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Variations in the Isotopic Composition of Common Lead and the History of the Crust of the Earth

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Variations in the Isotopic Composition
of Common Lead and the History of
the Crust of the Earth

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June 1955

Submitted by George L. Bate in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

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ABSTRACT

Isotopic analyses have been completed on 161 samples in a reconnaissance of lead minerals from all the major continents, the majority coming from North America. The analyses were made with a 6-inch radius, 60° Nier-type, direction-focussing mass spectrometer utilizing lead tetramethyl vapor for sample introduction. Intercalibration analyses show that relative abundances of the three heavier isotopes, Pb^{206} , Pb^{207} , Pb^{208} , obtained with the spectrometer agree to .5% with those reported by other investigators. Agreement on the lightest and least abundant isotope, Pb^{204} , is generally within 1%.

The majority of previous investigators have studied isotopic composition of lead ores relative to their age and genesis on the basis of the simplest possible model, herein referred to as the step-differentiation model, which assumes broad uniformity of crustal conditions affecting lead mineralization and neglects secondary effects. On the basis of this model, isotopic compositions of the common leads reported in this work are generally in agreement with their geologic age. Data for a few dated samples have been fitted to the step-differentiation model by a least squares analysis. The constants required for best fit are in good agreement with those obtained by earlier workers, but incorporation of meteoritic lead composition as primeval lead composition leads to an age of the earth's crust which is considerably larger than those obtained without meteoritic lead data.

This discrepancy has led to formulation of a model which permits continuous differentiation of the earth's crust throughout geologic time in an exponential manner. The constants introduced are evaluated independently of lead ore data and these calculations show that the maximum age of the earth is approximately 5.3 billion years, this being the time when terrestrial lead had the composition of meteoritic lead. In like manner it is shown that the major portion of the differentiating forces was expended in a time somewhat in excess of a billion years.

The isotopic composition of a number of leads is found to diverge markedly from that predicted on the basis of the step-differentiation model, and these anomalies are delineated together with their characteristics. Special consideration is given to the Joplin-type anomaly which is characterized by a moderate excess of the radiogenic isotopes, and is found to be prevalent throughout the several lead districts of the Mississippi Valley. To account for this anomaly, a hypothesis is advanced which involves inhomogeneous extraction of lead from original or contaminating sources. In this process it is pictured that on the basis of the known tendency of uranium and thorium to concentrate in interstitial rock material, their lead end-products are more easily removed in solution than lead inside mineral grains and thus give rise to leads with anomalously high radiogenic isotope content. Calculations based on the excess Pb^{206} and Pb^{207} in a number of the Mississippi Valley anomalous leads give an apparent age of about 2 billion years for the excess lead in these samples.

Average isotopic compositions for the anomalous Mississippi Valley leads and for other regions in the United States are tabulated. Consideration of other possible factors affecting isotopic composition leads to the conclusion that age, source, and mode of extraction are the main factors controlling isotopic constitution of lead in common lead minerals.

Introduction

The isotopic analyses of lead from twenty-five lead minerals reported by Nier and co-workers^{1, 2} in 1938-1941 showed that the isotopic composition depends upon geologic origin. Nier postulated that the variations are due to the addition of radiogenic lead (i.e. Pb^{206} , Pb^{207} , Pb^{208} formed from radioactive decay of U^{238} , U^{235} and Th^{232} respectively) to "uncontaminated lead" during geologic time. He also suggested that this "uncontaminated lead" should be identified with primeval lead, (German "Urblei") which may be loosely defined as the lead present at the time of formation of the earth's crust. The remaining stable lead isotope, Pb^{204} , is not known to be produced by any radioactive decay and all Pb^{204} existing today is therefore regarded as primeval. Accumulation of nuclear data and advances in nuclear theory since the Nier analyses have not revealed any process in nature whereby appreciable amounts of Pb^{206} , Pb^{207} and Pb^{208} may be formed (or destroyed), other than by the uranium and thorium decay schemes.

The current view on the geochemical occurrence of lead may briefly be described as follows. Lead in nature is found either dispersed as rock lead or concentrated as mineral lead. Since rocks also contain dispersed uranium and thorium in varying concentrations, it is seen that the isotopic composition of rock lead changes with geologic time due to the accretion of radiogenic lead from the decay of uranium and thorium. Rock lead may be extracted and separated from the host rock by various geochemical processes of differentiation and, depending on the efficiency of separation from the uranium and thorium, three types of minerals containing lead may be recognized: (1) common lead minerals, (2) uranium and

thorium minerals, and (3) mixed lead minerals.

If the separation of lead from a rock mass is essentially complete, common lead minerals are formed. In this case the lead isotopic composition does not change with time after the formation of the minerals and may reflect the isotopic composition of the rock lead from which it was formed at the time of mineralization. Common lead is most frequently found as galena, PbS . Uranium and thorium minerals contain lead from radioactive decay of the parent elements. The isotopic composition of the lead in these minerals changes with time and together with chemical analyses for lead, uranium and/or thorium, may be used to determine the age of the minerals by the several procedures of the lead-uranium method of age determination. These minerals may contain some common lead incorporated at the time of formation. Finally, if common lead and significant radiogenic lead are both present it is designated a mixed lead mineral. In this case the isotopic composition is independent of time although the $207/206$ ratio of the radiogenic component may give an indication of the time of formation.

Nier's common lead analyses formed the basis of a number of theoretical papers³⁻¹¹, in which it was attempted to establish the following: (1) A satisfactory model to account for lead ore formation from the rocks of the earth's crust; (2) a value for the age of the earth's crust; (3) the isotopic composition of primeval lead; and (4) a relation between the isotopic composition of mineral lead and the age of the mineral. The last three items follow from the type of model proposed in (1). McCrady¹¹ has reviewed the papers prior to his publication.

More recently a new fund of common lead isotopic data has begun to be published by laboratories in Canada¹²⁻¹⁵, Germany¹⁶⁻¹⁷ and the U.S.S.R.¹⁸. These data, together with Nier's original results have received further analytical

treatment by Damon^{19, 20} and have been summarized by Houtermans²¹. The various workers in the field have consistently cited the need for more lead isotopic abundance data.

The present work was undertaken with the purpose of (1) conducting a reconnaissance of common lead minerals of world-wide distribution to add to the growing fund of lead isotopic abundance data, and (2) to catalog in more detail the variations in isotopic composition of common lead in the United States. The data obtained provide the basis for a number of theoretical conclusions: (1) New limits on the possible variations in isotopic composition in various geologic settings can be defined. (2) This makes it possible to identify anomalous leads with greater certainty. (3) A revised model of crustal differentiation can be proposed. (4) The age of the earth's crust can be reassessed. (5) The relative abundances of uranium and thorium to lead in the earth's crust can be reevaluated. (6) It is possible to limit the speculation on the mechanism and origin of lead-ore formation. In summary, the acquisition of new common lead isotopic data permits further study of the history of the earth's crust, both in the broader aspects of crustal formation and composition, and in the local aspects of mineral formation throughout geologic time at various differentiating foci.

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The authors are especially indebted to the Offices of the Geological Survey of South Africa and of Southern Rhodesia for their excellent cooperation in providing a suite of common lead minerals from various pre-Cambrian strata in southern Africa. Dr. L. T. Nel, Director and Dr. B. Wasserstein of the Geological Survey of South Africa provided eight samples together with a description of their geological environment, from the Union of South Africa. A similar set of samples from

Southern Rhodesia with descriptions was supplied by Dr. R. M. Tyndale-Biscoe, Acting Director, assisted by Dr. A. M. Macgregor, of the Geological Survey of Southern Rhodesia.

The original mass spectrometer tube was designed and constructed by H. R. Owen. W. R. Eckelmann worked out the initial chemistry of lead tetramethyl preparation. Technical assistance on routine operations was necessarily extensive. J. Gaetjen, R. Nuckolls, J. Miller and M. Trautman assisted with tetramethyl preparation; D. Miller, W. Knox and J. Hoover helped with routine spectrometer operation; M. Feely, L. Tryon, J. Averill and A. Toleno assisted with the abundance computations. The valued assistance of our instrument makers, W. Tamminga and F. Gwinner, is also acknowledged with appreciation. W. F. Kelly assisted with bibliographic research on the geologic origin of various lead deposits.

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Mineral Selection

The choice of common lead minerals was restricted largely to those available in the various mineralogical collections so generously placed at the disposal of this laboratory. The samples were selected with as widespread distribution both in geographic location and geologic setting and age, as possible. Several suites of samples were chosen with a common geologic environment but with different mineral form, different mineral associations, etc., in order to search for possible effects on isotopic composition. In one case, two samples were taken from opposite ends of a large galena crystal in order to check possible isotopic fractionation with crystal growth. In some cases more than one sample was taken from a given locality with the purpose of checking variations in random samples.

It will be noted (see Table II) that for some of the localities selected, common lead analyses have previously been reported in the literature. The Lamont data for these localities are included here however, not only to permit comparison with the earlier analyses, but also to present the whole body of data accumulated with the use of one mass spectrometer at this laboratory. By way of summary for the 161 samples shown, a total of 121 localities are represented, 100 of which are new localities, without previously published common lead analyses.

Although the mineralogical collections were invaluable for the acquisition of samples, the value of some of the samples is diminished because of the lack of full description of the geographic and geologic source. A typical difficulty encountered is that some samples were originally collected from small mines whose operation ceased many years ago; consequently little or no further information can be obtained at the present time. In any event, the table contains all the pertinent information as to geographic origin and mineral association obtainable with each specimen.

Experimental Procedure

Chemical Preparation of Lead Tetramethyl

In order to introduce the lead into the mass spectrometer in gaseous form it was necessary to synthesize lead tetramethyl $\text{Pb}(\text{CH}_3)_4$ from the mineral lead samples. The general technique has been described in the literature²² and consists briefly of: preparation of pure lead chloride from the lead mineral; Grignard reaction with lead chloride; hydrolysis of excess Grignard agent; separation of ether solution of tetramethyl from water solution; separation of tetramethyl from ether by fractional distillation, completed by evaporation of excess ether under reduced pressure, until the vapor pressure corresponding to that for lead tetramethyl was observed on a mercury manometer. With an initial charge of about .3 gram lead chloride, the final yield of tetramethyl was of the order of a few hundredths milliliter by volume, sufficient for several runs of the spectrometer.

Contamination Effects

The possibility of appreciable lead contamination from the chemical reagents employed was ruled out on the basis of the following considerations. Only reagents of the highest purity commercially available were used and the possible lead content specified was very small compared to the amount of lead in the sample. Moreover, any lead present in the reagents would have been, most likely, common lead, and since the isotopic composition of common leads varies over small limits only, the effect on the isotopic composition of the sample would have been negligible. This conclusion was verified by two pieces of experimental evidence.

(1) An intercalibration sample was received in the form of metallic lead, and the typical chemical procedure in its entirety was used to prepare the lead tetramethyl

required for the analysis. The isotopic composition obtained was very close to that reported by other investigators for the identical sample (see Table I). (2) An even more conclusive proof was demonstrated in the following manner. A lead iodide salt was divided into two portions, one of which was converted into lead chloride for the Grignard reaction. Since the Grignard reaction will also take place with other halides, the remaining iodide portion was utilized directly for the Grignard reaction. The lead isotopic compositions of the two tetramethyls thus prepared were identical within limits of experimental error, and it was therefore concluded that contamination from inorganic reagents, the most likely source of contaminant, was negligible.

It was found that heavy organic residues were present in the tetramethyl sample, which could contribute to ion signals in both the Pb^+ spectrum and in the trimethyl spectrum. These impurities exhibited low vapor pressures relative to $\text{Pb}(\text{CH}_3)_4$ and were a source of trouble only if the sample container was heated. It was found that initially all of the $\text{Pb}(\text{CH}_3)_4$ could be transferred to the manifold by putting liquid air on a finger in the manifold while the sample container remained at room temperature. This process did not introduce any appreciable contaminants into the leak of the mass spectrometer.

Possible Fractionation

Further tests were conducted to detect any fractionation effects in the chemical procedure. It may be noted that in the last two steps of ether removal by fractional distillation and by evaporation, the effect of isotopic fractionation would be such as to favor removal of the lighter isotopes and thereby increase the percentage composition of the heavier isotopes in the residual sample. For the typical sample,

the fractional distillation reduced the volume of the ether solution by a factor of about 4 and the final evaporation involved a volume reduction by a factor of about 100. Although the predicted fractionation at the boiling temperature of the mixture based on the mass difference of the $\text{Pb}^{204}(\text{CH}_3)_4$, $\text{Pb}^{206}(\text{CH}_3)_4$, $\text{Pb}^{207}(\text{CH}_3)_4$, $\text{Pb}^{208}(\text{CH}_3)_4$ molecules, is negligibly small, two experimental tests were resorted to for the final proof. These tests simply consisted of repeating the fractionation and evaporation process two times, one process at a time, after adding a volume of ether equal to that just removed. Any effect originally present would have been multiplied by about a factor of 3, but although the tests were repeated several times on two different samples, no change from the original isotopic composition could be detected.

It is believed therefore, that errors in the data due to contamination or isotopic fractionation in the chemical preparation process are well within the experimental error reported.

Instrumentation of Mass Spectrometer

The mass spectrometer employed for the isotopic analyses was a direction-focussing 60° sector type instrument of glass-metal construction with 6" radius, previously made at this laboratory after a design originally reported by Nier²³. Following several modifications a mass resolution of better than 1 part in 220 was obtained, together with other characteristics suitable for work with the Pb^+ spectrum. A later re-alignment of the entrance and exit slits gave a mass resolution of nearly 1 part in 300, which permitted satisfactory operation in the range of the trimethyl spectrum.

The most important modification consisted of the utilization of a new source, designed essentially after that described by Palmer and Aitken²⁴ (Figure 1). The exit slit of the source was made .075 mm wide, and the entrance slit at the collector was made .3 mm wide in order to give maximum signal with optimum resolution. With these slit configurations the typical ion current at mass 208 was of the order of 10^{-11} ampere.

In order to avoid Hg^{204} at mass number 204, an oil diffusion pump was initially used to provide high vacuum in the tube. However, on prolonged use, increasingly large backgrounds of organic origin were encountered in the mass range of the lead spectrum, particularly at mass number 207. This background was essentially eliminated on replacement of the oil diffusion pump with a mercury diffusion pump. The 3-stage mercury pump also lowered the ultimate vacuum of the system to an indicated pressure (Research Corp. ionization gauge) of 5×10^{-8} mm Hg., as well as providing a considerable improvement in the pumping speed of the system. The forevacuum was maintained by a mechanical pump of 58 lpm free air capacity and rated with an ultimate vacuum of .1 micron.

A commercial high voltage supply (Beva Model 301) proved very satisfactory for the high voltage required for ion acceleration. The accompanying voltage divider loop was designed for our particular source requirements and is shown schematically in Figure 2. The electromagnet and magnet supply were also commercial items.

The emission regulator was slightly modified from a design reported in the literature²⁵. The schematic circuit is shown in Figure 3. The time constant

SOURCE ASSEMBLY FOR MASS SPECTROMETER

Figure 1. Source Assembly for Mass Spectrometer

Figure 2. Schematic of High Voltage Divider Circuit for
Mass Spectrometer Source

SCHEMATIC OF HIGH VOLTAGE DIVIDER CIRCUIT FOR MASS SPECTROMETER SOURCE

EMISSION REGULATOR CIRCUIT FOR MASS SPECTROMETER

Figure 3. Emission Regulator Circuit for Mass Spectrometer

of the control circuit was highly sensitive to the value of condenser C_1 and values larger than $.01 \mu\text{f}$ were found to give rise to regenerative conditions.

A commercial vibrating reed electrometer (Applied Physics Corp. Model 30) gave satisfactory amplification of the ion currents received at the collector. A voltage signal was developed in the usual manner by passing the ion current through a grid resistor of large resistance. The optimum value of 10^{11} ohms for the grid resistor was obtained by compromising the requirement of maximum signal with that of minimum noise for the greatest amplification used. The resultant time constant was larger than desired and necessitated a relatively slow scanning rate in order to allow the full signal to be developed at the peak heights.

With later improvement of the resolution and sensitivity which permitted use of the trimethyl spectrum, a grid resistor of 10^{10} ohms was found to be very satisfactory. This change substantially reduced the input time constant of the detecting system and permitted more rapid scanning.

The output of the vibrating reed electrometer was fed to a pen and ink recorder through a decade resistance box which served as a voltage multiplier. The gain control on the electrometer, together with the following voltage multiplier bridge permitted a complete range of amplification of ion current signals. The linearity of amplification of the combined system was checked by applying known signals from a standard potentiometer to the reed input.

The sample introduction system was made as simple as possible. In order to avoid contamination (from mercury or organic vapors) from diffusion pump vapors, the vacuum in the sample manifold was supplied solely by a mechanical pump followed by a liquid air trap. With an ultimate vacuum rating of $.1$ micron

Hg, the mechanical pump gave good pumping characteristics. It was found that tetramethyl vapor was readily absorbed on all types of stopcock grease, and it was therefore necessary to use a metal manifold with all-metal needle valves.

The sample pressure was reduced by admitting the gas into the spectrometer through a viscous leak. The leak was made by drawing out glass capillary tubing, giving a final capillary of some 30" in length with an average diameter of about 4 mils. A specially constructed gas inlet system for transfer of the gas from the low pressure side of the leak into the ion source proper is shown in Figure 4. This system provided for a highly efficient transfer of the gas, with the result that typical analyses were made at indicated tube pressure of $1 - 4 \times 10^{-7}$ mm Hg.

Operating Characteristics of Mass Spectrometer

Resolving Power

A useful and perhaps more definitive index of resolving power than the customary mass resolution, is the quantity Q defined by Geiss¹⁷, e.g., as the ratio of the ion current minimum between the peaks at mass numbers 207 and 208, to the maximum ion current at mass number 208. The optimum value obtained for our spectrometer was $Q \approx .05\%$, while for the average analysis the value of Q might be as high as $.3\%$. However, it was shown that for even higher values of Q the effect on the peak heights and therefore on the apparent isotopic composition varied only in a secondary manner with Q .

Extensive tests were made to determine the factors affecting Q , inasmuch as the resolving power occasionally became very poor, with no known change of

Figure 4. System for Transfer of Sample Gas to Ionization Chamber

SYSTEM FOR TRANSFER OF SAMPLE
GAS TO IONIZATION CHAMBER

the control parameters. No dispersion due to pressure effect alone could be established and none would be expected since the indicated tube pressure during analyses never exceeded 5×10^{-7} mm Hg. Variation of the position of the aligning magnet, of the source plate potentials, and of the electron accelerating potential affected primarily the intensity of the ion beam, and had little if any effect on the resolving power. It was observed however, that the resolution invariably decreased when considerable impurity (primarily ether) was present in the sample and moreover the apparent dispersion increased during an analysis. It was finally concluded that the primary cause of loss of resolution was the accumulation of surface charge on the walls of the tube. The fact that small ion currents (about 10^{-11} ampere maximum) were employed, made the instrument especially sensitive to surface charge accumulation. Preventive measures to avoid surface charge effects consisted of maintenance of clean metallic surface conditions within the tube, and of regular heating of the tube between runs.

In general, the resolving power of the instrument is considered more than adequate for the lead isotopic abundance reconnaissance undertaken in this work. Even for work on a regional basis the inherent resolution is sufficient, unless differentiation of isotopic compositions to better than .3% is required.

Background and Noise Effects

With the introduction of a mercury pump the background mass spectrum was reduced to a negligible level. After extended use a background common lead spectrum was consistently present, but since the 208 peak height was of the order of 1 mv, the background effect was disregarded in comparison to actual

sample signal, for which in a typical analysis the 208 peak height lay in the range of .5 - 1 volt. A substantial background signal was rarely observed in the trimethyl spectrum. The tube was baked for about 15 minutes between runs primarily to dissipate surface charge accumulated within the tube, and this procedure also had the beneficial effect of essentially eliminating memory effect from the preceding sample. The pumping speed of the vacuum system was such that on sample removal, peak heights were decreased by a factor of several hundred within a few minutes' time.

