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ORE LEAD ISOTOPE RATIOS IN A CONTINUOUSLY CHANGING EARTH

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A critical re-assessment of the construction of simple ore lead isotopic development curves is follwed by three fresh approximations, all designed to involve the minimum possible number of assumptions. All are based on the Russell-Reynolds algorithm, which in its simplest form involves knowledge only of ratios, not of ages. We apply the calculations to a restricted class of ore leads, and employ the latest constant values for the U and Th isotopes.

Model I treats all data as being of equal weight, and shows that the deletion or inclusion of the Canyon Diablo meteorite data makes no difference to the derived parameters.

Model II demonstrates that essentially the same parameters result if the simple curve is forced through the meteorite point; i.e. questions about homogeneity or otherwise of "initial terrestrial" Pb are unimportant to the regression.

Model III makes allowance for the known discrepancy in young "model ages" by providing for a steady linear change in U/Pb and Th/Pb. The additional assumption of one fixed time point proves necessary. An age close to 430 m.y. for Captains Flat, N.S.W., yields acceptable age estimates for most other deposits investigated. No claim is made for the uniqueness of this solution, but the derived evidence for steady growth in U/Pb accompanied by a slight decline in Th/U, seems compatible with a crustal source for the lead ores concerned.

1. Introduction

It has long been recognized that Pb isotope ratios in many ores and rocks are approximately age-dependent. Among the more recent attempts to fit the simplest algebraic description of this trend are those of Stacey et al. [1] and Cooper et al. [2], who applied a "single-stage" curve to much the same data, with methods which may have been similar. The recent improved value for the U and Th decay constants [3,4] and the precise remeasurement of troilite Pb [5] have prompted several workers [6–8] to re-examine the situation with models of varying complexity. All agree with earlier authors that the single-stage model is inadequate, and offer a variety of modifications which they claim lead to a better fit to known information.

However, we are not satisfied. Many of these and other recent publications seem to lack essential details of the methods used. From what we can read we sometimes infer the use of assumptions with which we do not agree, even the possibility of algebraic or logical error. We have therefore decided to begin afresh, to state our postulates as we see them, re-examine the available evidence, and base our curve-fitting upon the minimal number of assumptions. We use, of course, the new constants for U and Th decay, but wish to point out that, although the numerical values change, these new constants do not by themselves significantly alter previously observed trends.

1.1. Critique

(1) Isotopic ratios are the only facts in which we feel complete confidence. They are subject to experi-

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mental bias, but several contemporary techniques are known to yield results close to the "true" value. Some earlier measurements, particularly the precise "intercompared gas source" data from the University of British Columbia, can be normalized reasonably well to their "true" values (see below).

(2) Ore (and rock) data tell us about the Earth. Earlier authors have argued for a connection between this, meteorites and the Moon, but a fresh re-examination of their compatibility is desirable before any combination is made.

(3) Many (but not all) Pb isotope ratios seem to exhibit a general age dependency, but the true geological ages applicable to these ratios are much less certain. For example the quoted "ages" for all the cited Precambrian ores are metamorphic ages (Table 3 and section 3). Do we really know what happens to a pre-existing ore during a high-grade metamorphic event? In any case the stratigraphic relationship of ore to dated rock is not always clear. Indeed, in some of the cited papers the Precambrian ores are listed with ages which appear to have been influenced by previous "model age" calculations. Such age estimates should never be used in the choice of model parameters!

(4) Terrestrial "common leads" (rock initial ratios and ores) may be subdivided qualitatively into two isotopic sets: those which conform to the age-dependent sequence and those which do not. The former have the extra general property of isotopic uniformity on the tens-of-kilometres scale, the latter exhibit a site-to-site variability which often results in a linear display on the standard diagrams. Classification is sometimes difficult, although extreme cases are easily distinguished. Ideally the latter "anomalous" class should be excluded from the growth-curve calculations. Paragraph 3 suggests that model age is not a good rejection criterion; significant deviation of a lone sample from the average curve may be a relevant clue, but it should not be used indiscriminately. *

(5) Every algebraic description of the isotopic trend among the age-dependent common leads involves assumptions about Earth history.

