. Antweiler, K. L. Buck, *Econ. Geol.* **56**, 1 (1961); and *Petrologic Studies,* Geol. Soc. Am. special vol. (1962), pp. 115–131.
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Strontium-90 Accumulation on Plant Foliage During Rainfall

Abstract. *Accumulation of strontium-90 in field-grown crops was measured during the spring of 1962. Each rainfall markedly increased the strontium-90 content of the crops, except when the plants were very small. Accumulation between rains was comparatively small, about equal to the expected uptake from the soil.*

Much of the strontium-90 in agricultural crops in recent years has accumulated by direct deposition of fallout on the plants (*1*). During early 1962, the rate of strontium-90 fallout was greater than that in previous years. During this period the effect of rainfall on accumulation of strontium-90 in crops was studied.

Four crops were grown at a humid location (Everglades Experiment Station, Belle Glade, Florida) and an arid one (Southwestern Irrigation Field Station, Brawley, California). Sweet corn, cabbage, and potatoes were grown at both locations. In addition, snap beans were grown at Belle Glade and soybeans at Brawley. One acre of each crop was grown according to recommended commercial practices in each area.

The crops were sampled several times weekly during a 6-week period of active vegetative growth in April and May. At least three randomly selected subplots of 4 square meters each were harvested to make up each crop sample. The sample was cut at from 5 to 7 cm above the ground. Care was taken to avoid soil contamination, but the samples were not washed. They were dried and ground at the field locations. At the end of the sampling period, nine samples of each crop were selected for strontium-90 analyses. At Belle Glade, the selected samples were those taken immediately before and after three rainy periods which occurred during the sampling period, and at nearly equal intervals between rains. Since no rainfall occurred at Brawley, the selected samples were those taken at nearly equal intervals over the entire sampling period.

Concurrently with crop sampling, samples were taken to determine strontium-90 concentrations in rainfall, air, and soil at each location. Rainfall was collected in pans, in which a layer of dilute strontium nitrate solution was maintained. Dust that settled in the pans during dry periods was analyzed in addition to the rainfall samples. Airborne strontium-90 was collected by drawing air through a highly efficient cellulose-asbestos filter, 20 cm in diameter, at the rate of about 1200 m^3/day. Core samples of soil were taken in several increments to a depth of 45 cm at Belle Glade and 35 cm at Brawley.

The strontium-90 content of the samples was determined at Beltsville, Maryland. Crop samples were dry-ashed and dissolved in HCl. Rainfall samples were evaporated to dryness and digested in 6*N* HCl, as were the air filters. Soil samples were extracted with 1*N* $Sr(NO_3)_2$ to obtain only the exchangeable strontium-90. All strontium-90 determinations were made after radioactive equilibrium had been re-established by separating the yttrium-90 daughter and following its radioactive decay.

All crops increased many times in dry weight during the sampling period. At both locations, sweet corn attained the greatest weight at the final harvest, 840 g/m^2 at Belle Glade, and 560 at Brawley. The corresponding weights at the first harvest were 45 and 20 g/m^2. Similar weight increases were obtained with the other crops. The final harvest weights (g/m^2) were: at Belle Glade, snap beans, 340; cabbage, 230; potatoes, 150; at Brawley, cabbage, 300; soybeans, 150; and potatoes, 110. The weights of all crops increased steadily over the sampling period without marked increases after rainfall at Belle Glade or irrigation at Brawley.

Strontium-90 contents on an area basis (Fig. 1) were obtained by multiplying the concentration in each sample times the corresponding yield from the