The use of a mercury diffusion pump necessarily introduced a background mercury spectrum which, under conditions of sustained baking, could not be entirely eliminated. However, since Hg^{204} constituted about only 1% of the signal at mass number 204, it is evident that errors in the Hg^{204} correction can contribute only errors of the second order to the Pb^{204} abundance.

The maintenance of a low noise level in the amplifying system depended in a critical manner upon proper shielding of the ion collector. With optimum shielding the noise level was of the order of .05 mv, which is quite negligible for the heavier isotopes and is not serious for the smaller Pb^{204} isotope, the signal for which rarely was less than 10 mv. The usual stability problem in a high-gain d.c. amplifier was not encountered with the vibrating reed electrometer, due to the reed method of changing the d.c. signal into an a.c. signal. The short term drift of the particular vibrating reed electrometer used was stipulated not to exceed .004 mv/sec, well within the required accuracy of analysis.

Drift in Ion Beam Intensity

With the higher value of input grid resistor previously noted, the time constant of the amplifying system was about 1 sec. With the relatively slow scanning rate required to permit full development of signals, the time required to scan through the lead spectrum from mass number 202 was about six minutes. Coupled with a drift rate in ion current of about .2% per minute, this factor was probably the major source of experimental uncertainty. The magnitude of the effect was substantially reduced, however, by applying a drift correction based on the assumption of a linear variation, to the recorded peak heights. This assumption was justified on the basis of the following two considerations. First, direct observation of drift by "sitting" on a peak showed that the drift rate was essentially linear. In the second place, the isotopic composition calculated with drift correction was identical to within .1% to that obtained without drift correction, the major difference being that the deviations were substantially reduced. Since the spectra were scanned alternately up-mass and down-mass, a composition calculated without drift correction would be expected to cancel the drift effect if the drift rate were linearly uniform. The fact that identical composition was obtained with both methods of calculation was taken as an indirect verification of linearly uniform drift rate.

Hydride Formation

A variable of particular importance in using the Pb^+ spectrum from $\text{Pb}(\text{CH}_3)_4$ vapor is the formation of PbH^+ . The efficiency of hydride formation is pressure and temperature dependent. However these variables are not known to change appreciably during the course of an analysis, and the hydride efficiency was in

fact never observed to change significantly during a run and was remarkably constant from day to day for long periods of time. The hydride efficiency is calculated from the ratio of the peak height at mass number 209, due to the hydride $\text{Pb}^{208}\text{H}^+$, to the peak height at mass number 208.

The hydride factor was found to be very sensitive to the electron accelerating voltage, which was variable over a range of about 90 volts. The isotopic composition of a sample was shown to be independent of the electron accelerating voltage, E_e , and hence independent of the hydride efficiency. It was found that the ion current increased with electron accelerating voltage to a maximum at about 40 volts, and then decreased on further increase of electron accelerating voltage. Higher values of the electron accelerating voltage were found to give rise to unstable source conditions and most of the analyses were therefore made with $E_e = 40$ volts. For this value of E_e , the efficiency of hydride formation was approximately 10%.

The operating performance of the spectrometer may finally be evaluated on the basis of the reproducibility of isotopic composition of a given sample. A reference standard sample of tetramethyl was analyzed nearly 40 times during the course of sample analyses, involving a time span of approximately one year. The average deviation of an analysis from the mean was about .2% for the heaviest isotopes and nearly .5% for Pb^{204} . These variations were usually within the deviation of each individual analysis. The greatest deviation observed was about .4 % for the heaviest isotopes and 2% for Pb^{204} .

Operational Procedure for Isotopic Analyses

The sample schedule was arranged so that no sample was analyzed twice in the same day, at the same time providing for a change in sample order on repeat analyses. With but few exceptions, all samples were analyzed at least twice. Two analyses usually gave results within the average deviations of each other and a third analysis was made if this condition was not met. Most of the analyses consisted of 10 single-peaked spectra or the equivalent.

The purity and amount of sample were initially checked by the nature of the spectrum obtained with a given sample manifold pressure and resulting tube pressure. Any sample purification further required was accomplished by pumping off repeated portions of the ether-rich vapor. For the typical analysis a sample pressure of about .5 mm Hg was required.

Allowing for tube bake-out between runs, the usual routine permitted 5 analyses during a 10 hour period. The reference tetramethyl standard was analyzed at various intervals to detect possible changes in performance of the instrument. For several of the Nier samples the reference tetramethyl was run before and after each analysis.

In general, the large number of analyses per unit time is the main advantage of the tetramethyl method. Without such a facility the number of samples herein reported would not have been possible.

Calculation of Abundances from the Pb^+ Spectrum

The sequence of computation for calculating the isotopic abundance from an analysis of the Pb^+ spectrum consists of: (1) correction of 204 peak for Hg^{204} ; (2) correction for drift in ion current intensity; (3) correction for resistance of secondary multiplier bridge coupled with (4) reduction to common scale on the

basis of amplification factors used; (5) reduction to percentage composition; and finally (6) hydride correction.

Mercury Correction

The mercury correction was made in the usual manner by computing the amount of Hg^{204} from the amount of Hg^{202} at mass number 202, using the known ratio of $\text{Hg}^{204}/\text{Hg}^{202}$. The measured ratio of $\text{Hg}^{204}/\text{Hg}^{202}$ from background spectra agreed with the value cited in the literature within the experimental error; however, the accepted value was used in the calculations due to the large uncertainty in the measured ratio, resulting from the small signals involved. As noted previously, the amount of Hg^{204} in the typical analysis was about 1% of the total 204 peak; hence any reasonable uncertainty in the $\text{Hg}^{204}/\text{Hg}^{202}$ ratio would have a very small effect on the Pb^{204} abundance. It was observed, however, that for some extreme cases in initial test analyses for which Hg^{204} comprised about half the signal at mass 204, the Pb^{204} abundance was experimentally identical to that later obtained with Hg^{204} down to the one per cent level. This was taken as evidence that the ratio used for $\text{Hg}^{204}/\text{Hg}^{202}$ was correct.

Drift Correction

Occasionally the change in ion current intensity during an analysis was so small that the drift correction was not necessary; but for most analyses it was necessary to apply the drift correction in order to obtain a true picture of the deviations. Since the 208 peak was the largest, the drift correction was applied so that all other peak heights were computed to give their true values at the time the 208 peak was recorded. The correction was computed by pairing spectra scanned

up-mass and down-mass and obtaining for each set an average drift rate from the percentage changes in peak height of the three heavier isotopes. The remainder of the calculation follows in a straightforward manner and, as noted before, is perfectly valid providing the drift rate is uniformly linear.

Scale Correction

When adjusting for the scale of amplification used, an additional small correction was made for the resistance of the voltage multiplier bridge following the vibrating reed electrometer. The resistance employed on the voltage multiplier varied from 10 to 90 ohms (to supply signal to a 10 mv recorder from maximum 1 ma reed current), which was not negligible compared to the electrometer output loop resistance of 2000 ohms. The correction follows directly from an elementary application of Ohm's law.

Hydride Correction

The true abundance of the isotopes is calculated from the peak heights observed on the recorder chart in the following manner. Let 204', 206', 207', 208' and 209' represent the observed peak heights of these isotopes (204' excludes Hg^{204}) and let 204, 206, 207, and 208 represent the corresponding true abundances. Both sets of numbers express percentage composition. The true hydride factor may then be written as:

$$C = 209'/208 = \text{Pb}^{208}\text{H}^+/\text{Pb}^{208+}.$$

From the nature of the hydride formation, the following equations can be written:

$$204' = 204 - C(204) = (1-C) 204 \quad (1)$$

$$206' = 206 - C(206) = (1-C) 206 \quad (2)$$

$$207' = 207 - C(207) + C(206) = (1-C) 207 + C(206) \quad (3)$$

$$208' = 208 - C(208) + C(207) = (1-C) 208 + C(207) \quad (4)$$

Now writing $k = \frac{C}{C/(1-C)}$, the foregoing equations become:

$$204 = (.1 + k) 204' \quad (5)$$

$$206 = (1 + k) 206' \quad (6)$$

$$207 = (1 + k) 207' - k (206) \quad (7)$$

$$208 = (1 + k) 208' - k (207) \quad (8)$$

Equations (6), (7), and (8) are actually three non-linear equations in the unknowns 206, 207, and 208, for which the exact analytical solution becomes somewhat cumbersome. This difficulty may be avoided and the roots may be obtained with the desired accuracy by using repeated approximations. For the first approximation $k' = 209'/208'$, and corresponding values of 206', 207', and 208' are calculated. The next approximation of k is $k'' = 209'/(208' - 209')$ and corresponding values of 206'' and 207'' and 208'' are computed. This is then followed with $k''' = 209'/(208'' - 209')$, etc., until the required precision is obtained. Usually the closure is so rapid that two approximations suffice.

For a given analysis, 204', 206', 207', 208', and 209' are actually the averages of percentage compositions of the individual scans comprising the analysis. For each average ion abundance an average deviation is computed. The average deviations of the true composition will have added uncertainty due to the error in the 209' peak. The effect of the hydride error was calculated for each analysis, but invariably the contribution to the error in the true composition was found to be small, usually negligible. The relative error in 209' never exceeded 1% and the resulting uncertainty contributed to the true abundances of the lead isotopes rarely approached .1%.

It is to be noted that the foregoing hydride correction assumes that the hydride efficiency obtained for Pb^{208} applies to the remaining lead isotopes. A possible systematic effect violating this assumption would consist of a mass discrimination in hydride formation. If such an effect did exist, the hydride factor for Pb^{204} would differ to the greatest extent from that obtained by Pb^{208} . However, even for Pb^{204} , the greatest possible effect on k , assuming a functional dependence as the square root of the ratio of the masses, would not exceed 1%. A systematic error in the hydride factor of this order of magnitude would introduce an uncertainty in the true abundances well within the experimental error reported.

Calculation of Abundances from the $\text{Pb}(\text{CH}_3)_3^+$ Spectrum

In the trimethyl mass region (mass numbers 248 through 254) there is no interference from mercury. The drift and scale corrections are made in an identical manner to that described under the calculation of abundances from the Pb^+ spectrum. The hydride effect is present but to a lesser extent than in the case of the Pb^+ spectrum. Additional corrections must be made in the $\text{Pb}(\text{CH}_3)_3^+$ spectrum for the $\text{C}^{13}/\text{C}^{12}$ effect and for the loss of a hydrogen atom.

The analytical expressions for the $\text{Pb}(\text{CH}_3)_3^+$ spectrum may be developed as follows. Let 249', 251', 252', 253', and 254' represent the observed signals at these mass numbers. Also, designate by 249, 251, 252, and 253 the true abundances of Pb^{204} , Pb^{206} , Pb^{207} , and Pb^{208} , respectively, appearing at the indicated mass numbers in the trimethyl spectrum. The $\text{C}^{13}/\text{C}^{12}$ ratio and hydride formation have the same effect of increasing the observed signal at mass number $(m + 1)$, at the expense of the signal at mass number m . Let p therefore represent

the fraction of the true signal at mass number m appearing at mass number $(m + 1)$ due to the combined effects of hydride formation and C^{13} appearance.

Similarly, let q represent the fraction of the true signal at mass number m lost to mass number $(m - 1)$ due to the loss of one hydrogen atom. Neglecting second order effects, the observed spectrum may be analytically expressed as follows:

$$249' = 249 - p(249) - q(249) = 249(1 - p - q) \quad (9)$$

$$251' = 251 - p(251) - q(251) + q(252) = 251(1 - p - q) + q(252) \quad (10)$$

$$252' = 252 - p(252) - q(252) + p(251) + q(253) = 252(1 - p - q) + p(251) + q(253) \quad (11)$$

$$253' = 253 - p(253) - q(253) + p(252) = 253(1 - p - q) + p(252) \quad (12)$$

$$254' = p(253)$$

Writing $r = p + q$ and $s = \frac{r}{1 - r}$, equations (9) through (12) may be implicitly solved for 249, 251, 252, 253:

$$249 = (1 + s)249' \quad (13)$$

$$251 = (1 + s)251' - q(1 + s)252 \quad (14)$$

$$252 = (1 + s)252' - p(1 + s)251 - q(1 + s)253 \quad (15)$$

$$253 = (1 + s)253' - p(1 + s)252 \quad (16)$$

As with the Pb^+ spectrum, equations (13) through (16) may be solved by repeated approximations. q was found to have a value consistently in the neighborhood of 1%. Small variations in this value would have a negligible effect on the final abundances. The value of p was fairly constant at 3.2%. If the C^{13}/C^{12} ratio is taken as .011, then the trimethyl hydride effect amounted to about 2.1%. This value is considerably larger than that of 0.33% reported by Dibeler and Mohler²⁶ and that of .08% reported by Collins, Russell and Farquhar¹³. The different values 0.33%, .08% and 2.1% are due presumably to differences in temperatures

of the sources, in geometric configurations of the electron beam, and in conditions of secondary emission.

The corrections in the trimethyl spectrum are therefore about one-third that in the Pb^+ spectrum. This is particularly important for the analysis of radiogenic lead where the correction factors from preceding and following common lead analyses must be assumed to be constant.

Results

Intercalibration Experiments

In the absence of a lead standard of known absolute isotopic composition, the only possible recourse to check possible systematic discrimination by a given mass spectrometer is to make comparison analyses of samples analyzed on other spectrometers. Unfortunately, at the time of research herein reported, no systematic program of comparison of lead samples at different laboratories was yet in effect, with the exception of the circulation of a reference lead sample by the United States Geological Survey. However, through the excellent cooperation of interested investigators, a number of samples were obtained which provide the basis for a correlation of the performance of our instrument with that of instruments at other laboratories.

The largest suite of samples for comparison purposes was provided by Dr. J. P. Marble in the form of a number of the identical lead salts used by Nier in his work^{1,2} previously referred to. The United States Geological Survey has recently circulated a "standard" lead sample for intercalibration purposes, and through the courtesy of Dr. L. R. Stieff, a portion of the U.S.G.S. "standard" was provided for this work. This identical sample has also been analyzed at Toronto, Canada, and at Harwell, England. Finally, two more samples were obtained which had been analyzed at Toronto and Oak Ridge.

The comparison of analyses of identical samples is displayed in Table I. All of the Lamont analyses shown are based on the Pb^+ spectrum, but later analyses of our reference standard in the trimethyl region gave results identical to those obtained on the basis of the Pb^+ spectrum. The comparison is even more significant in view of the different methods used for sample introduction. The lead was

Table I

Intercalibration and Comparison Analyses

Sample Specification		Isotopic Composition						
Source	Locality	Analysis by	204	206	207	208	208/204	208/206
Great Bear Lake, Galena		Nier No. 1	1.48	23.59	22.66	52.3	35.3	2.22
		Lamont No. 4	1.45(4)±.004	23.61±.08	22.59±.05	52.34±.05	35.75	2.217
Broken Hill, N.S.W., Galena		Nier No. 2	1.47	23.64	22.66	52.2	35.5	2.21
		Lamont No. 137	1.44(5)±.005	22.49±.04	22.49±.04	52.56±.06	36.37	2.236
Joplin, Mo., Galena I		Nier No. 7	1.26	27.29	20.02	51.4	40.8	1.88
		Lamont No. 73	1.25(1)±.004	27.26±.04	19.92±.03	51.57±.04	41.22	1.892
Joplin, Mo., Galena II		Nier No. 8	1.27	27.47	20.01	51.3	40.3	1.87
		Lamont No. 74	1.24(7)±.006	27.25±.06	19.90±.03	51.60±.07	41.38	1.894
Joplin, Mo., Galena III		Nier No. 14	1.23	27.47	19.87	51.43	41.8	1.87
		Lamont No. 75	1.23(5)±.004	27.38±.04	19.88±.03	51.50±.04	41.70	1.881
Metalline Falls, Wash., Galena		Nier No. 9	1.32	25.55	20.83	52.3	39.5	2.05
		Lamont No. 22	1.31(1)±.003	25.52±.04	20.75±.05	52.42±.05	39.98	2.054
Wallace, Id., Cerussite		Nier No. 10	1.48	23.80	22.40	52.32	35.26	2.198
		Lamont No. 23	1.41(7)±.006	24.22±.05	22.01±.04	52.35±.05	36.94	2.161
Tucson Mts., Ariz., Wulfenite and Vanadinite		Nier No. 11	1.37	25.20	21.27	52.17	38.1	2.07
		Lamont No. 36	1.35(0)±.007	25.00±.06	21.15±.04	52.50±.07	38.89	2.100
Casapalca, Peru, Bournonite		Nier No. 16	1.36	25.48	21.08	52.07	38.15	2.043
		Lamont No. 120	1.33(6)±.004	25.19±.04	21.06±.03	52.41±.04	39.23	2.081
Casapalca, Peru, Galena		Nier No. 17	1.35	25.42	21.13	52.11	38.62	2.050
		Lamont No. 121	1.33(3)±.004	25.22±.06	20.98±.07	52.47±.07	39.36	2.080

Table I, Continued

Sample Specification		Isotopic Composition						
Source	Locality	Analyses by	204	206	207	208	208/204	208/206
U.S.G.S. "Standard"		Harwell	1.45(5)±.007	23.64±.05	22.61±.03	52.30±.07	35.95	2.212
		Toronto	1.44(0)±.009	23.69±.02	22.54±.04	52.33±.04	36.34	2.209
		Lamont	1.44(4)±.007	23.50±.04	22.55±.04	52.52±.05	36.37	2.235
Goldfields No. 1, Sask., Can.		Oak Ridge	1.059	41.33	19.66	37.97	36.54	.9187
		Toronto	.981	42.25	19.52	37.26	37.98	.8819
		Lamont	1.02(6)±.007	41.05	19.86±.05	38.06±.09	37.10	.9038
Goldfields No. 2, Sask., Can.		Oak Ridge	1.35	26.64	21.34	50.67	37.53	1.902
		Toronto	1.31	26.98	21.32	50.39	38.47	1.868
		Lamont	1.31(5)±.004	27.10±.04	21.35±.04	50.23±.05	38.20	1.854

volatized from solid lead salts in the instruments used by Nier, Oak Ridge, and Harwell, while lead tetramethyl vapor was employed at Toronto and Lamont. The Toronto results also include analyses based on the lead trimethyl spectrum, in addition to the Pb^+ spectrum. It is significant that in spite of the considerable differences in chemistry, in method of ion formation, etc., the results are comparable to within a fraction of a per cent for the heavier isotopes, and to the order of a per cent for Pb^{204} . The greater divergence of values for Pb^{204} is to be expected from the relatively small signals obtained at mass number 204.

The results from the various laboratories are of further interest in that different geometry was used for beam collimation and focussing. The Nier spectrometer and the Toronto spectrometer were both 180° instruments while the Lamont, Harwell and Oak Ridge spectrometers are 60° instruments. In all cases magnetic scanning was used.

The Lamont analyses are averages of at least three runs in most cases. The Wallace, Idaho, cerussite was analyzed about a dozen times, for reasons enumerated below. The Pb^{204} composition is shown with parentheses about the fourth significant figure in order to emphasize that Pb^{204} does not have associated with it the same relative precision as in the case of the heavier isotopes.

A very close comparison of the Lamont analyses with the Nier analyses is not possible since Nier's numbers are stated to have a probable error of about .5%. It is observed that with the exception of Nier's sample No. 10 (Lamont No. 23), the compositions for the heavier isotopes generally agree within .5%, while the divergence for Pb^{204} may approach 2%, but more usually about 1%. A greater spread is to be expected for the Pb^{204} values, but it nevertheless

seems evident (see especially the seventh column in Table I) that relative to Nier's values, Pb^{204} is suppressed in the Lamont analyses. Such an argument based on comparison of Pb^{204} compositions alone would not be conclusive; however, the same trend is definitely reflected in the heavier isotopes (note especially the last column in Table I). Although the differences involved lie within the experimental uncertainty, the statistical weight of the numbers shows a trend toward a lower abundance of the lighter isotopes in the Lamont analyses as compared with those of Nier.

The distinct discrepancy between the analyses on the cerussite from Wallace, Id. (Nier No. 10) has no explanation. The sample was repeatedly analyzed under varying conditions, but the isotopic composition consistently differed as shown from that reported by Nier. It is suggested that the sample had in some manner become contaminated.