(6) We are not sure, even in individual cases, whether ore Pb development took place in crust or mantle, or a combination of the two. Arguments for the rejection of a purely mantle origin have been summarized by Richards [9].

(7) Most models pre-suppose an initial isotopic homogeneity in all Earth Pb. The formulation by Armstrong and Hein [10] suggests that this may not be necessary.

(8) It is generally agreed that reality was in no way as simple as any "single-stage" description; even slightly more elaborate models can not be regarded as any better than a useful approximation. None is unique.

(9) In view of this complexity, we re-explore a model which involves the least number of assumptions.

1.2. Procedure

We have therefore chosen to begin with the Russell-Reynolds [11] method. It invokes knowledge only of the ratios, not of ages, and does not need any assumptions of relationship between terrestrial and meteorite systems. We follow Cooper et al. [2] in imposing one further requirement, exclusion of any samples which we suspect might belong to the second, "anomalous" isotopic class (for further discussion, see below). The selected data are then normalized to the NBS Standard Pb SRM981 through the value established [2] for the Broken Hill Galena Standard.

In Model I the single-stage equations are regressed in two steps first through terrestrial samples only, and then treating the Canyon Diablo point as an extra, equal partner. This leads on to Model II, which forces the curve through the meteorite data of Tatsumoto et al. [5]. Model III is a demonstration that a minor amendment to the simple single-stage model (one which is geologically reasonable) suffices to bring derived model ages into acceptable agreement with geological ages, as far as they are known, and to remove an oft-reported discrepancy on the 208/204–206/204 diagram.

2. Data selection and adjustment

We follow precedent by concentrating upon ore leads, under the influence of two implicit assumptions. First, if it is true that ore leads represent the average

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* This point is given added weight in a new manuscript just received from B.R. Doe and R.E. Zartman ("Plumbotectonics").

TABLE 1

Ore lead isotope ratios

Sample	$^{206}/204$	$^{207}/204$	$^{208}/204$	Reference
Daylight Mine	12.431(1)	14.065	32.270	[20]
French Bob's Mine	12.461	14.077	32.285	[1]
Geneva Lake	14.002	14.870	33.716	[1]
Cobalt; upper end of mixing line	14.857(1)	15.148	34.412	[22]
Sudbury Errington Mine Toronto #359	15.489(1)	15.303	35.338	[27]
Southwest Finland	15.676(1)	15.328	35.233	[28]
Broken Hill	16.003(1)	15.390	35.660	[2]
	16.007	15.397	35.675	[1]
Mount Isa	16.108(1)	15.454	35.834	[39]
	16.120	15.454	35.850	[15]
McArthur River	16.156	15.474	35.887	[15]
Sullivan	16.526(1)	15.504	36.195	[54]
Balmat	16.906(1)	15.525	36.449	[55]
	16.935	15.505	36.423	[1]
Captains Flat	18.065(1)	15.614	38.157	[39]
Cobar C.S.A. Mine	18.105(1)	15.626	38.161	[39]
Bathurst	18.178(1)	15.629	38.118	[39]
	18.204	15.655	38.122	[1]
Halls Peak	18.378(1)	15.602	38.362	[39]
White Island	18.772(2)	15.598	38.662	[39]
Manitouwadge Willroy #332	13.286(2)	14.411	33.119	[39]
#371	13.360(2)	14.427	33.193	[16]
MG-38a	13.211(2)	14.401	33.069	[1]
Geco vein #372	29.870(2)	17.548	46.949	[39]
Flin Flon #648	15.315(2)	15.106	34.846	[14]
Mine #660	15.745(2)	15.228	35.297	[14]
Chisel Lake Mine #652	15.387(2)	15.116	34.940	[14]
Snake Lake #660	15.709(2)	15.256	35.176	[14]

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(1) Data used by Cooper et al. (1969).