A comparison with more recent instrumentation is provided by the remaining analyses shown in Table I. For the U.S.G.S. "standard" the Toronto analysis is an average of five runs, four of which utilized the trimethyl spectrum and the fifth the Pb^+ spectrum²⁷. The Harwell analysis is an average of seven runs - three based on the PbCl^+ spectrum, two on the PbI^+ spectrum and two on the Pb^+ spectrum. Two analyses are shown for the Lamont measurements, and although the operating conditions were not highly satisfactory, circumstances prohibited further analyses prior to this publication.

In general, the analyses on the U.S.G.S. standard agree to about .3% for the heavier isotopes and the probable error in values for Pb^{204} is less than 1%.

For the remaining two samples the Lamont analyses are roughly intermediate between those reported by Oak Ridge and Toronto. The Goldfields No. 1 sample

has an anomalous composition and the discrepancies between the analyses are considerable. However, this sample was known to contain a small amount of uranium and the spread in composition reported may merely reflect inhomogeneity of samples. The Goldfields No. 2 is a more typical common lead and for this case the Lamont and Toronto values are in good agreement.

More data and greater precision are necessary for conclusive comparisons, but at this point there is just a suggestion that instruments utilizing volatilization of lead from the solid state give analyses tending to suppress the heavier isotopes, compared with analyses obtained with tetramethyl vapor. The internal precision claimed for the Lamont data is of the order of .2% for the heavier isotopes and .5% for Pb^{204} . On the basis of the foregoing comparisons, the Lamont analyses are comparable to those of the laboratories cited within .5% for Pb^{206} , Pb^{207} , and Pb^{208} and to within 1% for Pb^{204} .

Tabulation of Isotopic Analyses

The isotopic abundance data for the samples analyzed are tabulated in Table II according to geographic distribution. Of the 161 analyses shown, the majority are for samples from the North American continent. Unless otherwise noted, the mineral samples were obtained from the Economic Geology Collection and from the Systematic Mineralogical Collection, both of the Department of Geology of Columbia University. Most of the analyses were made with the Pb^+ spectrum. Those based on the trimethyl spectrum are denoted with an asterisk (*).

Although the experimental uncertainties for the various analyses do not vary greatly, they are shown as average deviations for each analysis in order to show to some extent the analyses with which greater precision can be associated. In

Table II
Isotopic Abundances of Common Lead

Sample Specification		Isotopic Composition					
No.	Locality	Mineral Description	204	206	207	208	207/206 208/206
North America							
Alaska							
1	Ketchikan	Galena	1.000 1.33(0)±.002	18.95 25.20±.05	15.89 21.13±.05	39.35 52.34±.08	.8385 2.077
2	Fish Creek Mining Property 5 miles north of Hyder	Galena	1.000 1.33(5)±.006	19.33 25.81±.07	15.64 20.88±.03	38.93 51.97±.07	.8090 2.014
Canada							
Northwest Territories							
3	Barren Grounds	Galena	1.000 1.35(6)±.004 1.00	18.35 24.88±.05 16.13	15.74 21.34±.03 15.43	38.66 52.42±.07 35.75	.8577 2.107
4 ^a	Great Bear Lake	Galena	1.46(4)±.004	23.61±.08	22.59±.07	52.34±.05	.9568 2.217
British Columbia							
5	Sullivan Mine, Kimberly	Galena and Sphalerite	1.000 1.40(0)±.004	17.31 24.24±.04	15.91 22.27±.06	37.21 52.09±.08	.9187 2.149
6	St. Eugene Mine, 200' level E. Kootenay District	Galena	1.43(7)±.006	16.41 23.58±.07	15.59 22.40±.06	36.59 52.58±.09	.9500 2.230
7	St. Eugene Mine, 1300' level East Kootenay District	Fine-grained Galena	1.44(2)±.006	16.48 23.76±.05	15.44 22.26±.05	36.44 52.54±.07	.9369 2.211

^aIdentical lead salt used by Nier from this locality. All of the Nier samples were provided through the kind cooperation of Dr. J. P. Marble, National Research Council.

Table II, Continued

No.	Locality	Mineral		204	206	207	208	207/206	208/206
		Description							
Saskatchewan									
8 ^b	Ace Mine, 2nd level Goldfield	Galena	1.000	14.36	14.96	34.49			
		concentrate	1.54(3)±.004	22.15±.04	23.09±.06	53.22±.06	1.042	2.403	
9 ^b	Ace Mine, 6th level Goldfield	Clausthalite	1.000	40.01	19.36	37.10			
		concentrate	1.02(6)±.007	41.05±.08	19.86±.05	38.06±.09	.4838	.9272	
10 ^b	Beaver Lodge Uranium Mine	Impure							
		Clausthalite	1.000	25.47	17.23	36.30			
		concentrate	1.25(0)±.008	31.84±.03	21.54±.04	45.37±.05	.6765	1.425	
11 ^b	Con Group, YY Concession Goldfields	Clausthalite	1.000	16.35	15.47	35.26			
		concentrate	1.46(9)±.007	24.02±.05	22.72±.05	51.79±.04	.9459	2.156	
12 ^b	Pitch Ore No. 8 Goldfields	Cleaned	1.000	20.61	16.24	38.20			
		Clausthalite	1.31(5)±.004	27.10±.04	21.35±.04	50.23±.05	.7878	1.854	
13 ^b	Reno Group No. 6 Goldfields	Clausthalite	1.000	28.96	17.56	36.51			
		concentrate	1.19(0)±.005	34.46±.07	20.90±.05	43.45±.08	.6065	1.261	
Ontario									
14	Eganville		1.000	23.28	16.00	42.24			
		Galena	1.21(2)±.005	28.21±.06	19.39±.06	51.19±.08	.6873	1.815	

^bSample supplied by Dr. S. C. Robinson, Canadian Geological Survey, numbered as follows: No. 6 - R 653; No. 7 - R 457; No. 8 - R 642; No. 9 - R 554; No. 10 - R 530; No. 11 - R 643.

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
15 ^c	Eldorado Mine	Galena	1.000	14.82	15.15	34.47		
	Porcupine District		1.52(8)±.002	22.65±.04	23.15±.03	52.67±.03	1.022	2.325
16	Cobalt	Galena	1.000	14.84	15.19	34.59		
			1.52(4)±.004	22.62±.02	23.15±.03	52.71±.04	1.023	2.330
17	Worthington Mine	Galena	1.000	25.98	16.99	52.18		
	Sudbury		1.04(9)±.06	27.02±.06	17.67±.04	54.27±.07	.6540	2.009
C(26) ^d	Worthington Mine	Galena	1.00	26.00	16.94	52.51		
	Sudbury		1.04	27.04	17.62	54.30	.6516	2.008
18	Victoria Silver Mine	Galena	1.000	17.79	15.92	37.70		
	Sault St. Marie		1.38(1)±.002	24.57±.03	21.99±.03	52.06±.04	.8950	2.119
19	Ivigtut	Galena with chalcopyrite, etc., from	1.000	14.69	14.83	34.92		
		pegmatite	1.52(8)±.004	22.45±.03	22.66±.06	53.36±.08	1.009	2.377
N(13) ^e	Ivigtut	Galena	1.00	14.75	14.70	34.5		
			1.54	22.71	22.63	53.12	.9965	2.339
R(18) ^f	Ivigtut	Galena	1.00	14.85	14.94	35.07		
			1.51(8)	22.54	22.68	53.24	1.006	2.362

^cObtained from the American Museum of Natural History, New York, N. Y.

^dAnalysis reported by C.B. Collins, R.D. Russell and R.M. Farquhar, "The Maximum Age of the Earth's Crust", Canadian Journal of Physics, 31: 402-418, March, 1953.

^eAnalysis reported by A.O. Nier, R.W. Thompson and F.B. Murphey, "Variations in the Relative Abundances of the Isotopes of Common Lead, from Various Sources", J. Amer. Chem. Soc., 60, 1571, (1938). Not an identical sample.

^fAnalysis reported by R.D. Russell, R.M. Farquhar, G.L. Cumming and J. Tuzo Wilson, "Dating Galenas by Means of Their Isotopic Constitutions", Transactions American Geophysical Union, 35, 301-309, (1954). A small error in the percentage composition is reproduced here without correction.

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
United States								
Western United States								
California								
20	San Antonio	Bournonite with Sphalerite and Pyrite	1.000 1.30(4)±.006	19.86 25.90±.07	16.23 21.16±.04	39.60 51.64±.08	.8170	1.995
21 ^g	Sulphide Queen Deposit, Mt. Pass	Galena in Fluorite, Barite, etc.	1.000 1.44(6)±.004	16.26 23.51±.03	15.55 22.49±.03	36.34 52.55±.04	.9566	2.235
Washington								
22 ^a	Metalline Falls	Galena	1.000 1.31(1)±.003	19.47 25.52±.04	15.83 20.75±.05	39.98 52.42±.05	.8131	2.054
Idaho								
23 ^a	Wallace	Cerussite	1.000 1.41(7)±.006	17.09 24.22±.05	15.53 22.01±.04	36.94 52.35±.05	.9088	2.161
24	Minnie Moore Mine Bellevue	Velvet Galena	1.000 1.23(3)±.008	21.11 26.03±.09	16.51 20.36±.07	42.48 52.38±.08	.7822	2.012
25	Minnie Moore Mine Bellevue	Velvet Galena	1.000 1.24(5)±.007	20.96 26.09±.04	16.21 20.18±.04	42.16 52.49±.08	.7735	2.012
26	Minnie Moore Mine Bellevue	Cubic Galena	1.000 1.25(8)±.004	20.79 26.15±.05	16.21 20.39±.04	41.49 52.20±.06	.7797	1.996

^gSample provided by P. S. Barton, Geology Dept., Columbia University.

Table II, Continued

No.	Locality	Mineral Description	204					207					208					207/206					208/206				
27	Minnie Moore Mine, Stope 952, 900' level Bellevue	Velvet	1.000		20.94			16.24					42.01					52.39±.09		.7756			2.007				
		Galena	1.24(7)±.006		26.11±.06			20.25±.04					52.39±.06														
28	Minnie Moore Mine, Stope 952, 900' level Bellevue	Cubic	1.000		20.91			16.65					41.64														
		Galena	1.24(7)±.006		26.07±.05			20.76±.05					51.92±.06														
29	Sunshine Mine, Kellogg 3700' F.W. at U-vein, 60' to Jewell crosscut Montana		1.000		16.84			15.40					36.79														
		Galena	*1.42(8)±.005		24.05±.06			21.99±.05					52.53±.07														
30	Gray Eagle Mine, Basin Nevada		1.000		18.24			15.62					38.67														
		Galena	1.36(0)±.004		24.80±.07			21.25±.05					52.59±.05														
32	Virginia City Eureka	Fine-grained Galena	1.000		19.80			16.24					39.71														
			1.30(3)±.010		25.80±.04			21.16±.04					51.74±.04														
33	Galena after Silurian Limestone		1.000		18.60			15.75					39.17														
			1.34(2)±.006		24.96±.07			21.13±.04					52.57±.06														
34	Horn Silver, Frisco Godiva Mine, Tintic District	Fine-grained Galena	1.000		18.22			15.55					38.59														
			1.36(3)±.007		24.84±.04			21.20±.04					52.60±.08														
34	Minium		1.000		18.50			15.69					38.99														
			1.34(8)±.003		24.94±.04			21.15±.03					52.56±.05														

*Analysis based on trimethyl spectrum

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Arizona								
35	Deer Trail Mine	Galena	1.000	18.37	15.75	38.51		
	Marysvale		1.35(8)±.006	24.95±.04	21.39±.03	52.30±.03	.8573	2.096
Tucson Mts.								
36 ^a		Wulfenite and Vanadinite	1.000	18.52	15.67	38.89		
			1.35(0)±.007	25.00±.06	21.15±.04	52.50±.07	.8460	2.100
New Mexico								
37 ^h	Kearney Mine, Hanover	Galena	1.000	17.57	15.34	37.88		
			*1.39(3)±.005	24.48±.08	21.37±.07	52.76±.10	.8730	2.155
38 ^h	Mine on west edge of Black Range, San Lorenzo	Galena	1.000	17.77	15.37	37.95		
			*1.38(7)±.008	24.65±.09	21.32±.08	52.64±.11	.8649	2.135
Colorado								
39	Pelican Mine, Clear Creek Co.	Argentiferous Galena	1.000	18.07	15.62	39.66		
			1.34(5)±.006	24.31±.07	21.01±.04	53.34±.09	.8643	2.194
40	Freeland Mine, Idaho Springs	Galena	1.000	18.78	15.72	38.79		
			1.34(6)±.005	25.28±.05	21.16±.06	52.21±.08	.8370	2.065
41	Freeland Mine, Idaho Springs	Galena	1.000	18.65	16.17	39.26		
			1.33(2)±.004	24.84±.04	21.54±.04	52.29±.06	.8671	2.105
42	Chaffee, Chaffee Co.	Galena	1.000	19.22	15.69	39.34		
			1.32(9)±.004	25.54±.04	20.85±.05	52.28±.08	.8164	2.047

^h Sample provided by H. L. Barnes, Geology Dept., Columbia University

*Analysis based on trimethyl spectrum.

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
43	Ute Mine, Hinsdale Co.	Galena	1.000 1.34(6)±.005	19.03 25.61±.03	15.74 21.18±.05	38.53 51.86±.06	.8270	2.025
44	Modonna Mine	Galena	1.000 1.31(9)±.007	19.77 26.08±.06	15.56 20.52±.04	39.48 52.08±.07	.7868	1.997
Mississippi Valley Illinois-Iowa-Wisconsin District								
45	Galena, Ill.	Galena	1.000 1.23(6)±.007	21.92 27.09±.07	16.08 19.87±.04	41.91 51.80±.07	.7335	1.912
46	Marsden Mine, Galena, Ill.	Galena	1.000 1.22(6)±.005	22.43 27.50±.06	16.22 19.88±.08	41.92 51.39±.10	.7229	1.869
47	Galena, Ill.	Cerussite	1.000 1.26(9)±.004	21.24 26.96±.04	16.04 20.36±.05	40.51 51.41±.05	.7552	1.907
48	Dubuque, Ia.	Galena	1.000 1.22(7)±.005	22.24 27.29±.04	16.08 19.73±.05	42.18 51.75±.06	.7230	1.896
49	Hunt 's Diggings near Dubuque, Ia.	Galena	1.000 1.22(6)±.003	22.20 27.22±.04	16.11 19.75±.04	42.25 51.80±.06	.7256	1.903
50	Dubuque, Ia.	Galena	1.000 1.23(3)±.004	22.07 27.21±.05	16.13 19.89±.04	41.91 51.67±.08	.7310	1.899
51	Dubuque, Ia.	Galena and Calamine	1.000 1.22(8)±.005	22.11 27.15±.04	16.16 19.85±.05	42.16 51.77±.05	.7311	1.907
52	California Mine, Cuba City, Wisc.	Galena and Sphalerite	1.000 1.24(1)±.008	21.65 26.87±.05	16.35 20.29±.04	41.58 51.60±.07	.7551	1.820

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
53	Galena, Wisc.	Galena and Sphalerite	1.000 1.22(1)±.004	22.48 27.45±.06	16.13 19.69±.04	42.29 51.64±.06	.7173	1.881
54	Hazel Green, Wisc.	Galena	1.000 1.20(9)±.007	22.73 27.48±.10	16.15 19.53±.04	42.83 51.78±.07	.7107	1.884
55	Hazel Green, Wisc.	Galena	1.000 1.23(2)±.003	22.17 27.31±.05	16.01 19.73±.03	41.99 51.73±.05	.7224	1.894
56	Hazel Green, Wisc.	Galena and Sphalerite	1.000 1.21(7)±.008	22.58 27.48±.07	16.18 19.69±.04	42.41 51.61±.06	.7165	1.878
Southern Illinois - Kentucky District								
57	Cave-in-Rock, Ill.	Galena and Fluorite	1.000 1.30(7)±.005	19.97 26.10±.05	15.64 20.44±.05	39.90 52.15±.07	.7831	1.998
58	Galatin Co., Ill.	Galena and Fluorite	1.000 1.29(5)±.005	20.20 26.16±.04	15.83 20.50±.04	40.19 52.04±.04	.7836	1.989
Central Missouri District								
59	Collins Spring Mine Morgan Co., Mo.	Galena and Cerussite	1.000 1.29(5)±.005	20.11 26.04±.09	16.45 21.30±.06	39.66 51.36±.09	.8180	1.972
Southeastern Missouri District								
60	St. Joe Mine Bonnetterre, Mo.	Galena	1.000 1.31(3)±.004	20.13 26.43±.05	15.82 20.77±.03	39.22 51.49±.06	.7858	1.948
61	Central Mine, Flat River, Mo.	Galena	1.000 1.28(3)±.006	20.82 26.71±.05	16.02 20.56±.05	40.10 51.45±.08	.7697	1.926

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
62	Columbia Lead Mine, Flat River, Mo.	4"Galena Crystal	1.000 1.21(4)±.005	22.31 27.09±.08	16.27 19.75±.05	42.79 51.95±.08	.7291	1.918
63	Columbia Lead Mine, Flat River, Mo.	Opposite end of Sample 62	1.000 1.22(2)±.006	22.20 27.13±.06	16.18 19.77±.04	42.45 51.88±.06	.7287	1.912
64	Federal Lead Co. Flat River, Mo.	Table Concentrates	1.000 1.28(8)±.005	20.74 26.71±.04	15.99 20.60±.04	39.91 51.40±.05	.7712	1.924
65	Federal Lead Co., Flat River, Mo.	Jig Concentrates	1.000 1.34(7)±.007	18.74 25.24±.04	15.68 21.12±.04	38.82 52.29±.09	.8368	2.072
66	St. Joseph	Octahedron Galena	1.000 1.22(4)±.007	22.70 27.78±.07	15.99 19.57±.05	42.02 51.43±.07	.7045	1.1851
67	Mine LaMotte, Madison Co.	Galena	1.000 1.27(1)±.007	21.12 26.85±.10	16.22 20.62±.05	40.33 51.26±.08	.7680	1.909
Tri-State District								
68	Joplin, Mo.	Galena	1.000 1.20(6)±.004	23.10 27.86±.06	16.41 19.79±.03	42.40 51.14±.06	.7103	1.836
69	Joplin, Mo.	Galena	1.000 1.29(4)±.007	20.07 25.97±.05	16.28 21.06±.05	39.94 51.68±.06	.8109	1.990
70	Joplin, Mo.	Galena with Sphalerite	1.000 1.23(7)±.004	22.32 27.61±.03	15.97 19.75±.03	41.55 51.40±.03	.7153	1.862
71	Joplin, Mo.	Galena	1.000 1.23(0)±.005	22.38 27.53±.06	16.04 19.73±.04	41.88 51.51±.09	.7167	1.871

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
72	Joplin, Mo.	Galena and Calamine	1.000 1.24(5)±.006	22.06 27.47±.06	15.93 19.83±.06	41.33 51.46±.08	.7219	1.873
73 ^a	Joplin I, Mo.	Galena	1.000 1.25(1)±.004	21.79 27.26±.04	15.92 19.92±.03	41.22 51.57±.04	.7307	1.892
74 ^a	Joplin II, Mo.	Galena	1.000 1.24(7)±.006	21.85 27.25±.06	15.96 19.90±.03	41.38 51.60±.07	.7303	1.894
75 ^a	Joplin III, Mo.	Residues	1.000 1.23(5)±.004	22.17 27.38±.04	16.10 19.88±.03	41.70 51.50±.04	.7261	1.881
76	Southwestern Mo.	Galena in Cannel Coal	1.000 1.24(2)±.003	21.96 27.27±.04	16.06 19.95±.04	41.50 51.54±.07	.7316	1.890
77	Southwestern Mo.	Galena	1.000 1.23(9)±.003	22.07 27.34±.06	16.05 19.89±.07	41.59 51.53±.07	.7275	1.885
78	Granby Mines, Newton Co., Mo.	Galena	1.000 1.23(1)±.007	22.11 27.22±.06	16.08 19.80±.04	42.04 51.75±.07	.7274	1.901
79	Big Chief Mine, Okla.	Etched Galena with pink dolomite and marcasite	1.000 1.23(0)±.008	22.17 27.27±.08	16.06 19.76±.05	42.06 51.74±.10	.7246	1.897
80	Goodwin Mine, Okla.	Galena	1.000 1.23(7)±.004	22.22 27.49±.05	16.10 19.92±.03	41.51 51.35±.05	.7246	1.868
81	See Sah Mine, Okla.	Galena with Chert and Sphalerite	1.000 1.24(4)±.006	21.92 27.27±.05	16.17 20.12±.04	41.29 51.37±.05	.7378	1.884