(2) Data plotted in Fig. 1 & 2 but not used in calculation.

of the Pb extracted from a sizeable volume of crust [12], then it seems possible that their ratios are less susceptible to later perturbation than those of rocks. Second, it just might be that some rocks belong to a different development system [13]. *

The data in Table 1 are basically the same as those used by Cooper et al. [2], but have been subjected to a slightly different normalization. These authors calculated correction factors from the ratio of their double-spike-controlled measurement of the Broken Hill Galena Standard to the precise (but fractionated) values reported from the University of British Columbia. So too did Stacy et al. [1] with the results of their triple-filament measurements. Both groups then used these factors as constant multipliers to obtain "absolute" values for other data. In fact the intercomparisons made by the Russell group have been made on the basis of differences between the observed ratios; hence corrections to absolute value should be made in the same way. The two methods of data reduction do not produce very different results except for extreme isotope ratios but we feel that in order to test the growth curve models carefully one should use the method of differences for the adjustment of these data. It should be noted that the British Columbia group now apparently use this technique when comparing gas-source results [14].

To these data we have added a selection of "absolute" ratios from Stacey et al. [1], and some others, also measured in Russell's laboratory [15], which provide a few more points on the growth curve and give an indication of the range of error expected for between-laboratory comparisons after corrections have been applied.

We do not feel it is fruitful to enter fully into arguments about the suitability of each sample included in the analysis. One could question almost any of the data on one ground or another. However, some comments may be appropriate. Many calculations (most recently [6,8]) include points for Manitouwadge and/or Flin Flon which have been used to support the conclusion that a large range of growth curve parameters is required. One of the basic requirements for inclusion of the Pb from a particular orebody in the analysis is that it be uniform in composition; this ensures that the Pb is truly representative of the source at the time of ore formation. Recent analyses by Slawson and Russell [14] clearly demonstrate that there is a large range of isotope ratios from the Flin Flon mine. This is perhaps not surprising since Pb occurs there only in trace amounts. Similarly it has been known since the original analyses of Ostic [16] that the Manitouwadge mines show some of the "anomalous" characteristics which Russell and his coworkers have specified on many occasions. From the three least-radiogenic analyses of Manitouwadge Pb shown in Table 1 and plotted in Fig. 1 (all on different samples) it is clear that real inter-sample variations exist, and are related to the highly radiogenic sample from the late vein at Geco Mine. Thus it is hard to defend the choice of any particular sample as the real end-member of a mixing sequence. We have therefore omitted these data from all the calculations.

Two different samples from the Barberton area are included. Recent work by Saager and Koeppel [17] indicates that these leads may also be members of an anomalous suite, but since here the anomalous lead line essentially parallels the growth curve, inclusion of the data is still defensible on grounds similar to those used by Russell and Reynolds [11] for young leads. We expect to obtain a good approximation to the growth curve even though the apparent ages of the leads may be in error. We have used here the least-radiogenic of the published data on Barberton Pb samples.

3. Geological ages

With one exception noted below, the age estimates quoted in the first column of Table 3 are not used in any of our calculations. The indicated uncertainties and the following summary have been obtained by going back to the original literature descriptions, and are included in support of our previous statement that not all ages are as well known as we would like. For the most part we have tried to correlate stratigraphic

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* The work of Doe and Zartman (previous footnote) leads us to accept that we have chosen samples characteristic of what they are calling "average orogene", which yields an average mixture of material from continental and upper mantle ("asthenosphere") sources. It may be argued that "primitive Earth" Pb should come closer to fitting such a definition than does "fractionated mantle". In such case Canyon Diablo Pb may well be an acceptable member of this set.

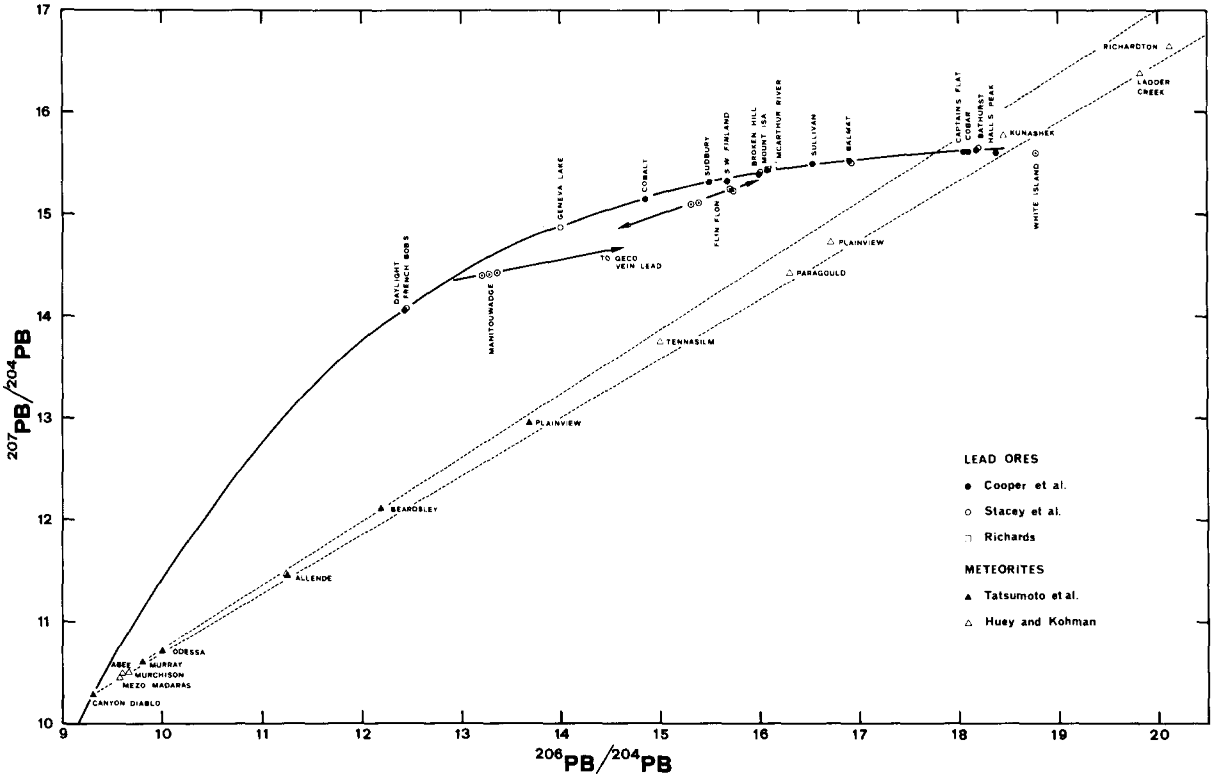

Fig. 1. ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios for some ore leads and meteorites. Solid curve is best-fitting single-stage growth curve; arrows are secondary isochrons; circles with central dot not included in analysis.

evidence with Rb–Sr or zircon U–Pb ages of related rocks; "lead model age" estimates have been studiously avoided. In some cases geological extrapolations of many kilometres are involved. Rb–Sr ages have been corrected to $\lambda_{Rb} = 1.42 \times 10^{-11} yr^{-1}$.

Barberton Mountain Land, South Africa. Daylight and French Bobs. The Pb is among minor sulphides in Au–Ag mines, apparently occurring within metasedimentary rocks of the Swaziland Sequence. These rocks are intruded by diapiric plutons dated between 3400 and 3200 m.y. [18,19] and have been affected by a general metamorphism, no later than 3000 m.y. On evidence not stated, Ulrych et al. [20] therefore ascribe an age 3000–3200 m.y. to the mineralization. No closer age specification appears justifiable.

Geneva Lake, Ont. Stratiform deposit in Archaean volcanics just to the northwest of Sudbury. Information is scarce. One data by Fairbairn et al. [21] suggests a corrected minimum age 2500 m.y.

Cobalt, Ont. There appear to be two ages of mineralization. The older material is stratiform in Keewatin volcanics, the younger is in veins of dominantly silver-arsenide which cut the Nipissing diabase. The sample we have quoted ("exact location unknown": [22]) is presumed to belong to the latter group. More than 300 km to the south, the Nipissing diabase has been tentatively dated at 2170 ± 200 m.y. [23] which corrects to 2125 m.y. The galena could be slightly younger than this [24].

Sudbury, Ont. The "nickel irruptive" consists of two layers: an inner micropegmatite dated [25] at 1680 m.y. (corrected age) and the outer ore-bearing norite, which Souch et al. [26] estimate to be just over a corrected age 1860 m.y. Krogh and Davis [56] report a zircon age 1844 m.y. for the norite. The lead [27] was associated in trace amounts with the ore.