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Arkansas District								
82	Kellogg Mine	Argentiferous	1.000	18.61	15.69	38.78		
		Blende	1.35(0)±.004	25.12±.06	21.18±.04	52.35±.06	.8432	2.084
83	Lawrence Co.	Galena and	1.000	21.89	16.07	41.55		
		Calamine	1.24(2)±.004	27.19±.03	19.96±.04	51.61±.04	.7341	1.898
84	Montgomery Co.	Lead-Silver	1.000	18.36	15.61	38.56		
		Ore	1.36(0)±.002	24.97±.03	21.23±.03	52.44±.04	.8502	2.100
85	Morning Star Mine, Rush Creek Dist.	Galena and	1.000	22.73	16.18	41.86		
		Sphalerite	1.22(3)±.001	27.80±.03	19.79±.03	51.19±.04	.7119	1.841
East-Central United States								
Kentucky								
86	Lexington	Galena with						
		barite, calcite	1.000 1.29(5)±.004	20.22 26.18±.05	15.93 20.63±.04	40.07 51.89±.06	.7880	1.982
87	Lexington	Galena	1.000 1.30(9)±.002	19.91 26.06±.03	15.91 20.82±.02	39.58 51.81±.04	.7989	1.988
		Tennessee						
88	Mascot Mine, Mascot	Galena with						
		Sphalerite in brecciated Limestone	1.000 1.31(6)±.004	19.56 25.74±.05	15.77 20.75±.03	39.66 52.19±.05	.8061	2.028
89	McMinnville, Warren Co.	Lead-Zinc	1.000	20.04	15.85	39.74		
		Ore	1.30(5)±.004	26.15±.06	20.69±.05	51.86±.09	.7912	1.983

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Eastern United States								
New England								
Maine, New Hampshire								
90	Deer Island, Me.	Fine-grained Galena with Chalcopyrite	1.000 1.36(3)±.006	18.19 24.79±.08	15.74 21.46±.03	38.44 52.39±.07	.8657	2.113
91	Denboe Pt., Me.	Galena	1.000 1.35(6)±.006	18.38 24.92±.05	15.63 21.19±.04	38.74 52.53±.07	.8503	2.108
92	Denboe Pt., Me.	Argentiferous Galena in quartz	1.000 1.36(3)±.007	18.40 25.08±.06	15.65 21.33±.04	38.32 52.23±.08	.8505	2.083
93	Warren, Grafton Co., New Hampshire	Lead-Zinc Ore	1.000 1.34(6)±.008	18.53 24.94±.10	15.96 21.48±.10	38.80 52.23±.09	.8613	2.094
Massachusetts								
94	Pembroke	Schistose Galena	1.000 1.33(9)±.006	18.83 25.22±.06	15.77 21.12±.07	39.07 52.32±.09	.8374	2.075
95	Leverett	Galena in Barite	1.000 1.32(7)±.005	19.05 25.28±.08	15.96 21.18±.05	39.34 52.21±.08	.8378	2.065
96	Newbury	Galena	1.000 1.21(0)±.006	22.93 27.74±.07	16.30 19.72±.06	42.42 51.33±.05	.7109	1.850
97	Fallon Quarry, Quincy	Galena in pegmatite	1.000 1.35(9)±.007	18.41 25.02±.04	15.75 21.40±.03	38.43 52.22±.06	.8553	2.087
Connecticut								
98	Middletown	Galena	1.000 1.34(4)±.005	18.64 25.05±.07	15.83 21.28±.06	38.94 52.33±.06	.8495	2.089

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
99	Middletown	Galena	1.000 1.33(8)±.005	18.76 25.10±.06	15.84 21.19±.05	39.14 52.37±.08	.8442	2.086
100	Darien	Fine-grained Galena with Chalcopyrite	1.000 1.34(6)±.007	18.60 25.04±.09	15.79 21.26±.07	38.89 52.35±.10	.8490	2.091
101	Roxbury	Galena	1.000 1.35(9)±.007	18.38 24.98±.07	15.70 21.34±.06	38.50 52.32±.06	.8543	2.094
102	Roxbury	Galena with chalcopyrite in quartz	1.000 1.30(8)±.009	19.27 25.21±.06	16.23 21.23±.03	39.95 52.25±.08	.8421	2.073
New York-Pennsylvania-New Jersey								
103	Canajoharie, N.Y.	Galena	1.000 1.35(5)±.008	18.51 25.08±.04	15.65 21.21±.03	38.63 52.35±.04	.8457	2.087
104	Ellenville, N.Y.	Galena	1.000 1.34(4)±.005	18.81 25.28±.04	15.68 21.08±.05	38.91 52.30±.07	.8339	2.069
105	Ellenville, N.Y.	Galena	1.000 1.34(7)±.004	18.75 25.25±.06	15.59 21.00±.05	38.90 52.40±.07	.8317	2.075
106	Mt. Hope Mine, Guymard	Galena	1.000 1.33(2)±.005	18.90 25.18±.06	15.82 21.07±.04	39.35 52.42±.06	.8368	2.082
107	Wallkill Lead Mine, Orange Co., N.Y.	Galena in Sandstone	1.000 1.34(0)±.005	18.74 25.11±.07	15.69 21.03±.04	39.19 52.52±.08	.8375	2.092
108	Sullivan Co., N.Y.	Galena	1.000 1.34(2)±.006	18.90 25.37±.05	15.67 21.03±.03	38.94 52.26±.07	.8289	2.060
109	Perkiomen Mine, Phoenixville, Pa.	Galena	1.000 1.34(6)±.004	18.71 25.19±.04	15.61 21.01±.05	38.97 52.45±.05	.8341	2.082

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
110	Wheatley Mine, Phoenixville, Pa.	Galena	1.000 1.33(9)±.005	18.83 25.22±.08	15.79 21.14±.05	39.06 52.30±.09	.8382	2.074
111	Wheatley Mine, Phoenixville, Pa.	Galena and Anglesite	1.000 1.34(6)±.004	18.75 25.24±.03	15.71 21.14±.03	38.83 52.27±.05	.8376	2.071
112	Phoenixville, Pa.	Galena	1.000 1.32(8)±.007	18.83 25.01±.07	15.93 21.15±.08	39.54 52.51±.08	.8457	2.100
113	Friedensville, Pa.	Galena	1.000 1.30(9)±.007	19.30 25.26±.07	16.71 21.87±.09	39.39 51.56±.10	.8658	2.041
114 ⁱ	Franklin, N.J.	Galena	1.000 1.41(5)±.004	17.12 24.23±.05	15.74 22.27±.05	36.81 52.08±.06	.9191	2.149
N(20) ^j	Franklin, N.J.	Galena	1.000 1.43	17.15 24.45	15.45 22.03	36.53 52.09	.9009	2.130
115 ⁱ	Franklin, N.J.	Cerussite	1.000 1.39(1)±.002	17.15 23.85±.04	15.49 21.55±.03	38.25 53.21±.04	.9036	2.231
116	Mt. Gilboa, Hunterdon Co. N.J.	Galena	1.000 1.28(3)±.005	20.30 26.05±.05	15.99 20.51±.03	40.65 52.16±.06	.7873	2.002
117	Henderson	Galena from Pegmatite	1.000 1.34(8)±.004	18.58 25.05±.03	15.78 21.27±.03	38.82 52.33±.04	.8491	2.089
118	Silver Hill Mine, Davidson Co.	Fine-grained Galena	1.000 1.34(9)±.005	18.30 24.68±.05	16.26 21.94±.05	38.57 52.03±.09	.8890	2.108

ⁱSample supplied by American Museum of Natural History, New York, N.Y. Museum numbers correspond to our numbers as follows: no. 114-15078; no. 115-21253; no. 130-219401 no. 131-24082; no. 136-18373; no. 140-16536; no. 141-23051; no. 160-20846.

^jAnalysis reported by A.O. Nier, R.W. Thompson, and B.F. Murphey, "The Isotopic Composition of Lead and the Measurement of Geological Time, III," Phys. Rev. 60, p. 112-116, (1941). Not an identical sample.

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Central and South America								
Mexico								
119	Jesus Maria Mine El Carmen, Durango	Galena with	1.000	19.12	15.92	39.20		
		Covellite	1.32(9)±.006	25.41±.05	21.16±.04	52.10±.08	.8327	2.050
N(21) ^J	Durango,	Galena	1.000	18.71	15.70	38.5		
		Anglesite	1.35	25.31	21.24	52.1	.8391	2.06
Peru								
120 ^a	Casapalca	Bournonite	1.000	18.85	15.76	39.23		
			1.33(6)±.004	25.19±.04	21.06±.03	52.41±.04	.8360	2.081
121 ^a	Casapalca	Galena	1.000	18.92	15.74	39.36		
			1.33(3)±.004	25.22±.06	20.98±.06	52.47±.07	.8319	2.080
Europe and Asia								
Spain								
122	Compania Minero, Los Guindos, La Carolina, Province Jaen	Coarse Cubical Galena	1.000	18.27	15.65	38.72		
			1.35(8)±.006	24.81±.04	21.25±.03	52.58±.07	.8565	2.119
123	Compania Minero, Los Guindos, La Carolina, Province Jaen	Fine - grained Galena	1.000	18.21	15.62	38.49		
			1.36(4)±.003	24.84±.05	21.30±.03	52.50±.05	.8575	2.114
124	Compania Minero, Los Guindos, La Carolina Province Jaen	Galena	1.000	18.35	15.72	38.80		
			1.35(4)±.004	24.84±.04	21.28±.04	52.53±.05	.8567	2.115
125	Huelva	Galena	1.000	18.27	15.59	38.40		
			1.36(5)±.006	24.94±.06	21.28±.04	52.42±.07	.8532	2.102
England								
126	Derbyshire	Galena	1.000	18.57	15.67	38.83		
			1.35(0)±.004	25.07±.03	21.16±.04	52.42±.05	.8440	2.091

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Hungary								
127	Schemnitz	Galena	1.000 1.30(4)±.008	19.25 25.10±.06	16.07 20.96±.05	40.37 52.64±.09	.8351	2.097
Germany								
128	Freiberg, Saxony	Galena	1.000 1.29(6)±.006	20.32 26.34±.07	15.91 20.62±.04	39.92 51.74±.07	.7828	1.964
N(24) ^j	Freiberg, Saxony	Galena	1.000 1.38	18.07 24.93	15.40 21.25	38.0 52.4	.8522	2.10
Sweden								
129	Fahlun	Galena	1.000 1.46(3)±.005	15.89 23.24±.06	15.61 22.84±.03	35.86 52.46±.06	.9828	2.257
130 ⁱ	Langban	Native Lead	1.000 1.46(9)±.003	15.84 23.27±.03	15.55 22.85±.03	35.68 52.41±.04	.9820	2.252
N(22) ^j	Langban	Native Lead	1.000 1.47	15.83 23.32	15.45 22.76	35.6 52.4	.9760	2.25
Italy								
131 ⁱ	Mt. Vesuvius, collected from Fumarole on March 16, 1954	Cotunnite	1.000 1.33(9)±.002	19.04 25.50±.02	15.38 20.59±.03	39.26 52.57±.04	.8074	2.062
Yugoslavia								
132	Trepca	Galena in Sphalerite rich ore	1.000 1.29(5)±.006	19.38 25.10±.06	17.03 22.05±.05	39.81 51.55±.06	.8785	2.054
Greece								
133	Zinc Mines, Laurion	Galena	1.000 1.34(3)±.005	18.80 25.25±.04	15.67 21.05±.02	38.99 52.36±.06	.8337	2.074

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
U. S. S. R.								
134	Nertschinsk, Siberia	Galena	1.000 1.35(5)±.003	18.52 25.10±.02	15.70 21.28±.02	38.57 52.26±.03	.8478	2.082
135	Nertschinsk, Siberia	Cerussite	1.000 1.35(2)±.003	18.54 25.07±.04	15.72 21.25±.04	38.71 52.33±.05	.8476	2.087
Japan								
136 ⁱ	Ani Mine, Yugo	Galena	1.000 1.34(2)±.003	18.50 24.83±.04	16.04 21.52±.04	38.98 52.31±.07	.8667	2.107
Australia and Tasmania								
137 ^a	Broken Hill, N.S.W., Australia	Galena	1.000 1.44(5)±.004	16.27 23.51±.05	15.56 22.49±.04	36.37 52.56±.06	.9566	2.236
138	Rum Jungle Area, Australia	Cerussite	1.000 1.45(4)±.004	16.18 23.53±.03	15.50 22.54±.04	36.09 52.48±.04	.9579	2.230
139	Rum Jungle Area, Australia	Galena	1.000 1.44(6)±.008	16.31 23.59±.04	15.62 22.59±.06	36.22 52.37±.08	.9576	2.220
140 ⁱ	Dundas, Tasmania	Anglesite	1.000 1.33(5)±.006	18.66 24.91±.06	15.95 21.29±.04	39.30 52.46±.06	.8547	2.106
Africa								
Morocco								
141 ⁱ	Mibladen	Cerussite	1.000 1.34(8)±.005	18.38 24.77±.07	15.90 21.43±.03	38.91 52.45±.04	.8652	2.117
Belgian Congo								
142	Kengere	Cerussite	1.000 1.37(5)±.004	18.04 24.81±.03	15.67 21.55±.03	38.01 52.26±.04	.8686	2.106
C(2) ^k	Kengere		1.000 1.37(2)	17.58 24.13	15.94 21.88	38.34 52.62	.9067	2.181

^kAnalysis reported by C. B. Collins, R. M. Farquhar, and R. D. Russell, "Variations in the Relative Abundances of the Isotopes of Common Lead", Phys. Rev. 88, 1275-1276, (1952)^c

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
Southern Rhodesia								
143 ^m	S. T. Mine, near Bindura	Galena	1.000	14.16	15.06	34.22		
			*1.55(2)±.004	21.97±.07	23.37±.03	53.11±.08	1.064	2.417
144 ^m	Kingsley Hoard Mine, Bindura, Mazoe District	Galena	1.000	13.99	14.89	33.97		
			*1.56(6)±.005	21.91±.03	23.32±.02	53.20±.03	1.064	2.428
145 ^m	Hardy (Gold) Mine, Darwin District	Galena	1.000	14.02	14.74	33.85		
			*1.57(2)±.005	22.04±.03	23.17±.03	53.22±.03	1.051	2.415
146 ^m	St. Ives Mine, near Turli, Bubi District	Galena	1.000	13.74	14.57	33.69		
			*1.58(7)±.005	21.81±.05	23.13±.05	53.47±.03	1.061	2.452
147 ^m	Elba (Gold) Mine, Wankie District	Galena	1.000	16.79	15.46	37.97		
			*1.40(4)±.003	23.58±.05	21.71±.04	53.31±.06	.9207	2.261
148 ^m	Cobra (Gold) Mine, Gwanda	Galena	1.000	14.00	14.89	34.05		
			*1.56(4)±.003	21.89±.04	23.29±.07	53.26±.09	1.064	2.433
149 ^m	C.S.C. Mine, Wedza, Marandellas District	Galena	1.000	14.15	15.17	33.86		
			*1.55(8)±.005	22.04±.03	23.64±.02	52.76±.04	1.073	2.393
South Africa								
150 ⁿ	Ombonna 89, Otjiwarongo District	Galena	1.000	18.71	15.52	38.95		
			*1.34(8)±.003	25.22±.04	20.92±.06	52.51±.08	.8295	2.082
151 ⁿ	Leeuwenkoof 97, Pretoria District	Galena	1.000	14.92	15.06	34.21		
			*1.53(4)±.003	22.89±.03	23.10±.02	52.48±.05	1.009	2.293

^m Sample provided by Dr. R.M. Tyndale-Biscoe, Acting Director, and Dr. A.M. Macgregor of the Geological Survey of Southern Rhodesia.

ⁿ Sample provided by Dr. L.T. Nel, Director, and Dr. B. Wasserstein of the Geological Survey of South Africa. Survey Museum numbers corresponding to our sample numbers are as follows: no. 150-4523a; no. 151-4415; no. 152-4480; no. 153-3487; no. 155-758; no. 156-4512. Samples 154 and 158 are from Dr. Wasserstein's personal collection.

* Analysis based on trimethyl spectrum.

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
South Africa, Cont'd.								
152 ⁿ	Uitloop 291, Pot- gietersrust District	Galena	1.000 *1.52(1)±.003	14.97 22.77±.04	15.07 22.92±.03	34.71 52.79±.04	1.007	2.318
153 ⁿ	Stavoren Tin Mine, Potgietersrust District	Galena	1.000 *1.36(3)±.006	18.14 24.72±.04	15.76 21.48±.04	38.47 52.44±.03	.8689	2.121
154 ⁿ	Appelfontein 71, Zout- pansberg District	Galena	1.000 *1.44(7)±.007	15.94 23.07±.04	15.40 22.29±.03	36.76 53.19±.05	.9662	2.306
155 ⁿ	Rosetta Mine, Barberton District	Galena	1.000 *1.65(4)±.006	12.58 20.81±.03	14.11 23.34±.07	32.77 54.20±.08	1.122	2.605
C(21) ^d	Rosetta Mine, Barberton District		1.000 1.65	12.65 20.84	14.27 23.51	32.78 54.00	1.128	2.591
156 ⁿ	Dyasonsklip, Gordonia, about 15 mi. s.w. of Uppington	Galena	1.000 *1.38(0)±.003	18.09 24.97±.03	15.57 21.49±.06	37.80 52.16±.06	.8606	2.089
157 ^p	Keimos, Orange River Valley, Cape Province	Galena	1.000 *1.27(3)±.004	20.41 25.98±.06	15.66 19.93±.06	41.49 52.82±.09	.7671	2.033
158 ⁿ	East Geduld (Gold) Mine, Witwatersrand	Galena	1.000 *1.43(9)±.004	18.03 25.95±.05	15.98 22.99±.03	34.48 49.62±.05	.8859	1.912
159 ^q	Sub Nigel Mine, Witwatersrand	Galena	1.000 .795±.004	60.52 48.11±.06	24.05 19.12±.03	40.21 31.97±.04	.3974	.6645

^p Sample provided by Dr. A. Poldervaart, Geology Department Staff, Columbia University.

^q Sample provided by United States Atomic Energy Commission, Raw Materials Division

* Analysis based on trimethyl spectrum.

Table II, Continued

No.	Locality	Mineral Description	204	206	207	208	207/206	208/206
South Africa Cont'd.								
160 ⁱ	Tsumeb, Otavi	Anglesite	1.000 1.35(0)±.004	18.27 24.67±.03	16.07 21.69±.03	38.73 52.29±.04	.8792	2.120
161	Tsumeb, Otavi	Cerussite	1.000 1.35(2)±.003	18.27 24.70±.06	15.88 21.47±.03	38.82 52.48±.06	.8692	2.125

some cases, the uncertainty is somewhat larger than that indicated, owing to the fact that further analysis was necessary but prohibited because of sample loss. For most data, at least two runs were available and these were averaged together, weighting each run according to the number of scans comprising it and weighting each isotope inversely to the square root of the average deviation associated with it. Such a weighting procedure admittedly suffers statistically because of the small number of runs per sample, but is believed to serve at least as a good first approximation.