Southwest Finland. Average of Aijala, Attu, Korsnäs, Orijärvi and Pakila (Whittles [28], quoted in

[2]). The sulphides apparently occur in "metamorphic" veins within Svecofennian rocks in the extreme southwest of Finland, where anorogenic Rapakivi granites abound. Zircon ages [29] point to an age around 1900 m.y. for Svecofennian intrusives; Rb–Sr mineral ages tend to be younger, and indicate possible resetting during an event associated with the Rapakivi granites (age quoted, "about 1700 m.y."; also on zircon?).

Broken Hill, N.S.W. Massive Pb–Zn ore conformable to high-grade metasediments; the initial Pb ratios of the mine-sequence gneisses are the same as the ore ratios [30].

Corrected Rb–Sr isochron age of gneisses is 1660 ± 21 m.y. [31]. Neighbouring pegmatites [32] are younger, with corrected age 1510 ± 50 m.y.; their relationship to the ore is not known, but they are generally thought to post-date the original mineralization.

Mount Isa, Qld. Massive Pb–Zn ore in deformed sedimentary-tuffaceous sequence, of somewhat uncertain age. Farquharson and Richards [33] argue on structural grounds for an age which corrects to about 1680 m.y.; Plumb and Sweet [34] deduce from fieldwork and regional correlations that it should be closer to a corected age 1470 m.y. Truth may lie somewhere in between.

McArthur River, N.T. A massive pyritic Pb–Zn ore in a relatively undeformed sedimentary-tuffaceous sequence which has been correlated in age with Mount Isa [15].

Sullivan, B.C. A large stratiform Pb–Zn body within the Precambrian Aldridge Formation [35]. Its chronological position is confused, but the best fix has probably been given by Ryan and Blenkinsop [36] with a Rb–Sr isochron age for the Hellroaring Creek Stock, which corrects to 1305 ± 50 m.y. This stock cuts the Aldridge Formation. Thus the ore is likely to be at least as old as 1300 m.y.

Balmat, N.Y. A sulphide orebody, dominantly Zn, it is classed [37] as conformable and "formed during the retrograde stage of the last severe metamorphism", which Doe dated at (corrected) 1080 m.y. by Rb–Sr, 1013 m.y. by K–Ar (also corrected to the newest constant values).

Captains Flat, N.S.W. A massive stratiform fine-grained Pb–Zn–Cu–Fe body of volcanic association, Middle Silurian in age [38]. A similar volcanic sequence 60 km north, and its associated mineralization, is very close to 425 m.y. old (B.L. Gulson, personal communication).

Cobar, N.S.W. CSA Mine. A massive lenticular Cu–Pb–Zn body, said to be stratiform [39]. There appear to be distinct differences, geological as well as isotopic, between this and other deposits in the district [40], so the CSA data only have been selected. Age said to be Upper Silurian.

Bathurst, N.B. BMS No. 6 (2 samples) and No. 12. Stratiform fine-grained Zn–Pb–Cu–Fe body in an intensely folded volcanic complex, part of a regionally metamorphosed sequence of Middle Ordovician age [41]. Assigned age therefore 440–450 m.y.

Halls Peak, N.S.W. Stratiform Pb–Zn ore in a Lower Permian sediment-volcanic sequence (H.W. Gutsche, personal communication, 1967). Ostic et al. [39] assign it to the Upper Permian. Age therefore in range 240–280 m.y.

White Island, N.Z. Incrustation of $PbSO_4$ on lip of fumarole [39]. Zero age. See also Cooper and Richards [42] who show similar isotopic ratios for possibly Miocene mineralization in the same region.

4. Meteorite leads

Meteorite Pb analyses are relevant to the present discussion in two ways. Ratios for the least-radiogenic meteorite, Canyon Diablo, are usually used either as another point of equal weight to terrestrial ore Pb data [11] or as the assumed initial composition of Earth Pb from which all ores must evolve ([6] and others). In addition the slope of the isochron through meteorite leads is sometimes used to yield an age which may be applied as a known parameter in the growth curve equation [6,8].

Recent work by Tatsumoto et al. [5], Huey and Kohman [43] and Tilton [44] are probably the most reliable. In Table 2 we list a selection of data for those meteorites with $^{206}Pb/^{204}Pb$ ratios less than 22.0. Higher ratios were not included simply because they do not add to the present discussion. These data are also plotted in Fig. 1. They demonstrate the point emphasized by Tatsumoto et al. [5] that there is clear evidence for variations in the apparent age of meteorites. The widely divergent points for Beardsley and Ladder Creek define a significant range of meteorite isochrons, and emphasize the need for caution in as-

TABLE 2

Some meteorite lead isotope ratios

Sample	$^{206}/204$	$^{207}/204$	$^{208}/204$	Reference
Canyon Diablo	9.307	10.294	29.476	[5]
Odessa	9.995	10.691	30.087	[5]*
Murray	9.806	10.594	29.939	[5]
Allende	11.250	11.451	31.352	[5]
Beardsley	12.193	12.106	31.973	[5]
Plainview	13.682	12.958	33.447	[5]**
Abee	9.605	10.492	29.807	[43]
Murchison	9.666	10.499	29.699	[43]
Allende	11.233	11.466	31.458	[43]M-85-A-v
Plainview	16.729	14.736	36.458	[43]M-1-D-v**
Richardton	20.123	16.656	39.853	[43]M-9-B-v
Mezö-Madaras	9.589	10.459	29.731	[43]
Tennasilm	15.012	13.753	35.237	[43]
Paragould	16.309	14.422	36.094	[43]M-88-A-v-1
Kunashek	18.457	15.785	37.492	[43]
Ladder Creek	19.826	16.377	39.508	[43]M-22-D-v

* possibly contaminated?

** finds; all others falls.

cribing any particular significance to the slope of the mean regression line. At best it only represents a mean age which may not be particularly relevant to the Earth. These extreme possible meteorite isochrons, shown as dotted lines, emphasize the difficulties with young ore leads. Observed Palaeozoic ores all lie within the range of possible zero ages defined by the meteorites, and the Recent lead from the White Island fumerolic incrustation appears "younger" than all the possible meteorite ("zero-age") isochrons.

5. Single-stage model calculations

This then is the final point in our defence of the procedure outlined in the Introduction. We have reprogrammed the Russell-Reynolds algorithm for curve fitting as outlined in [2] so as to facilitate analysis, and have estimated errors for the fitted curves in two different ways, since acceptance or rejection of the single-stage model is based not only on the ages obtained for the ore leads but on the associated errors as well. Any systematic disparity between the "known" ages of ore deposits and those calculated from a model must indicate shortcomings in the model. If the ages obtained agree within the assessed errors then we can accept the model as adequate and from the curve deduce an age for the troilite Pb ratios, which we might then be prepared to compare with other solar system age estimates. If the model ages for ore leads do not agree with the geologic ages, then the model is inadequate and we must not ascribe any significance to the "age of the Earth" deduced from the troilite Pb ratios.

5.1. Single-stage Model I

Following the method of Russell and Reynolds [11] as used in [2] we write:

$$^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = X = a + \alpha V(1 - e^{\lambda t}) \qquad (1a)$$

$$^{207}\mathrm{Pb}/^{204}\mathrm{Pb} = Y = b + V(1 - e^{\lambda' t}) \qquad (1b)$$

$$^{208}\mathrm{Pb}/^{204}\mathrm{Pb} = Z = c + W(1 - e^{\lambda'' t}) \qquad (1c)$$

where t is measured from the present, a, b and c are the present-day ratios; and $V = {}^{235}\mathrm{U}/^{204}\mathrm{Pb}$, $W = {}^{232}\mathrm{Th}/^{204}\mathrm{Pb}$ (present-day values). Constants used are $\lambda = 0.155125 \times 10^{-9}\ \mathrm{yr}^{-1}$, $\lambda' = 0.98485 \times 10^{-9}\ \mathrm{yr}^{-1}$ [3], $\lambda'' = 0.049475 \times 10^{-9}\ \mathrm{yr}^{-1}$ [4], $\alpha = {}^{238}\mathrm{U}/^{235}\mathrm{U}$ (present) = 137.88 [45].