As noted previously, not all of the localities represented are "new" in that isotopic analyses have not previously been reported for the given source. For those sources from which samples have already been analyzed, the previous analyses, where available, have also been given for comparison purposes. Analyses by other investigators on identical specimens are included only in Table I, and all the "outside" analyses reported in Table II are on non-identical samples from the same locality. It is interesting to note that for three such samples in particular, namely nos. 17 (Sudbury, Ont.), 19 (Ivigtut, Greenland), and 130 (Langban, Sweden), the agreement with the Toronto and Nier analyses is better than that generally obtained for that between analyses of identical samples in Table I.

For each analysis the isotopic composition is reported in two ways - with $\text{Pb}^{204} = 1.000$ in the first line, and with the normal percentage composition in the second line. The corresponding deviations are not shown for the first manner of presentation, but may be calculated if desired from the deviations given with the percentage composition. It is evident that such deviations will be larger than the latter because of the combination with the large uncertainty in Pb^{204} .

For further comparison of the Lamont analyses, the ratios $\text{Pb}^{207}/\text{Pb}^{206}$ and $\text{Pb}^{208}/\text{Pb}^{206}$ are shown in the last two columns as arbitrary indices. These quantities, it is to be noted, are not affected by the large uncertainty in Pb^{204} .

The classification of the lead minerals as common lead (i.e., containing no radioactive elements) was loosely made on a mineralogical basis; it was not considered necessary to actually monitor any of the samples for possible radioactivity. It was known however, that the suite of Goldfields samples (Nos. 9-13) contained small amounts of uranium. These samples are not common leads, but rather mixed leads, but are included in the table to illustrate the possible variations in the isotopic composition of lead minerals in the region where they are formed from an environment containing high concentrations of radiogenic lead. Samples 9, 10, and 13 clearly show the presence of radiogenic lead, while sample 12 has an anomalous common lead composition and constitutes an interesting transition into the common lead field.

An arbitrary but useful display of the variations in isotopic composition of lead may be had by utilization of a triangular diagram as shown in Figure 5. Here the percentage compositions (recalculated to 100%) of the three heaviest isotopes, Pb^{206} , Pb^{207} , Pb^{208} , are plotted in the usual triangular mode (there are actually only two independent variables). The field in Figure 5 is arbitrarily bounded by the vertex points of 32%, 28% and 60% of Pb^{206} , Pb^{207} and Pb^{208} respectively, and this field will be referred to as the (normal) common lead field. The position of the common lead field in the total field is shown in Figure 6, together with a plot of some samples whose composition falls outside the common lead field. The chief advantages of the triangular mode of repre-

Figure 5. Common lead field. Points represent data of Table II. Curves are plotted on the basis of step-differentiation model with constants assumed as shown.

Figure 6. Total lead composition field showing normal common lead field, together with several samples falling outside the normal field. Sample numbers shown with the points correspond to those of Table II.

sensation are that (1) the variations of the three variables may be simultaneously displayed and (2) in this particular case, the variations are independent of the uncertainty in Pb^{204} , to the first order.

Although the uncertainty in Pb^{204} introduces a larger error than that associated with the remaining lead isotopes, it is nevertheless necessary to consider the variations in isotopic composition with reference to Pb^{204} as well. A convenient and useful representation is shown in Figure 7, where the ratios $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{208}/\text{Pb}^{204}$ are plotted against the ratio $\text{Pb}^{206}/\text{Pb}^{204}$ for each sample.

For both the plots in Figures 5 and 7, samples of very similar composition have been averaged together and are represented by one point. That the variations in composition are more or less regular is evident from inspection of both diagrams. In Fig. 7 in particular, it is seen that as $\text{Pb}^{206}/\text{Pb}^{204}$ increases, $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{208}/\text{Pb}^{204}$ increase regularly, with the latter "curve" showing the greatest gradient. The curves that appear in the graphs show possible correlation of the variables with time, as discussed in following sections.

Figure 7. Plot of y_m and z_m against x_m . Points represent data of Table II, and curves are plotted on the basis of the step-differentiation model with constants assumed as shown.

Age Relations for Various Earth Models

The interpretation of lead abundances pertaining to events in earth history must necessarily depend on the model proposed to represent the time dependence of the isotopic abundances of rock lead. A simple model, herein referred to as the step-differentiation model, requires the complete differentiation of the crust, essentially into its present form in a very short time interval subsequent to the accretion of the planet. Another possible model would involve a continuous differentiation of the earth's outer shell with time. A general expression for the rate of differentiation would assume some exponential relationship involving a decreasing rate of differentiation from the time of formation of the earth. Least likely would be a model involving a maximum in the differentiation rate or an increase with time.

Derivation of Step-Differentiation Model

Consider the production of radiogenic lead Pb^{206} from U^{238} in a given geochemical environment in a permanent crust. If, for convenience, time t is measured positively back into geologic history from the present, then the differential equation for uranium decay may be written

$$dN^{238} = -\lambda N^{238} dt \quad (17)$$

where N^{238} is the number of U^{238} atoms at time t in the specified environment, and λ is the decay constant for U^{238} . Specifically, the variation of the ratio of N^{238} to N^{204} , the number of Pb^{204} atoms, is required and if it is assumed that N^{204} is constant with time, equation (17) may in turn be written

$$dP = \lambda P dt \quad (18)$$

where $P = N^{238}/N^{204}$. Integrating equation (18) and taking $P = P_0$ at $t = 0$, one obtains

$$P = P_0 e^{\lambda t}. \quad (19)$$

Using similar notation the differential equation for variation of $x = N^{206}/N^{204}$ where N^{206} is the number of atoms of Pb^{206} in the designated matrix,

$$dx = -\lambda P dt \quad (20)$$

Substitution of the explicit time dependence of P from equation (19) gives

$$dx = -\lambda P_0 e^{\lambda t} dt. \quad (21)$$

Integration of equation (21) yields

$$x = -P_0 e^{\lambda t} + C, \quad (22)$$

where C is the constant of integration.

Depending on the boundary conditions specified to determine C , equation (22) may be reduced to several final forms. Two sets of boundary conditions are most commonly used. (a) At $t = 0$ (present time) $x = \alpha_0$, the presently observed value of N^{206}/N^{204} in the crustal environment under consideration. $\alpha_0 = \alpha_c + \alpha_r$ where α_c is the primeval or initial ratio of N^{206}/N^{204} at time $t = t_c$ (time of earth formation = time of crust formation according to this model), $\alpha_r = N^{206}/N^{204}$ due to production of radiogenic Pb^{206} in this matrix throughout geologic time. Equation (22) then becomes

$$x = \alpha_0 - P_0(e^{\lambda t} - 1). \quad (23)$$

(b) At $t = t_c$, $x = \alpha_c$. For this case equation (22) reduces to

$$x = \alpha_c + P_0(e^{\lambda t_c} - e^{\lambda t}) \quad (24)$$

The exact significance of t_c in equation (24) depends on the particular cosmogonical theory invoked to account for the origin of the solar system and of the earth in particular. According to a currently accepted view the earth

initially accreted from undifferentiated matter very similar in composition to meteoritic material. Increased temperatures at the surface possibly due to impact during the late stages of planet formation caused the differentiation of a thin basaltic layer (5 km) now preserved under the ocean sediments. Subsequent differentiation produced the iron-nickel core and the granitic continental layers. The step-differentiation model requires all of this differentiation to have occurred in a short time interval close to the formation of the earth.

The composition of meteorites has been fairly well established and of pertinent interest here is the datum that the lead to uranium ratio is of the order of 80:1 in average meteorites²⁸ (obviously for $t = 0$). Assuming that the age of meteorites is roughly that of the earth, i.e. 5×10^9 years, then the initial lead to uranium 238 ratio was approximately 40:1. Noting that the present ratio of lead to uranium in the most mafic rocks measured^{29, 30} is about 10:1, it is seen that the rate of accumulation of radiogenic lead relative to Pb^{204} in primordial material was about one fourth that of the slowest rate observed in present crustal rocks. Or, stated alternately, the increase in the ratio of $\text{Pb}^{206}/\text{Pb}^{204}$ in meteorites from $t = t_c$ to $t = 0$ could not exceed 2%.

On the other hand, in an environment such as the present basaltic or granitic crust the rate of generation of radiogenic lead would be sufficient to change the isotopic composition of total lead by a readily measurable amount in the period of earth history. t_c is therefore understood as that post-differentiation time remote in earth history at which radiogenic lead relative to Pb^{204} began to be produced in the "crust" at a rate comparable to that in the present crust.

α_c in equation (24) is the ratio of Pb^{206} to Pb^{204} at time t_c ; this lead isotopic

composition is called primeval. (For the purposes of this discussion, an arbitrary, technical distinction will be made between the words "primeval" and "primordial". "Primordial" is used with reference to the pre-differentiation era, for describing the earth and its materials in their elemental, accreted form and "primeval" is associated with an arbitrary post-primordial point of time remote in earth history.) If a relatively short time elapsed before the assumed step-differentiation took place, then the primeval lead composition is essentially identical to that of lead, assumed to be primordial, found in meteorites.

It may be observed that equation (24) does not necessarily imply the existence of a solid crust at time t_c . Although the existence of a solid crust at that time is very probable, equation (24) merely requires the existence and continuation of a crust with a geochemical composition comparable to the present crust.

Discussion in the literature²⁻¹¹ on the significance of α_c and t_c is often vague, and the definitions stated here are not necessarily identical with those of the previous writers. The present definitions are made to promote maximum clarity for the considerations at hand.

Turning to the geochemical processes of lead ore formation, the extraction of lead from a given crustal matrix (source rocks) and the accompanying lead mineralization at time t_m (assuming negligible lapse of time between the two events) terminates the growth curve of the three radiogenic lead isotopes and "freezes" the isotopic composition obtaining in that environment at time t_m . Each common lead mineral under the conditions assumed reflects an isotopic composition characteristic of its age t_m , and the Pb^{206} composition may be displayed in equations (23) and (24) as

$$x_m = \alpha_0 - P_0 (e^{\lambda t_m} - 1), \quad (25)$$

and

$$x_m = \alpha_o + P_o (e^{\lambda t_c} - e^{\lambda t_m}). \quad (26)$$

In similar manner, equations analogous to (25) and (26) may be derived for the isotopes Pb^{207} and Pb^{208} . Employing typical notation, the two complete sets of equations are:

$$\begin{aligned} x_m &= \alpha_o - P_o (e^{\lambda t_m} - 1) \\ y_m &= \beta_o - \epsilon P_o (e^{\lambda' t_m} - 1) \\ z_m &= \gamma_o - W_o (e^{\lambda'' t_m} - 1) \end{aligned} \quad (27)$$

$$\begin{aligned} x_m &= \alpha_c + P_o (e^{\lambda t_c} - e^{\lambda t_m}) \\ y_m &= \beta_c + \epsilon P_o (e^{\lambda' t_c} - e^{\lambda' t_m}) \\ z_m &= \gamma_c + W_o (e^{\lambda'' t_c} - e^{\lambda'' t_m}). \end{aligned} \quad (28)$$

y_m and z_m are the respective time-dependent ratios N^{207}/N^{204} and N^{208}/N^{204} , where N^{207} and N^{208} are the numbers of atoms of Pb^{207} and Pb^{208} ; β_o and γ_o are the presently observed ratios N^{207}/N_o^{204} and N_o^{208}/N_o^{204} respectively. β_c and γ_c are the respective ratios N^{207}/N^{204} and N^{208}/N^{204} obtaining at time t_c . ϵ is the present value of N^{235}/N^{238} and W_o is the contemporary value of N^{232}/N^{204} where N^{235} and N^{232} refer to U^{235} and Th^{232} atoms. All quantities refer to the crustal environment specified for equation (17). The decay constants for U^{235} and Th^{232} are denoted by λ' and λ'' , respectively.

If now the values of $\alpha_o, \beta_o, \gamma_o, P_o$, and W_o are assumed to be the same in all portions of the earth's crust which serve as the sources of common lead deposits, and if it is further assumed that the only change of the lead to uranium ratio therein is due to radioactive decay, then the use of the isotopic composition of common lead minerals of known age in equations (28) would permit an accurate evaluation of t_c . Although the actual situation is more complicated than this simple

picture affords, it is worthwhile to make such a calculation to describe a limiting case. The limitations of the proposed calculation may be clarified by an enumeration of the implicit and explicit assumptions employed.

Assumptions:

(1) The decay constants λ , λ' , and λ'' have been constant throughout earth history, and are reliably represented by the values obtained in the laboratory today. Moreover, ϵ is constant throughout the crustal environments considered.

(2) The amount of equivalent radiogenic lead represented by the unstable elements lying between the end members of the three radioactive decay series is at all times negligible once secular equilibrium has been reached.

(3) Each of the three radioactive decay series is closed so that none of the member elements has been added or removed by extraneous processes throughout geologic time.

(4) The amount of the radiogenic lead isotopes created or destroyed by natural processes other than the decay schemes delineated, is negligible. Moreover, Pb^{204} has not been produced or removed in nature throughout geologic time.

(5) Uranium to lead and thorium to lead ratios are uniform in zones of lead extraction.

(6) The only change of uranium and thorium relative to Pb^{204} in the designated zones of the crust throughout earth history is that occasioned by radioactive decay.

(7) The process of rock lead extraction must involve a complete mixing of the radiogenic lead and primeval lead present in the rock, and is therefore homogeneous.

(8) The possibility of significant chemical fractionation of the isotopes of lead

is negligible for all conceivable thermochemical environments of lead extraction and ore mineralization.

(9) The time required for both the processes of extraction and mineralization is negligibly small compared to the time of accumulation of the radiogenic lead.

(10) The time interval between extraction and mineralization of lead is insignificant relative to the time of accumulation of the radiogenic lead.

(11) In the process of transport from lead source to site of mineralization, the ore-carrying solutions are not contaminated by lead of extraneous origin.

(12) The amount of common lead minerals and/or radiogenic lead minerals in the source rocks due to previous mineralizing activity must be small compared to the total amount of lead involved.

(13) The two sets of constants $\alpha_o, \beta_o, \gamma_o$ and $\alpha_c, \beta_c, \gamma_c$ are constant in the portions of the crust involved in lead ore formation.

Insofar as the assumptions are not met, the validity of the application of equations (27) and (28) to common lead minerals of diverse origin can be questioned. It is virtually certain that conditions (1), (2), (4), (8), (9), and (10) are fulfilled in nature. Assumption (3) is probably valid, but note must be taken of the possible migration of radon (half-life 3 1/2 days) in the U^{238} decay chain. The remaining items merit further consideration and will be discussed later.

Comparison of Common Lead Isotopic Data with the Step-Differentiation Model

A qualitative comparison of the data with the step-differentiation model is exhibited by the curves projected with the data in Figures 5 and 7. The particular curves shown include the isotopic composition of meteoritic lead reported by Patterson²⁸, et.al., as the composition of primeval lead. In Figure 5, the curves enter the bottom of the field for old leads and the compositions move up along the indicated loci as the age of mineralization becomes increasingly younger.

The curves represent equations (28), with selected values of the constants to bring the curves into the domain of the points representing the data. For all cases, the composition of primeval lead referred to²⁸ is $\alpha_c = 9.4$, $\beta_c = 10.3$ and $\gamma_c = 29.2$. For the curves labelled mafic, the values of P_0 and W_0 are taken as 7.95 and 32.3 respectively, and corresponding values for the siliceous curves are 11.7 and 51.1, respectively. These values for P_0 and W_0 are based on abundances of uranium, thorium and lead in various types of crustal rocks reported by Evans and Goodman²⁹, and Sandell and Goldich³⁰, using the modern common lead abundance of Quaternary sediments reported by Patterson³¹, et.al., to obtain the amount of Pb^{204} in contemporary rock lead. The remaining pair of curves designated as "average of lead sources" is plotted with $P_0 = 9.92$ and $W_0 = 38.3$, which are values reported by Collins¹³, et.al., as the average required for a least squares fit of a number of common lead minerals to the primary earth model. The values of t_c employed range as shown from 4.0×10^9 yrs. to 4.5×10^9 yrs. The values used for the constants ϵ , λ , λ' , λ'' , are those reported by Fleming, Ghiorso and Cunningham³².

For the curves in both Figures 5 and 7, the terminal point at the upper end

of each curve represents modern lead composition obtainable with the given parameters. From this qualitative comparison it is seen that, assuming the validity of equating primeval lead to the meteoritic lead composition reported, the data may be considered to be generally compatible with the step-differentiation model for values of t_c between 4.0×10^9 yrs. and 4.5×10^9 yrs., and with values of P_0 and W_0 corresponding to those of siliceous, continental rocks of the earth's crust.

Least Squares Fit of Dated Samples to Step-Differentiation Model

A more quantitative treatment of the data is obtained by means of a least squares fit to the equations (27) for the step-differentiation model. Such a procedure involves, however, the introduction of an added uncertainty, the geologic ages of the common lead minerals.

Age Considerations

The difficulty of assigning reliable ages to common lead minerals necessarily restricts the analysis to a relatively small number of samples, for which sufficiently good dating criteria exist. Some 16 Lamont samples have been so dated and, together with three of the Toronto analyses added to give a more even spread on the time scale, are shown with the assigned geologic ages in Table III. The data and evidence for the ages used in this table are contained in the references.

Most of the post-Cambrian samples are dated from position in the stratigraphic column, since the errors involved although large percentage-wise, do not have a pronounced effect on the constants determined by least squares analysis. For one or two post-Cambrian samples, such as no. 117 from Henderson, N.C., for example, ages of radioactive minerals of contemporary

Table III

Ages For Common Lead Minerals

No.	Source Locality	Isotopic Composition ($Pb^{204}=1.00$)			Geologic Age (in m. y.)
		206	207	208	
43	Ute Mine, Hinsdale Co., Colo. ^a	19.03	15.74	38.53	15±10
120	Casapalca, Peru ^b	18.85	15.76	39.23	25±10
119	Durango, Mex. ^c	19.12	15.92	39.20	25±10
133	Laurion, Greece ^d	18.80	15.67	38.99	70±20
111	Phoenixville, Pa. ^e	18.75	15.71	38.83	120±30
98	Middletown, Conn. ^f	18.64	15.83	38.94	170±15
82	Kellogg Mine, Ark. ^g	18.61	15.69	38.78	200±50
97	Fallon Quarry, Quincy, Mass. ^h	18.41	15.75	38.43	230±40
117	Henderson, N. C. ⁱ	18.58	15.78	38.82	340±20
C(10)	Katanga, Belgian Congo ^j	17.58*	15.94*	38.34*	630±30
115	Franklin, N. J. ^k	17.15	15.49	38.25	700±200
18	Sault Ste. Marie, Ont. ^l	17.79	15.92	37.70	700±300
21	Mountain Pass, Calif. ^m	16.26	15.55	36.34	925±200
137	Broken Hill, N. S. W. ⁿ	16.27	15.56	36.37	1,200±300
4	Great Bear Lake, N. W. T. ^j	16.13	15.43	35.75	1,450±100
129	Fahlun, Langban, Sweden ^o	15.86	15.58	35.74	1,600±200
130					
C(15)	Great Slave Lake, N. W. T. ^j	14.63*	15.27*	34.46*	1,900±300
8	Ace Mine, Goldfields, Sask. ⁱ	14.36	14.96	34.49	1,900±100
C(17)	Sioux Lookout, Ont. ^j	14.05*	14.92*	33.85*	2,600±500

^a W. Lindgren, Mineral Deposits, p. 499-508, New York, 1933

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^l H. C. Cooke, Regional Structure of Lake Huron-Sudbury Area, Symposium: Structural Geology of Canadian Ore Deposits, Jubilee Volume, Canadian Inst. of Min. Met., pp. 580-589, 1948.

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^o N. H. Magnusson, Zinc and Lead Deposits of Central Sweden, 18th International Geological Congress, loc. cit., pp. 371-379.

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mineralization are used. Radio-isotope ages are considered much more reliable than those obtained by the usual non-quantitative geologic methods and it is unfortunate that more such ages are not available.

For the pre-Cambrian samples, the inaccuracies of geologic dating become increasingly intolerable, and where possible these samples have been assigned ages from radio-isotope data on minerals of supposed contemporary mineralization. For four samples however, no. 115 from Franklin, N.J., no. 18 from Sault Ste. Marie, Ont., no. 137 from Broken Hill, N.S.W., and nos. 129 and 130 averaged from Fahlun and Langban, Sweden, no satisfactory radio-isotope ages for minerals of immediate association exist. The ages shown are those deduced on the basis of the best geologic evidence obtainable, and do not have as much reliability as the other minerals.