For given values of a, b and V, eqs. 1a and 1b define a single growth curve with parameter t. The perpendicular from the observed point to the tangent to the curve is used as an approximation to the perpendicular to the curve and is given by:

$$S = \frac{Y - b - V(1 - e^{\lambda' t})}{\sqrt{(1 + R^2)}}$$

where $t = \frac{1}{\lambda}\ln\left(1 - \frac{X - a}{\alpha V}\right)$ and R is the tangent to the curve at time t. If the slope of the curve is steep the time may be calculated from the Y ratio and the perpendicular distance from the X ratio. Parameters are chosen such that:

$$r = \sum S_i^2 = \text{a minimum} \qquad (2)$$

Since a direct least-squares solution is awkward, an array of values for a and b is used. For each (a,b) pair a value of V is calculated which yields the minimum residual, and a choice is made from the print-out array of the (a,b) pair which yield the minimum overall residual. This minimization is equivalent to selecting the best-fitting curve from a set of sub-parallel curves as illustrated in Fig. 3a.

To find the best-fitting curve for eqs. 1a and 1c, we use a slightly different approach. For a given parameter set, two points on the curve may be determined from the two values of t in eqs. 1a and 1c. Since the plot of X against Z is almost a straight line with slope near unity, we determine the perpendicular from the observed point to the chord between the two curve points corresponding to the two time values, and minimize the sum of squared perpendicular distances. Since the parameters a and V have been determined previously, the variables are c and W in eq. 1c.

We find the following values using the new decay constants and the corrected ratios of Table 1:

$a = 18.465 \pm 0.074 \quad b = 15.642 \pm 0.010$

$c = 38.507 \pm 0.095$

$V = 0.066413 \pm 0.00085 \quad (\alpha V \equiv \mu = 9.157)$

$W = 36.058 \pm 0.13$

Errors for a, b and V were estimated by the method of Ostic et al. [46] although as indicated below we believe their method overestimates some of the errors substantially. These parameters are not significantly different from those calculated with the old decay constants [2] which lie within the assigned error limits. The best-fitting curve still passes exactly through the troilite point in Fig. 1, but we now find exactly the same parameters whether or not we include Canyon Diablo data (with equal weighting) in the analysis. Adding the latter point does reduce the uncertainty in the present-day ratios by a factor of about two, since the curve is much more closely constrained.

For the plot of eqs. 1a and 1c in Fig. 2 we confirm earlier observations [2,22] that the best-fitting curve does not pass through the meteoritic value. However, the discrepancy is now somewhat smaller than obtained previously and is certainly no greater than the scatter of the ore lead points about this curve. This much greater scatter in Fig. 2 may be an indication that Earth Th/U ratios vary more widely than the U/Pb ratio, or it may just arise from a larger error in the $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ measurements.