Of the remaining pre-Cambrian samples, those considered to have the most reliable ages are numbers 10 from Katanga, Belgian Congo (Collins analysis), 4 from Great Bear Lake, N.W.T., 8 from Goldfields, Sask., and 15 from Great Slave Lake, N.W.T. (Collins analysis). Ages assigned on the basis of radio-isotope data can be very tenuous, if the common lead and radioactive minerals are not taken from the same deposit. This is illustrated in the case of the Sioux Lookout sample, Collins number 17. The age for this sample has been taken as that of the Huron claim pegmatite some 200 miles west of Sioux Lookout. But there is no guarantee that these minerals were deposited at the same time. Collins assigned an age of 2.48×10^9 yrs. for the Huron Claim pegmatite but a re-evaluation of the data³³ suggests a value of 2.6×10^9 yrs. as more probable. The geologic ages assigned to the Broken Hill, N.S.W. mineral range from a value of 0.9×10^9 yrs. assigned by Nier to 1.5×10^9 yrs.

given by Collins¹³ on the basis of age determinations made at Radium Hill.

While Nier's figure appears small, an age of 1.5 billion years predicated upon the assumption of contemporaneity of minerals from different rock masses is questionable; hence a compromise age of 1.2 billion years has been retained here as a first approximation.

For pre-Cambrian samples two factors may contribute to uncertainty in the age: (1) the uncertainty in the age itself due to recrystallization effects and the loss of lead³³; (2) contemporaneity of mineralization is difficult to establish unless the minerals under consideration come from the same rock mass. Certainly ages assigned on the basis of province-wide orogenic activity must be considered suspect.

Mathematical Analysis

The use of least squares analysis for common lead data has been amply discussed and illustrated by previous writers on the subject (see especially Bullard and Stanley⁸, E. McCrady¹¹, and Collins, Farquhar and Russell¹³).

Employing equations (27) with α_0 , β_0 , γ_0 , P_0 and W_0 as the parameters for the least squares fit, the normal equations may be written as

$$n\alpha_0 - P_0 \sum_{m=1}^n (e^{\lambda t_m} - 1) - \sum_{m=1}^n x_m = 0 \quad (29)$$

$$n\beta_0 - \epsilon P_0 \sum_{m=1}^n (e^{\lambda' t_m} - 1) - \sum_{m=1}^n y_m = 0 \quad (30)$$

$$n\gamma_0 - W_0 \sum_{m=1}^n (e^{\lambda'' t_m} - 1) - \sum_{m=1}^n z_m = 0 \quad (31)$$

$$\alpha_0 \sum_{m=1}^n (e^{\lambda t_m} - 1) - \sum_{m=1}^n x_m (e^{\lambda t_m} - 1) + \epsilon \beta_0 \sum_{m=1}^n (e^{\lambda' t_m} - 1) + \epsilon \sum_{m=1}^n y_m (e^{\lambda' t_m} - 1) - P_0 \sum_{m=1}^n (e^{\lambda t_m} - 1)^2 + \epsilon^2 \sum_{m=1}^n (e^{\lambda' t_m} - 1)^2 = 0 \quad (32)$$

$$\gamma_0 \sum_{m=1}^n (e^{\lambda'' t_m} - 1) - \sum_{m=1}^n z_m (e^{\lambda'' t_m} - 1) - W_0 \sum_{m=1}^n (e^{\lambda'' t_m} - 1)^2 = 0. \quad (33)$$

n is the number of samples fitted to the curves. The five unknowns may be solved for as follows:

$$\alpha_0 = \frac{1}{n} \left[\sum_{m=1}^n x_m + P_0 \sum_{m=1}^n (e^{\lambda t_m} - 1) \right] \quad (34)$$

$$\beta_0 = \frac{1}{n} \left[\sum_{m=1}^n y_m + \epsilon P_0 \sum_{m=1}^n (e^{\lambda' t_m} - 1) \right] \quad (35)$$

$$\gamma_0 = \frac{1}{n} \left[\sum_{m=1}^n z_m + W_0 \sum_{m=1}^n (e^{\lambda'' t_m} - 1) \right] \quad (36)$$

where P_0 and W_0 have the values -

$$P_0 = \left\{ (\sum x_m) \sum (e^{\lambda t_m} - 1) - n \sum x_m (e^{\lambda t_m} - 1) + \epsilon (\sum y_m) \sum (e^{\lambda' t_m} - 1) - n \epsilon \sum y_m (e^{\lambda' t_m} - 1) \right\} \div \left\{ n \sum (e^{\lambda t_m} - 1)^2 - [\sum (e^{\lambda t_m} - 1)]^2 + n \epsilon^2 \sum (e^{\lambda' t_m} - 1)^2 - \epsilon^2 [\sum (e^{\lambda' t_m} - 1)]^2 \right\} \quad (37)$$

$$W_0 = \frac{(\sum z_m) \sum (e^{\lambda'' t_m} - 1) - n \sum z_m (e^{\lambda'' t_m} - 1)}{n \sum (e^{\lambda'' t_m} - 1)^2 - [\sum (e^{\lambda'' t_m} - 1)]^2} \quad (38)$$

Using the values $\frac{1}{\epsilon} = 138$, $\lambda = 0.154 \times 10^{-9}$, $\lambda' = 0.972 \times 10^{-9}$ and $\lambda'' = 0.0499 \times 10^{-9}$ yrs.⁻¹ reported by Fleming, Ghiorso and Cunningham³², equations (34) through (38) give for the data of Table III the values shown for the first entry in Table IV. Also shown for comparison purposes in Table IV are several other sets of values for these constants. The data reported by Collins¹³, et.al., are derived from 17 common lead minerals, not all of which are different from the Lamont samples. The cotunnite from Mt. Vesuvius is probably the most modern lead "ore" specimen obtainable. It was estimated by the collector, Dr. B. H. Mason of the American Museum of Natural History, to have been deposited within a 36-hour period prior to collection (March 16, 1954).

Table IV

Comparison of Modern Lead Isotopic Abundances
and of Values for P_o and W_o

Source	α_o	β_o	γ_o	P_o	W_o
Least squares analysis of dated lead ores, this work	18.9	15.9	39.2	11.5	42.7
Least squares analysis of dated lead ores, Collins, ^a et.al.	18.4	15.6	38.4	9.92	38.3
Cotunnite collected from fumarole at Mt. Vesuvius, Italy, 1954, our sample 131	19.0	15.4	39.3		
Average of lead from Quaternary sediments, Patterson, ^b et.al.	18.9	15.7	38.8		

^a Collins, Russell and Farquhar, reference 13.

^b Paterson, Goldberg and Inghram, reference 31.

The last entry in the table, reported by Patterson³¹ and co-workers, is an average of the values obtained from the manganese nodule and from the red clay sample.

For further comparison of P_o and W_o , Table V shows values of these quantities computed for mafic and siliceous crustal rocks from the abundance data of Evans and Goodman²⁹, Sandell and Goldich³⁰, and Senftle and Keevil³⁴, using modern lead abundances reported by Patterson³¹, et.al. It should be observed that the values of P_o and W_o determined for Table V suffer from the fact that the lead abundances are not from the same sets of rocks for which the uranium and thorium abundances are reported.

The Lamont constants shown in Table IV are in general agreement with the other values shown and confirm the fact that, on the basis of the step-differentiation model, common leads have been extracted from a fairly siliceous environ-

Table V

Uranium and Thorium to Lead Abundances in Continental Rocks

Rock Type	Uranium Concentration	Thorium Concentration	Lead Concentration	P _o	W _o
Acid Igneous	3.0±0.3 ^a g/ton	13±2 ^a g/ton	19 ^b g/ton	11.8	50.9
Basic Igneous	.96±0.1 ^a	3.9±.6 ^a	9 ^b	7.94	32.3
Granitic	3.82 ^c	12.48 ^c	19 ^b	15.0	48.9

^a Evans and Goodman, reference 29
^b Sandell and Goldich, reference 30
^c Senftle and Keevil, reference 34

ment, as indicated by the values for P_o and W_o, corresponding to those observed in surficial, continental rocks today. The Lamont values for P_o and W_o exceed those of Toronto in particular by about 10%. The composition of modern lead from our least squares analysis is more nearly in agreement with that reported by Patterson than the Toronto values. However, it may be argued that Patterson's values may not necessarily be expected to agree with those deduced from the step-differentiation model by least squares analysis.

The abundances of Table III are plotted against age in Figures 8 and 9, together with the curves for the step-differentiation model, using the constants determined by least squares fit to the data. In view of the meaning of the step-differentiation model equations as defined in this paper, it again seems admissible to equate primeval lead composition to Patterson's meteoritic lead composition. This conclusion has been presented and discussed by Houtermans²¹. If therefore, the meteoritic lead abundances are read as ordinates on the solid curves in Figures 8 and 9, the corresponding abscissae give the following values of t_c (age of the earth's crust):

Figure 8. Plot of x_m and y_m versus time. Solid curve shows least squares fit of analyses in Table III to the step-differentiation model. Dashed curve is plotted with $k = .472 \times 10^{-9} \text{ yrs.}^{-1}$ and $\mu = .625 \times 10^{-9} \text{ yrs.}^{-1}$

Figure 9. Abundance of Pb^{208} relative to Pb^{204} versus time. Curve obtained from least squares fit of data in Table III to the step-differentiation model.

$$\begin{aligned}
 t_c &= 3.9 \times 10^9 \text{ yrs.}, \\
 t_c' &= 4.4 \times 10^9 \text{ yrs.}, \\
 t_c'' &= 4.2 \times 10^9 \text{ yrs.},
 \end{aligned}
 \tag{39}$$

from the curves $\text{Pb}^{206}/\text{Pb}^{204}$, $\text{Pb}^{207}/\text{Pb}^{204}$, and $\text{Pb}^{208}/\text{Pb}^{204}$, respectively.

An average value $t_c = 4.17 \times 10^9$ yrs. is obtained for the values in equation (39).

Ideally, the values of t_c obtained from each of the abundance curves should be equal. The fact that there is some spread in the values, equation (26), probably reflects inadequacy of the data, as well as the lack of realization of some of the assumptions invoked in setting up the step-differentiation model.

It should be emphasized that the evaluation of the constants in Table IV by least squares analysis does not in itself constitute a validation of the step-differentiation model, equations (27). The fitting procedure of the least squares treatment merely determines the best values of the constants for any given function such that the sum of the squares of the residuals is a minimum. Thus any information such as the age of the earth's crust, deduced from the step-differentiation or any other model must depend not only on the adequacy of the data, but also on the validity of the model itself.

As a final criticism, it must be noted that sufficient data do not yet exist for a highly reliable least squares analysis with any model. The least squares method is essentially a statistical analysis, and it follows that the number of samples should be large. In this particular case, the fit is especially sensitive to the older samples and it is evident that a much larger number of old pre-Cambrian samples is needed. The dependence of the results on the older samples may be illustrated by varying the age of the oldest sample, Collins no. 17 from Sioux Lookout. In a restudy of common lead ages, Allan, Farquhar, and Russell¹⁴

have obtained a new value for the age of the Sioux Lookout mineral by a mathematical procedure which does not utilize geological ages of pre-Cambrian common leads. The age so obtained is 2.31×10^9 yrs. If now this age is associated with the Sioux Lookout sample, the equations (34) through (38) give the following new values for the constants:

$$\begin{aligned}\alpha_o &= 18.9 \\ \beta_o &= 15.8 \\ \gamma_o &= 39.2 \\ P_o &= 12.4 \\ W_o &= 45.2\end{aligned}\tag{40}$$

Comparing with the original constants in Table IV, $\alpha_o, \beta_o, \gamma_o$, have not changed appreciably, whereas P_o and W_o have increased by almost 10%. The average value t_c , obtained with the new constants, equation (40), is $t_c = 3.98 \times 10^9$ yrs., a change of nearly 5%.

While the foregoing illustration represents an extreme case, it is nevertheless evident that in order to minimize the effects of error in any one given sample, it would be desirable to both decrease the possible uncertainty in age of old leads, and to increase substantially the number of dated common lead minerals with large t_m .

Model Embodying Continuous Differentiation of the Earth's Crust

Consider a model which allows for continuous differentiation of the crust, from an original primordial composition represented by chondrites, to a siliceous composition characteristic of granitic rocks today. The evidence for a step-differentiation is not altogether conclusive and moreover, with a proper analytical representation, the discrete differentiation should be contained in the continuous differentiation formulation, at least as a limiting case, if the boundary conditions so require.

Although differentiation of the whole crust is loosely referred to, the particular differentiation here designated is the change in geochemical composition of potential lead ore source material, and even more specifically, in the uranium to lead ratio of that material. Other portions of the crust are not directly involved, although it is conceivable that complementary changes were taking place simultaneously throughout the whole crust, or what was to become the crust.

The differentiation hypothesized does not distinguish between migration of uranium and/or lead from the mantle as opposed to changes within the crust (i.e., above the Mohorovicic discontinuity) as it is now known. The formulation merely admits of an open system and no specification is made as to the origin or destination of uranium and/or lead entering or leaving the system. It is quite likely, however, that since most of the earth's lead is below the Mohorovicic discontinuity and uranium is above it, some transfer between crust and mantle is involved. There may be superimposed additional effects of intra-crustal differentiation. Either or both effects are compassed within the proposed formulation.

It is to be emphasized that the geochemical composition of the environment of ore lead sources considered is correlated with time, rather than the amount of a given type of differentiated material with time.

Not many criteria are available to determine the proper generating function for the differentiation process. From the uranium to lead ratio found in rocks of varying SiO_2 content, it is generally observed that the U/Pb greatly increases from material of chondritic composition to those of granitic composition. Since therefore, old rocks of granitic composition are known, it would seem that the generating function is properly exponential in nature, with the high-gradient portion of the curve at the old end of the time scale. Also, if the differentiation reaction proceeds at a rate proportional to the inequilibrium concentrations, then an exponential dependence on time is not unreasonable. These arguments are not conclusive, but merely point to the exponential relationship as presently more plausible than other general expressions available.

The proposed function is qualitatively illustrated in Figure 10, where variations in the U/Pb ratio are projected against time. Also shown is the relationship postulated for the step-differentiation model. The effect of the decay of uranium is not included for the curves shown.

With the foregoing considerations in mind, the differential equation for the $\text{U}^{238}/\text{Pb}^{204}$ growth curve may be written as

$$\frac{dP}{dt} = \lambda P - ke^{\mu t}, \quad (41)$$

where the generating function, $ke^{\mu t}$, is quite arbitrary, beyond the exponential nature just noted. k and μ are constants to be determined and the remaining

Figure 10. Schematic illustration of possible variation of uranium to lead ratio in outer shell of earth with time for the models indicated, due to differentiation alone (effect of radioactive decay not included). The right terminal points of the curves are presumably at or near the beginning of earth history.

symbols are as previously defined. Since time is again measured positively back into earth history from the present, the generating function must provide negative increments with increasing t ; therefore, with the minus sign shown, k must necessarily be a positive number.

If the Laplace transformation of $P(t)$ be denoted by $P(s)$, then the Laplace transformation of equation (41) may be written as:

$$P(s) = \frac{P_0}{(s-\lambda)} - \frac{k}{(\lambda-\mu)} \left[\frac{1}{(s-\lambda)} - \frac{1}{(s-\mu)} \right] \quad (42)$$

where the initial boundary condition $P = P_0$ at $t = 0$ has been incorporated, and s is the complex variable. The inverse transformation of equation (42) immediately gives as the desired solution $P(t)$,

$$P = P_0 e^{\lambda t} - \frac{k}{(\lambda-\mu)} [e^{\lambda t} - e^{\mu t}] \quad (43)$$

The corresponding growth curve for Pb^{206}/Pb^{204} may be obtained by inserting $P(t)$ from eq. (43) into eq. (4):

$$dx = -\lambda P dt = -\lambda P_0 e^{\lambda t} + \frac{k\lambda}{(\lambda-\mu)} [e^{\lambda t} - e^{\mu t}] \quad (44)$$

and direct integration yields

$$x = -P_0 e^{\lambda t} + \frac{k}{(\lambda-\mu)} \left[e^{\lambda t} - \frac{\lambda}{\mu} e^{\mu t} \right] + C \quad (45)$$

The constant of integration C may be evaluated by applying the condition $x = \alpha_0$ at $t = 0$, and the growth curve may then be written

$$x = \alpha_0 - P_0 (e^{\lambda t} - 1) + \frac{k}{(\lambda-\mu)} e^{\lambda t} + \frac{k}{\mu} \left[1 - \frac{\lambda}{(\lambda-\mu)} e^{\mu t} \right]. \quad (46)$$

For the case of $Q = N^{235}/N^{204}$, the differentiation process would be expected to be the same as for U^{238}/Pb^{204} , since both nuclides have the same chemical properties, and possible chemical fractionation effects are probably negligible. Allowance must be made, however, for the difference in abundances of the uranium isotopes. An average value may be employed,

but the exact time dependent ratio of the isotopes introduces no great complication. The differential equation may therefore be written as

$$\frac{dQ}{dt} = \lambda' Q - \frac{\epsilon k}{e^{(\lambda - \lambda')t}} e^{\mu t} \quad (47)$$

where the present ratio of U^{235} to U^{238} is denoted by ϵ , and μ and k are the same quantities appearing in eq. (41). If again $\mathcal{L}[Q(t)] = Q(s)$ indicates the Laplace transformed function, then the Laplace transformation of eq. (47) may be written thus (with $Q = Q_0$ at $t=0$):

$$Q(s) = \frac{Q_0}{(s - \lambda')} - \frac{\epsilon k}{(\lambda - \mu)} \left[\frac{1}{(s - \lambda')} - \frac{1}{[s - (\mu - \lambda + \lambda')]} \right] \quad (48)$$

$\mathcal{L}^{-1}[Q(s)]$ yields the required solution $Q(t)$:

$$Q = Q_0 e^{\lambda' t} - \frac{\epsilon k}{(\lambda - \mu)} \left[e^{\lambda' t} - e^{(\mu - \lambda + \lambda')t} \right] \quad (49)$$

The differential equation for $y = \frac{N^{207}}{N^{204}}$ may now be written as

$$dy = -\lambda' Q_0 e^{\lambda' t} dt + \frac{\epsilon k \lambda'}{(\lambda - \mu)} \left[e^{\lambda' t} - e^{(\mu - \lambda + \lambda')t} \right] dt \quad (50)$$

Integration of eq. (50) and evaluation of the constant of integration as before gives

$$y = \beta_0 - Q_0 (e^{\lambda' t} - 1) + \frac{\epsilon k}{(\lambda - \mu)} e^{\lambda' t} + \frac{\epsilon k}{(\mu - \lambda + \lambda')} \left[1 - \frac{\lambda'}{(\lambda - \mu)} e^{(\mu - \lambda + \lambda')t} \right] \quad (51)$$

In the case of Th^{232}/Pb^{204} , the same differential equation will apply as for U^{238}/Pb^{204} , except that constants k'' and μ'' will not necessarily equal those used for uranium. With this difference the equation obtained for $W = Pb^{208}/Pb^{204}$ is identical in form to eq. (46). Applying the results to common lead of composition x_m, y_m, z_m mineralized at time t_m , the

the equations for the three isotopes may be written thus:

$$\begin{aligned}
 x_m &= \alpha_0 - P_0(e^{\lambda t_m} - 1) + \frac{k}{(\lambda - \mu)} e^{\lambda t_m} + \frac{k}{\mu} \left[1 - \frac{\lambda}{(\lambda - \mu)} e^{\mu t_m} \right] \\
 y_m &= \beta_0 - Q_0(e^{\lambda' t_m} - 1) + \frac{\epsilon k}{(\lambda - \mu)} e^{\lambda' t_m} \\
 &\quad + \frac{\epsilon k}{(\mu - \lambda + \lambda')} \left[1 - \frac{\lambda'}{(\lambda - \mu)} e^{(\mu - \lambda + \lambda') t_m} \right] \\
 z_m &= \gamma_0 - W_0(e^{\lambda'' t_m} - 1) + \frac{k''}{(\lambda'' - \mu'')} e^{\lambda'' t_m} + \frac{k''}{\mu''} \left[1 - \frac{\lambda''}{(\lambda'' - \mu'')} e^{\mu'' t_m} \right]
 \end{aligned} \tag{52}$$

It should be noted that the equations (52) representing the continuous differentiation model involve only the changing ratios of uranium and thorium to lead. Only insofar as these quantities serve as an index of general crustal differentiation can the results be generalized to speak of the crust as a whole. Moreover, the equations are limited to zones in the crust that serve as lead sources, but again the implications are probably more general. With the exception of the differentiation allowed for, the assumptions previously delineated for the step-differentiation model must also hold for equations (52).

The evaluation of the constants k , μ and k'' , μ'' presents some difficulty. A rigorous application of the method of least squares is not feasible since simultaneous equations are involved with the unknowns in exponential and other non-linear functions, and exact analytical solutions are very difficult, if not impossible, to obtain.

Although approximation methods are applicable the number of mathematical operations becomes extensive. In view of the fact that the constants are dependent on the pre-Cambrian samples to an even greater extent than with the step-differentiation model, the effort required to evaluate the constants was not considered warranted because of the small number of dated pre-Cambrian samples available.

A somewhat different approach permits the evaluation of k and μ together with a simultaneous evaluation of t_p , where t_p is the time at which terrestrial lead has the isotopic composition of meteoritic lead, and the uranium to lead ratio has the primordial value reported by Patterson²⁸, et al. If P_p , Q_p , α_p and β_p are the values of the ratios of U^{238} , U^{235} , Pb^{206} and Pb^{207} to Pb^{204} respectively, obtaining at time t_p , then the foregoing conditions may be analytically represented by the following equations:

$$P_p = P_o e^{\lambda t_p} - \frac{k}{\lambda - \mu} \left[e^{\lambda t_p} - e^{\mu t_p} \right] \quad (53)$$

$$Q_p = Q_o e^{\lambda' t_p} - \frac{\epsilon k}{(\lambda - \mu)} \left[e^{\lambda' t_p} - e^{(\mu - \lambda + \lambda') t_p} \right] \quad (54)$$

$$\alpha_p = \alpha_o - P_o (e^{\lambda t_p} - 1) + \frac{k}{(\lambda - \mu)} e^{\lambda t_p} + \frac{k}{\mu} \left[1 - \frac{\lambda}{(\lambda - \mu)} e^{\mu t_p} \right] \quad (55)$$

$$\begin{aligned} \beta_p = \beta_o - Q_o (e^{\lambda' t_p} - 1) + \frac{\epsilon k}{(\lambda - \mu)} e^{\lambda' t_p} \\ + \frac{\epsilon k}{(\mu - \lambda + \lambda')} \left[1 - \frac{\lambda'}{(\lambda - \mu)} e^{(\mu - \lambda + \lambda') t_p} \right] \end{aligned} \quad (56)$$

It will be observed that these equations are simply those of the growth curves of the continuous differentiation model, equations (43), (49) and (52), with the appropriate values of the variables inserted.

The assumptions inherent in equations (53) through (56) should be noted:

(1) the isotopic abundance of lead at t_p is that now observed in iron-meteorites (negligible U and Th); (2) the total uranium to total lead ratio in the earth at the time of its formation t_p , may be equated to that now found in stony and iron meteorites in their proper proportion; (3) the rate of differentiation has decreased exponentially since the time of planet formation. These assumptions are listed in order of decreasing certainty. They are all sufficiently reasonable,

however, to warrant calculation of the model.

The unknowns k , μ and t_p may be found by simultaneous solution of any three of the equations (54) through (56). The values of α_0 and β_0 employed are derived from the step-differentiation model (Table IV) by least squares analysis of the lead ore data. Their use here is justified not only by the agreement with the Patterson's Quaternary lead abundances and with the Vesuvius abundances, but also by the fact that the two models become essentially identical for small (modern) values of t_m . The value of P_0 is taken from Table V for acid igneous rocks, and is very close to those in Table IV. The values of P_p and Q_p are obtained from the primordial lead and uranium abundances for meteorites reported by Patterson²⁸, et al. by correcting for the natural decay of uranium in time t_p . We have, therefore:

$$\alpha_0 = 18.87$$

$$\beta_0 = 15.77$$

$$P_0 = 11.76$$

$$\frac{1}{\epsilon} = 138$$

$$\alpha_p = 9.41$$

$$\beta_p = 10.27$$

$$P_p = .6186e^{\lambda t_p}$$

$$Q_p = .004515e^{\lambda t_p}$$

With the values shown in equations (57), a graphical solution of the three equations (54), (55) and (56) gives the following values:

$$t_p = 5.28 \times 10^9 \text{ yrs.}$$

$$\mu = .625 \times 10^{-9} \text{ yrs.}^{-1}$$

$$k = .472 \times 10^{-9} \text{ yrs.}^{-1}$$

(58)

That the four equations (53) through (56) are compatible is indicated by the fact that a graphical solution of an alternate combination, equations (53), (55) and (56) gives a value of t_p equal to that of the first combination, equations (58), to within less than a percent, with a somewhat larger divergence in the values of k and μ .

It should be noted that the values of k , μ and t_p obtained in equations (58) depend only indirectly on the isotopic composition of lead ores, inasmuch as the values of α_0 and β_0 from Table IV were the only ones incorporated which depended in any way on common lead minerals. Because the continuous differentiation model allows for an increase in the uranium to lead ratio with decreasing t , it follows that in view of the fixed ratio postulated for step-differentiation model, the derived value for t_p should be larger than any previously obtained. If therefore the three assumptions initially noted are valid, $t_p = 5.3 \times 10^9$ years may be regarded as an upper limit for the age of the earth.

The growth curves for Pb^{206} and Pb^{207} relative to Pb^{204} are shown as the dashed curves in Figure 8, using the values of k and μ in equation (58).

The curves for the two models are identical for small values of t_m , but begin to diverge at about 2 billion years. The divergence becomes larger with increasing values of t_m . For the value of $\mu = .625 \times 10^{-9}$ yrs.⁻¹, the corresponding differentiation "half-life" is about one billion years. If the differentiation of uranium serves as an index of differentiation of all crustal material, then it follows that the major portion of the general differentiating forces was expended in the first billion years plus of earth history.

If at the end of this period, a sufficient amount of siliceous material was segregated in the outer shell so that the existence of a crust at that time could properly be spoken of, then it is seen that the age of the crust so obtained would correspond roughly to that obtained with the step-differentiation model, of the order of 4 billion years.

Comparison of Lead Isotope Constants and Age Derivatives with Previous Results

Values for α_c , β_c , γ_c , isotopic composition of primeval lead in the earth's crust, for α_p , β_p , γ_p , primordial lead isotopic composition, for t_c , age of the crust of the earth, and for t_p , age of the earth, obtained by other investigators are summarized for convenience together with those of the present work in Table VI.

Table VI

Values for Age of the Earth and its Crust and the
Isotopic Composition of Primeval and Primordial Lead

Author	t_c or t_p (1×10^9 yrs.)	Primeval or Primordial Lead Composition		
		$\alpha_{c,p}$	$\beta_{c,p}$	$\gamma_{c,p}$
S. K. Gerling ³	3.23	- - -	- - -	- - -
F. G. Houtermans ⁶	2.9	11.52	14.03	31.6
A. Holmes ⁵	3.35	10.95	13.51	- - -
H. Jefferys ⁷ , corrected by A. Holmes ⁹	2.87	- - -	- - -	- - -
E. C. Bullard and P. Stanley ⁸	3.29 $\pm$.2	11.86 $\pm$ 1.47	13.86 $\pm$.56	- - -
C. B. Collins ¹³ , et.al.	3.5	11.33	13.55	31.10
C. Patterson ³⁵	4.51 - 4.56	9.41	10.27	(29.16)
F. G. Houtermans ²¹	4.5 $\pm$.3	(Patterson's meteoritic lead composition assumed)		
This research	4.2 - 5.3	(Patterson's meteoritic lead composition assumed)		

In addition, it may be noted that Alpher and Herman¹⁰ have assigned an upper limit of 5.3×10^9 yrs. for t_c by computing the age required for $x_m = 0$,

and McCrady¹¹ has similarly obtained an upper limit of 5.07×10^9 yrs., required for $y_m = 0$. Both of these results are based on the Nier data. The new data presented in this paper do not significantly affect these maximal values. It is evident however that the validity of these limits rests on a constant uranium to lead ratio throughout earth history, such as is embodied in the step-differentiation model. If the possibility of differentiation effects with time are allowed for, it follows that the numbers obtained by Alpher and Herman¹⁰ and by McCrady¹¹ cannot be properly regarded as maximal values.

A survey of the methods used to obtain the data shown in Table VI reveals that with the exception of the continuous differentiation model of this research, all have been obtained on the basis of the step-differentiation model, used in one form or another. Patterson's values for t_p (4.5 and 4.6×10^9 yrs.) were obtained by calculating a Pb^{207}/Pb^{206} age for the radiogenic lead remaining after subtracting meteoritic lead from modern oceanic and basaltic leads. Due to the possibility of the system being open (i.e., allowing for differentiation effects with time, for example), the Patterson ages must be regarded as minimal, as he indicates. Patterson's meteoritic, modern oceanic and basaltic lead compositions are an important contribution to the study of earth history, and his method of calculating the age of the earth has the additional merit of averaging secondary changes of rock lead composition due to such possible phenomena as multiple orogenies, cycling through the sedimentary process, etc.

A brief inspection of the results tabulated in Table VI indicates that the data may be classed in two groups: group 1, consisting of the first six entries, for which t_c ranges from 2.9 to 3.5 billion years, average 3.2 billion years, and the values for α_c , β_c and γ_c , averages 11.4, 13.8 and 31.4 respectively, are substantially larger than those for meteoritic lead; the last three sets of data

constitute group 2 and the ages here are higher than those in the first group by at least a billion years.

Of the methods used to obtain the first group of results, that of Holmes is the most elaborate, but as Bullard and Stanley point out, uncertainties persist because the same data are repeatedly used in different combinations. The treatment by Bullard and Stanley is probably the most rigorous, if the propriety of their sample selection and the validity of their statistical assumptions be granted. The results of Collins, et.al, are obtained by the method of Bullard and Stanley with additional data, and have therefore a correspondingly increased reliability. It is important to note, however, that in spite of differences in the treatments, the results of the first six authors indicated in Table VI are in broad agreement. It may be stated here that the Lamont data, if treated by the same methods employed in the first group, would give substantially the same results indicated in this group.

The higher age values characteristic of group 2 must be attributed to the incorporation of meteoritic lead composition, which is used in all three methods for primordial lead isotopic composition. The younger age of 4.2 billion years resulting from this work and Houterman's result were obtained by using lead ore data to determine points on the young portion of the age curves model and are in general agreement with Patterson's values.

The most convenient explanation of the two sets of differing ages, on the basis of the present work, is that the crust was not formed in a negligibly small time, but there was required an extended time of the order of a billion years, as embodied in the continuous differentiation model, in order for a siliceous outer crust to be built up. As noted previously, this model was shown to admit an age of 5.3 billion years for the time at which meteoritic lead composition

obtained. From the dashed curves of Figure 8, the mean values of α_c and β_c for group 1 of Table VI give an age of about 3.6 billion years, which agrees roughly with the mean value of t_c , 3.2 billion years, for said group. Thus the continuous differentiation model gives a comparable age for the crust if the average of the lead isotopic compositions of group 1 is taken as the primeval lead isotopic composition prevailing in the early crust.

The idea of growth of the earth's crust in time is in itself not new. A hypothesis embodying the growth of continents has been advocated by J. Tuzo Wilson^{35, 36}. The possible relations between the continuous differentiation model and Wilson's hypothesis are evident, but it should be borne in mind that the model deals with the geochemical composition of the crust as a function of time rather than amounts and distribution of crustal material with time.

It is evident that a precise definition of the age of the earth on the basis of common lead isotopic compositions is not yet possible. This is due primarily to the uncertainty in the nature of the required model and the lack of well dated samples older than 2 billion years. The assumption that the isotopic composition of lead in the metal phase of meteorites is the same as that existing in the primordial earth has been questioned but is one of the most likely postulates in this problem.

On the basis of the preceding summary it is reasonable to believe that the age of the earth lies between a minimal figure of 4.5×10^9 years determined by Patterson³⁵ and a maximal value of 5.3×10^9 years as presented in this work.

The actual value may be regarded as depending primarily on the nature and time required for the geochemical differentiation which produced the earth's crust. Some evidence for a certain amount of differentiation at the time of formation of the earth, together with preliminary calculations for young ore leads of low radiogenic lead content indicates an age closer to the minimal value. Tentatively a best estimate of the age of the earth may be placed therefore at $4.8 \pm .2 \times 10^9$ years.

Regional Analysis of Common Leads

The large number of isotopic analyses completed in the course of this study adds considerably to knowledge of the regional variations of the isotopic composition of lead from common lead minerals. In a crude way the isotopic composition of samples from various localities follows an "age curve", i.e., a smooth curve of isotopic composition vs. age can be drawn which is closely approximated by a considerable number of the samples. On the other hand there are many samples which do not conform to this "normal" behavior and are termed "anomalous". Such variations are not unexpected. Significant differences in uranium and thorium to lead ratios are known. Most ore lead presumably originates from a fairly small volume element of the earth's crust, thus reflecting the local environment of origin. Thus in terms of the models previously discussed, P_0 and W_0 are not truly constants.

The distribution of samples from North America is shown on the map of Figure 11. The majority of samples analyzed in this work are from the North American continent, and of these the largest group is from the districts of the Mississippi Valley, as shown on the map. The majority of younger minerals are found in lead-zinc ore deposits associated with sedimentary rocks while the older samples are found in a metamorphic or igneous environment. Three samples (nos. 19, 97 and 117) are of pegmatitic origin.

Figure 11. Map of North America, showing sources of samples. Samples in Mississippi Valley districts: distr. 1, 12 samples; distr. 2, 1 sample; distr. 3, 8 samples; distr. 4, 2 samples; distr. 5, 14 samples; distr. 6, 2 samples.

It would be very useful to establish possible regional variations of P_o and W_o , and this could be done if the ages of the samples were accurately determined. However, for most samples, the uncertainty in the age more than accounts for the displacement from the time curve, and it is therefore not possible to obtain sufficiently reliable information to establish broad patterns.

The so-called anomalous leads may be divided into three basic groups: (1) the Joplin type, (2) the Athabasca type, and (3) the Ivigtut type.

(1) Joplin type. This group, first identified by Nier¹, is representative of the Mississippi Valley leads in general and a number of other leads. It is characterized by an excess of Pb^{206} , Pb^{207} and Pb^{208} over that expected from the age curve.

Virtually all the leads from the Mississippi Valley region show this anomaly. The high radiogenic content is not obtainable with reasonable values of the constants from any of the proposed models of crustal history. The ages of these deposits are generally no younger than Cretaceous and yet more radiogenic lead is contained than in modern leads ($t_m = 0$). To the south in Central Arkansas and to the east in the Kentucky-Tennessee district the anomalous character of the leads becomes much less pronounced and even disappears. Other leads which have a similar anomalous composition are: no. 14 from Eganville, Ont.; nos. 24 through 28 from Minnie Moore Mine, Bellevue, Id.; nos. 86 through 89 from Kentucky and Tennessee as borderline cases; no. 96 from Newbury, Mass.; no. 113 from Friedensville, Pa., as a borderline case; no. 116 from Hunterdon Co., N.J.; nos. 127 and 128 from Hungary and Germany, respectively; and no. 132 from Trepca,

Yugoslavia. This type of anomalous composition is discussed separately under Mississippi Valley leads.

Sample no. 17, from the Worthington Mine, Sudbury, Ontario, is an exaggerated case of the same type anomaly as the Mississippi Valley leads. However, although its radiogenic content considerably exceeds that of modern leads it is different from the Mississippi Valley leads in at least two respects; (1) the deposits are in an entirely different environment, in metamorphic rocks that are definitely pre-Cambrian in age: (2) the excess Pb^{208} is much larger than that usually found in the Mississippi Valley leads.

This sample shows that the Joplin type anomaly is not restricted to young leads but may have developed at almost any time in earth history.

The Sudbury deposits have been subjected to detailed studies utilizing lead isotopic analyses by Russell¹⁵, et al, and these authors conclude that radiogenic lead has been added to normal lead from a source with a thorium to uranium ratio of 5.2 (measured at the present time).

(2) Athabasca type. This group shows an appreciable excess of only Pb^{206} and Pb^{207} , thus indicating derivation at least in part, from a uranium-rich environment. The samples nos. 9 through 13 from the Goldfields, Sask., region are associated with pitchblende deposits. The high Pb^{206} and Pb^{207} concentration is due to lead removed from the pitchblende at the time of formation of the galena (PbS) or clausthalite (PbSe). Recrystallization effects in the Athabasca (Goldfields, Sask.) deposits have been shown³⁸

Study of the Witwatersrand deposits³⁹ indicates that the galena may occur as small blebs not in "atomic" contact with radioactive minerals. However, they are of sufficient proximity to the radioactive grains so that recrystallization could mix radiogenic lead with rock and hydrothermal lead in the formation of the common lead mineral.

(3) Ivigtut type. This group is characterized by low $\text{Pb}^{206}/\text{Pb}^{204}$, $\text{Pb}^{207}/\text{Pb}^{204}$, $\text{Pb}^{208}/\text{Pb}^{204}$ ratios compared to those predicted by the "age curves". Thus this lead was derived from an environment such that the $\text{Pb}/\text{U}+\text{Th}$ was higher than that for the "average ore lead".

The Ivigtut, Greenland sample no. 19 indicates an age from the age curves (compare isotopic composition with model curves in Figures 8 and 9) which is considerably in excess of the reported geologic age of about 600 million years (late pre-Cambrian). The Wallace, Id. cerussite, no. 23, is another Nier sample which is anomalous in the same way. There is some uncertainty as to the geologic age, but if the reported age of early Tertiary is accepted, there is definite conflict with the isotopic age which apparently is late pre-Cambrian.

The regional variations in isotopic composition of common leads for the United States are shown in Table VII, where averages have been computed for the arbitrary indices 207/206, and 208/206 shown in Table II. In computing the averages a few obvious anomalies have been deleted because of their undue effect on the averages. The anomalies for districts in the Mississippi Valley have been retained, however, since they constitute the established pattern for the region. The averages indicated generally reflect

the age of mineralization common to the region, excepting of course, the Mississippi Valley districts. For some of the regions a paucity of samples requires that larger uncertainties be associated with their averages than for those with a greater number of analyses. With the averages summarized in Table VII, semi-quantitative criteria are provided for determining the possible anomalous nature of common leads from any given region of those listed.

Table VII

Lead Isotopic Averages for Regions in the United States

Region	No. Samples	Sample Nos. of Anomalies Deleted	Average 207/206	Average 208/206
Rocky Mts.	8	23 - 28	.8427	2.088
Colorado	6		.8331	2.072
Mississippi Valley				
Ill., Ia., Wisc.	12		.7287	1.896
South. Ill., Ky.	2		.7833	1.994
S.E. Missouri	7	65	.7510	1.913
Tri-State Dist.	14		.7311	1.887
North Ark.	2		.7230	1.870
Ky. - Tenn.	4		.7961	1.995
Appalachian Mts.				
New England	12	96	.8498	2.088
Penn., New York	11		.8396	2.076
Southern	2		.8690	2.098

Joplin-Type Anomaly - The Mississippi Valley Leads

An important observation from the data of the present research is that leads from the whole Mississippi Valley, from the Wisconsin-Illinois-Iowa district down through the Missouri districts to Northern Arkansas, have the same anomalous character as the Joplin leads. This is an important fact which must be embodied in any hypothesis proposed to explain the anomalies.

Earlier attempts^{4, 19} to account for the character of the Joplin leads have generally invoked one of the following two factors: (1) a high uranium and thorium to lead ratio (in effect, anomalous P_O and W_O) in the rock sources from which the lead was extracted; (2) the presence of radioactive deposits at depth, which produced radiogenic lead which mixed with the ore-bearing solutions. The main objection to the first hypothesis is that the values required for the P_O and W_O anomalies are so large ($P_O = 28$ and $W_O = 82$, for example) that in comparison to values thus far observed in crustal rocks, they seem unrealistic. In light of the geographically extended nature of the Joplin-type anomaly as delineated by the isotopic analyses reported in this work, the second factor suggested must require either a very extensive deposit of such radioactive minerals, or a large lateral distance of transport by the ore-carrying solutions, neither of which seems a likely prospect. It seems more reasonable that differential extraction of rock lead is involved. This hypothesis will be developed in the following pages.

Geologic Setting

The geology of the ore districts of the Mississippi Valley may be described in general terms as follows, after Lindgren⁴⁰ and Behre, Heyl and McKnight⁴¹. The deposits have no conclusive association with igneous rocks and characteristically occur in limestones, dolomites, cherts (derived from limestone), or calcareous shales. Specifically, the Illinois-Iowa-Wisconsin deposits are found primarily in the Galena dolomite and the Decorah formation (Ordovician); in southeast Missouri the main ore-bearing strata are the Bonne-terre and Potosi dolomites of Upper Cambrian Age; the Boone formation and the Chester group (Mississippian Age) are the main sites of deposition in the Tri-State region. Lead and zinc are of secondary importance in the fluorite deposits in the southern-Illinois district and here the mineralization occurs in veins on faults that cut Mississippian limestones, and in tabular replacement deposits in the same limestones. The ore-bearing strata are usually capped by shale.

Galena and sphalerite are the essential minerals in the deposits, but the ore also contains small amounts of nickel, cobalt, iron, copper and cadmium. With the exception of a small amount of silver found in the upper Mississippi Valley deposits and in places in the associated fluorite ores in southern Illinois and locally in the ores of southeastern Missouri, silver is generally absent. Mineral associations indicate a shallow deposition at temperatures and pressures comparable to surface conditions. Dikes, small plugs and sills of basic igneous rocks occur in the southern Illinois-Kentucky district near the fluorite veins, and are of older age. The only

other evidences of adjacent igneous activity are findings of a siliceous breccia mass cutting Paleozoic rocks in southern Illinois, a granite intruded into the Paleozoic of Kansas, and a granite of probable Mesozoic age found at 1250 feet depth in the Bird-Dog Mine, Oklahoma.

The ores are found as irregular deposits near the surface and as tabular "blanket deposits" at depth, the deepest mines being 300 to 500 feet. The ore may occur disseminated in limestone or dolomite, in massive replacement deposits along the bedding, as veinlets or small cavity fillings, in fault breccias and in solution breccias and cavities, the different types commonly being intermixed. The rock strata tend to be flat-lying, showing little folding or faulting. Where fault and joint patterns exist, they control deposition; but deposits are found independent of such patterns. In regions of gentle folding, deposition is controlled by fracture zones on limbs of the folds; and a tendency to follow pitching troughs has been observed.

The genesis of the Mississippi valley deposits is still a matter of controversy. Early opinions favored the Paleozoic sedimentary beds as the source, with the deposition affected by meteoric waters. Others have suggested deposition from artesian waters. In more recent years, the evidence has been interpreted to indicate deposition by hydrothermal solutions. However, as Behre, Heyl and McKnight⁴¹ point out, no criteria have yet been discovered that finally substantiate any of these hypotheses.

General observations as to the nature of the anomaly of the Mississippi Valley leads, as deduced from the analyses in Table II, may now be enumerated in the following manner:

- (1) As noted previously, the anomalies are characterized by excess radiogenic content, the excess favoring Pb^{206}
- (2) The amount of radiogenic lead is not only high, but variably so. The variations are well outside the limits of experimental uncertainty in the isotopic composition. While the excess may run as high as 20% for Pb^{206} , it is to be noted that for many samples the radiogenic content is much lower, and no. 65, from Flat River, Mo., in particular has essentially no excess radiogenic lead and must be regarded as a normal lead.
- (3) The excess radiogenic content is not only variable in concentration, but also over relatively short distances. As an illustrative case, the variations of samples 61 through 65--all from one locality, Flat River, Mo.--may be noted.

It is believed that the second and third observations in particular, argue against the earlier hypotheses which were advanced to explain the Joplin-type anomaly.

As a preliminary to the detailed presentation of an alternate hypothesis, the nature of the distribution of lead, uranium and thorium

in ordinary rocks should be considered. It is well established^{42, 43} that lead, uranium and thorium atoms are distributed throughout the various mineral grains (or equivalent domains in a non-crystalline matrix) comprising any given rock; the amounts of the three elements may not only vary from grain to grain, but any one of the three may be selectively enriched in one or more mineral species. This fact is conclusively demonstrated for example in the study of the distribution of lead, uranium, and thorium in the Essonville granite by Tilton⁴⁴, et al.

Of further significance is the discovery by Hurley⁴⁵ and Brown⁴⁶ et al. that intergranular surfaces of granite may carry a significant fraction of the uranium and thorium in the rock. It follows that the radiogenic lead daughters likewise would be preferentially concentrated along intergranular surfaces. Qualitatively at least, it appears that a similar situation would prevail in other igneous and metamorphic rocks and to a certain extent in sedimentary rocks as well.

On the basis of the observed inhomogeneous distribution of uranium and thorium in rocks, the following hypothesis is postulated to account for the Joplin-type anomaly. It is simply that, either in initial extraction processes or in transit, solutions permeated large volumes of rock containing inhomogeneously distributed lead under such conditions that only part of the lead present was removed. As a result the radiogenic lead was preferentially extracted since it was most accessible to the action

of the solutions.

This situation is in marked contrast to that postulated for a normal lead--namely, that the lead be extracted uniformly by complete mixing of the total lead in the rock, and that no extraneous lead be added to the ore-carrying solutions in transport (see assumptions 7 and 11 on pages 65 and 66). Under low temperature conditions it is evident that with preferential concentration of radiogenic lead in intergranular regions, a uniform removal of the total rock lead would not be likely. As for the matter of transport, it is seen that for the cases where the ore channel is fairly well restricted, the amount of rock surface exposed to the solutions is relatively small so that there is little possibility of extraneous contamination by the process mentioned above.

With such a mechanism for the extraction or addition of inhomogeneously distributed lead by low-temperature solutions, a number of variable factors are at once suggested to account for the variations in isotopic composition of the mineralized lead, even over short geographic distances. These variables are enumerated as follows:

- (1) Variations in net lead content with rock facies.
- (2) Variations in the extent to which excess radiogenic lead is concentrated along intergranular boundaries.
- (3) Variable lengths of time during which the solutions are active.

- (4) Differing temperatures at which the lead is taken into solution.
- (5) Variations in pH and in other properties of the solutions affecting the solubility of the lead.
- (6) Variation in the extent to which a given rock volume has been "worked" by previous solutions.
- (7) For the case of "contamination" of solutions carrying ore from an original homogeneous source, variations in the ratio of "contaminating" lead to original lead due to factors not included in the foregoing.
- (8) The presence of radon, with a 3 1/2 day half-life, in the U^{238} decay chain may serve to give a selective mobility to the Pb^{206} daughter, due to the possibility of the radon escaping into intergranular regions before disintegration.
- (9) Variations of excess uranium to thorium in the intergranular regions, with resulting differences in the amounts of the interstitial lead daughters.

It is seen that items (1) through (7) affect the radiogenic isotopes indiscriminately, whereas factors (8) and (9) may give rise to preferential effects on the three heavier isotopes. Without detailed knowledge of

environments of lead ore genesis, it is difficult to assess the relative importance of the factors enumerated. However, general considerations would assign to variables (2), (3), (5), (6), (8) and (9) the greatest probable effects but not necessarily in the order named.

The simplest mechanism of the proposed hypothesis would involve incomplete extraction of the lead from a single source; variations in isotopic composition would arise with the passage of time, the first extractions being richest in radiogenic lead. The remaining possibilities are for ore (normal isotopic composition) carrying solutions to permeate lead-bearing strata and to be contaminated with the radiogenic lead most easily dissolved; or to mingle with other solutions which have previously acquired an excess of radiogenic lead under conditions of inhomogeneous extraction. Combinations of the foregoing possibilities may also arise. In any event, the applicability of the hypothesis to the Mississippi Valley leads seems favored by the geological evidence in that broad dispersion of the solutions through rock bodies is indicated by (1) the nature of extensive replacement ore bodies and of disseminated ore, (2) the fact that ore feeding channels have not been found, and (3) the presence of impermeable strata usually marking limits of ore deposition.

It appears that without further data, no conclusive predictions that could be made on the basis of the proposed hypothesis will solve the matter of origin of the deposits (hydrothermal, meteoric or artesian). Each of the

three cases could involve the production of anomalous leads by the mechanism hypothesized. These possibilities are briefly outlined below, together with their probable implications. These in turn may provide a basis for a more conclusive study of the deposits on a local basis, using isotopic analyses on samples procured under close geological control.

Case (1a). Hydrothermal origin without contamination.

The word hydrothermal as used here refers to the action of hot waters, but it is not implied that these waters have been derived at higher temperatures from normal igneous activity. In this latter instances, the contained lead would probably have been extracted homogeneously and would not show an anomalous isotopic composition. It is pictured then, that the lead was inhomogeneously extracted from fairly deep-seated sources (probably in the crystalline basement rocks) under hydrothermal conditions such that the radiogenic lead in intergranular regions most easily entered into solution and gave rise to an anomalous isotopic composition. There was probably one such major source associated with each of the main districts, but as a matter of speculation, there may have been more. The variations in isotopic composition observed over short geographic distances probably require either multiple sources or multiple deposition in the sense that the times of extraction from a single source differed. The latter explanation would assume a continuous process in which the total available lead was gradually impoverished as to its radiogenic isotopes due to the preferential removal of the latter. In any event,

since the ores have come from some distance and in this case are premised not to be contaminated in transport, it would seem that ore bodies genetically related would tend to have the same isotopic composition. If the path of deposition could be outlined, only a gradual change in isotopic composition would be expected at most, and a regular trend from higher radiogenic content with early deposition to lower radiogenic content with later deposition would be expected if changes in isotopic composition were found. Mixing of solutions from such sources would of course complicate the simple pattern outlined.

Case (1b). Hydrothermal origin with contamination.

If the hydrothermal solutions are derived primarily from igneous sources, the resultant homogeneous extraction would yield lead of essentially "normal" isotopic constitution. These solutions somewhere in their upward movement could undergo broad diffusion through rock strata, and in this process would be selectively contaminated by radiogenic lead from these rocks. Depending on how near these contaminating sources were to the site of deposition, variations in isotopic composition would arise over short geographic distances. Introduction of the time element and other variables previously enumerated would produce similar results. In general, the variations in isotopic composition so produced would not follow as regular a pattern as suggested for the previous case.

Case (2). Meteoric origin. If atmospheric water in percolating down through rock strata could remove lead in solution, it is evident that under such low temperature conditions the extraction would very likely be inhomogenous and an anomalous lead composition would be obtained. Variations in the isotopic composition would again tend to show an irregular pattern, depending as they would on the nature of the various factors affecting solution.

Case (3). Artesian origin. This situation is very similar to Case 2 but with a minor difference. Less random variations in isotopic composition might be expected because of greater possibility of mixing through lateral circulation.

Additional geochemical studies which may contribute to further evaluation and applicability of the proposed hypothesis are: (1) measurement of isotopic composition of the sulphur from the various deposits; (2) study of the distribution of uranium, thorium and lead relative to granular structure, in sedimentary rocks.

A final point of interest is the apparent age of the source rocks. If the most contaminated samples of Mississippi Valley lead are used and the modern isotopic component of "average lead" employed to correct for the rock leads the difference will reflect the Pb^{206} , Pb^{207} and Pb^{208} added by the differential extraction process. The ratio $\text{Pb}^{207}/\text{Pb}^{206}$ of this excess radiogenic lead should give an approximation to the age of the rocks from which this lead was derived. The results are listed in Table VIII. Thus the age of the source rocks appears to be 2,000 m.y.

Table VIII

Age of Mississippi Valley lead source rocks
 (Modern lead assumed $204=1.00$ $206=18.9$ $207=15.7$ $208=39.1$)

<u>Sample No.</u>	<u>"Excess"</u>			<u>Excess</u>
	<u>Pb²⁰⁶</u>	<u>Pb²⁰⁷</u>	<u>Pb²⁰⁸</u>	<u>Pb²⁰⁷/Pb²⁰⁶</u>
Iowa-Ill. - Wis.				
45	3.0	.4	2.8	.13
46	3.5	.5	2.8	.14
47	2.3	.3	1.4	.13
48	3.3	.4	2.9	.12
49	3.3	.4	2.9	.12
50	3.2	.4	2.8	.125
51	3.2	.45	2.9	.14
53	3.6	.4	2.9	.11
54	3.8	.45	3.7	.12
55	3.3	.3	2.9	.09
56	3.7	.5	3.3	<u>.135</u>
			Av.	.12 ± .01
S.E. Missouri				
62	3.4	.6	3.7	.18
63	3.3	.5	3.3	.15
66	3.8	.3	2.9	<u>.08</u>
				.14 ± .04
Missouri-Kansas-Oklahoma				
68	4.2	.7	3.3	.165
70	3.4	.3	1.4	.09

Table VIII (cont'd.)

<u>Sample No.</u>	<u>Pb²⁰⁶</u>	<u>Pb²⁰⁷</u>	<u>Pb²⁰⁸</u>	<u>Pb²⁰⁷/Pb²⁰⁶</u>
Missouri-Kansas-Oklahoma				
71	3.5	.3	1.8	.09
72	3.2	.2	1.2	.06
75	3.3	.4	1.6	.12
77	3.2	.35	1.5	.11
78	3.2	.4	2.9	.125
79	3.3	.35	3.0	.105
80	3.3	.4	2.5	.12
85	3.8	.45	2.8	<u>.12</u>
				.11 ± .02
			Weighted Av.	0.12 ± .01
			Apparent age of source rocks	2,000 m. y.

Although the maximum spread in apparent age from the individual $^{207}/^{206}$ ratios ranges from 1200 to 2600 m.y., most of this spread is no doubt due to experimental uncertainty since the excess radiogenic Pb^{207} abundances are not known to better than 25%.

Ivigtut Type Anomaly

Although the most reasonable explanation for this type of anomaly is the origin in an environment of higher $\text{Pb}/\text{U}+\text{Th}$ than "average lead", another hypothesis based on inhomogeneous lead extraction is possible. If a given rock mass has been "worked" by solutions under such circumstances that much of the more accessible radiogenic lead has been removed, there would result a rock mass with a deficiency of radiogenic lead. If now at some subsequent time the same rock mass is heated to higher temperatures, any lead homogeneously extracted would be low in radiogenic lead. Since the fraction of the total lead in a rock that is in the intergranular spaces is small, it would be impossible by this mechanism to obtain large "negative" anomalies of the Ivigtut type. This mechanism appears statistically unlikely.

Additional Possible Factors Affecting Isotopic Composition

Although rigorous conclusions must await controlled sampling, the analyses in Table II seem to indicate that isotopic composition is not affected directly by type of mineral, crystal habit, chemical associations, or the like. The suite of samples nos. 24 through 28 from the Minnie Moore Mine, Bellevue, Id., exhibits only small variations in isotopic

composition, in spite of differences in crystal habit and origin in the mine. The anglesite and cerussite samples from Tsumeb, S. Africa, nos. 160 and 161, exhibit very similar chemical compositions; and note may also be made of the identical isotopic compositions of the galena and cerussite from Nertschinsk, U.S.S.R., nos. 134 and 135. The occurrence of lead in two or more different types of minerals in the same deposit is often due to weathering effects on one original mineral. There is no reason to suppose that such chemical phenomena would affect the isotopic composition of the lead.

On the other hand, the galena and cerussite, nos. 114 and 115 from Franklin, N.J., show distinctly different compositions. It is concluded therefore, that differences in isotopic composition with nature of mineral or mineral association, reflect differences in age or origin of the lead involved--the variations in mineral form and environment do not involve processes which produce appreciable fractionation of the lead isotopes.

An indication that mineral association reflects conditions of lead-ore genesis with resulting implications for isotopic composition, may be found in consideration of the following four samples: no. 39, from Clear Creek Co.,; no. 82, from Kellogg Mine, Ark., no. 84, from Montgomery Co., Ark.; and no. 92, from Denboe Pt., Maine. Each of these minerals is associated with silver, and it is observed moreover, that the isotopic compositions are consistently normal, i.e., in keeping with their approximate geologic age on the basis of the ~~step differentiation~~ model. The presence

of silver is taken to reflect ore genesis under mesothermal or hypothermal conditions.⁴⁷ In the light of previous discussion, a more homogeneous extraction of lead is likely under these conditions of intermediate to high temperatures. Consequently, anomalous compositions due to inhomogeneous extraction of rock lead are not very probable. The fact of the normal isotopic constitutions of the four argentiferous samples, especially the two from Arkansas which are not far from districts showing anomalous leads, is in keeping with these conclusions.

With reference to possible fractionation with crystal growth, the meager evidence resulting from this work (see samples 62 and 63) is negative. Cannon⁴⁸ has reported a 10% variation in isotopic composition within a single crystal. This crystal exhibited marked zoning however, and appears to have an unusual origin. There is little reason to suspect appreciable effects on the isotopic composition of lead due to chemical fractionation, hence variations within a single crystal indicate changes in the source of the solutions from which the ore is deposited.

Conclusions

Isotopic analyses of lead minerals of world-wide distribution have been found generally consistent with their ages of mineralization. The selected, dated samples treated by least squares analysis on the basis of the step-differentiation model yield constants consistent with the concept of lead ore derivation from essentially continental, siliceous rocks in contrast to extremely deep-seated sources. The age of the earth's crust obtained by use of meteoritic lead composition in conjunction with the step-differentiation model may be questioned in view of the possibility of continuous differentiation of the earth's outer layers throughout geologic time. On the basis of this possibility, a continuous differentiation model has been developed which gives 5.3 billion years as the maximum age of the earth (when terrestrial lead had the composition of meteoritic lead) and the age of the earth's crust is indicated to be over a billion years younger.

Probably the most important single factor affecting the validity of these conclusions is the matter of differentiation early in earth history. In a secondary way, these results also depend on the full significance of primordial abundances of the elements observed in meteorites, on the relation of terrestrial material to meteoritic material, and on the cosmogony of the solar system in general. Definitive criteria are needed to establish what conditions of the earth's outer layer constitute the earliest existence of a crust.

It is evident that a larger number of well-dated pre-Cambrian samples is needed before a highly definitive evaluation of any of the proposed models can be made. 20 such samples concentrated along the older end of the time scale would permit a substantial statistical treatment. An improved precision of the constants would be permitted thereby and the results obtained would have greater certainty, but are not expected to differ in kind from those previously derived. It may be questioned whether a sufficient number of very old, dated samples can be procured to decide between the continuous differentiation model and the step-differentiation model on the basis of lead ores alone.

Average isotopic compositions have been tabulated for the major regions of the United States. Anomalies have been delineated and are indicated to arise primarily from differences in origin and age of the lead. A hypothesis of inhomogeneous extraction of lead from original or contaminating sources has been advanced to account for the Joplin-type anomaly prevalent in the Mississippi Valley districts. On the basis of this hypothesis, calculations of the apparent age of the excess radiogenic lead in these anomalous samples lead to a figure of 2 billion years. This result argues in favor of extraction from sources below the sedimentary column in these particular districts.

The possibility of inhomogeneous extraction of certain ions from rock masses under low temperature conditions is not original with this work, but has received new corroboration from the nature of the isotopic analyses of pertinent leads reported herein, on the basis of the assumed

hypothesis. While the hypothesis is compatible with the known geology of the ores involved and with the broad conditions outlined by this research, further investigation along the lines suggested is needed for its conclusive evaluation. Such investigation has of necessity been beyond the scope of the reconnaissance nature of this work.

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