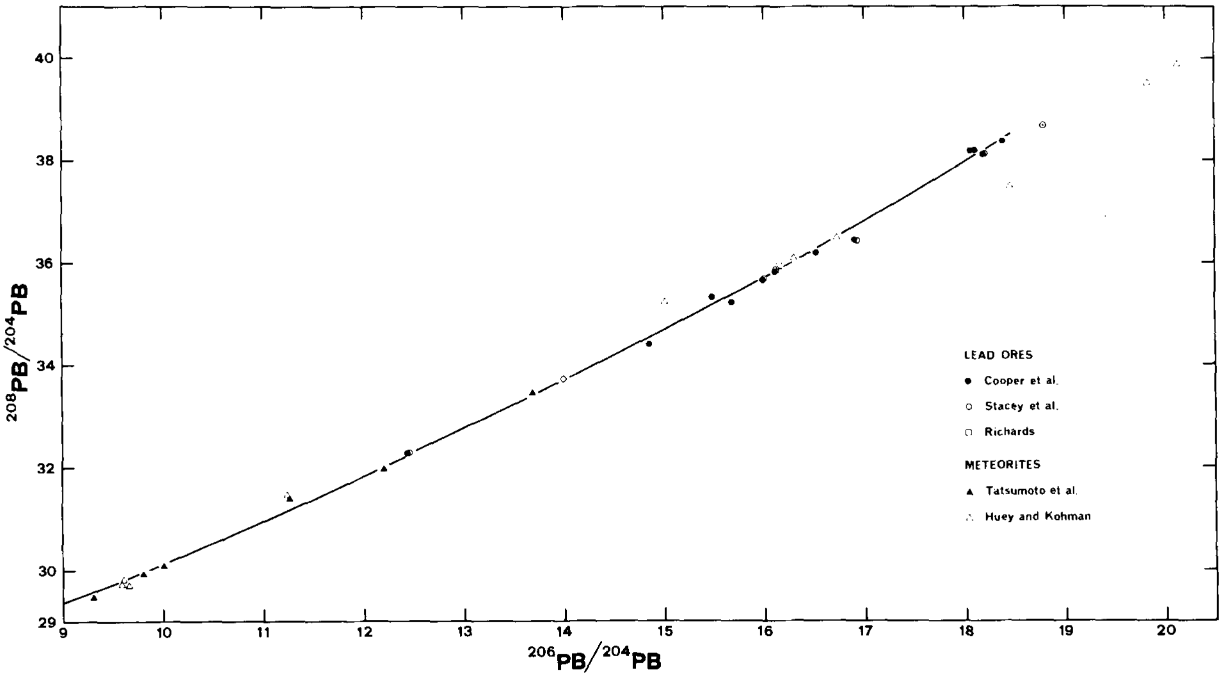

Fig. 2. $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios. Solid curve is best-fitting single-stage growth curve (unconstrained). Circle with central dot as in Fig. 1.

In Fig. 1 it is clear that exactly the same value of V will not fit all the data (for example Broken Hill, Mount Isa and McArthur River require significantly different V's). Nevertheless the curve fits the ratios remarkably well as a first approximation. For the model the mean residual for the 20 data points used is 0.020. This average error is hardly greater than that of a realistic assessment of the experimental errors. Assuming X and Y ratios have errors of about equal magnitude the above mean deviation implies that the individual ratios have mean errors $0.020/\sqrt{2} = 0.014$, i.e., about 0.1%.

Without commenting on its significance at this time, we note that the above parameters a, b and V imply a value $t_0 = 4469$ m.y. for Canyon Diablo lead.

5.2. Single-stage Model II

Since the unconstrained analysis above clearly indicates that Canyon Diablo lead fits the ore lead growth curve exactly, it is then justifiable to force the curve through that point. This is equivalent to assuming a uniform initial Pb for the Earth system (see paragraph 7 in subsection 1.1) and amounts to finding the best-fitting member of the family of curves illustrated in Fig. 3b. In this case the equations may be written as:

$$X = a_0 + \alpha V(e^{\lambda t_0} - e^{\lambda t}) \tag{3a}$$

$$Y = b_0 + V(e^{\lambda' t_0} - e^{\lambda' t}) \tag{3b}$$

and we now minimize:

$$r = \sum \{[X - a_0 - \alpha V(e^{\lambda t_0} - e^{\lambda t})]^2 + [Y - b_0 - V(e^{\lambda' t_0} - e^{\lambda' t}]^2\} \tag{4}$$

with V and t_0 as the free parameters. In this case the incidental variable t is determined from the conventional isochron equation, hence the value of r obtained from eq. 4 will be greater than that found from eq. 2. In Fig. 4 we show the $V - t_0$ point corresponding to the minimum residual and also the contour for $r = 2r_{\min}$ (eq. 4). The chosen data yield:

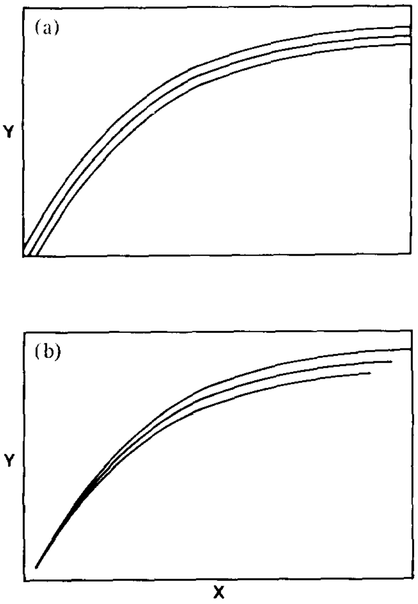

Fig. 3. (a) Curve-fitting of single-stage growth curve with no constraints. (b) Curve-fitting with growth curve forced through a_0, b_0.

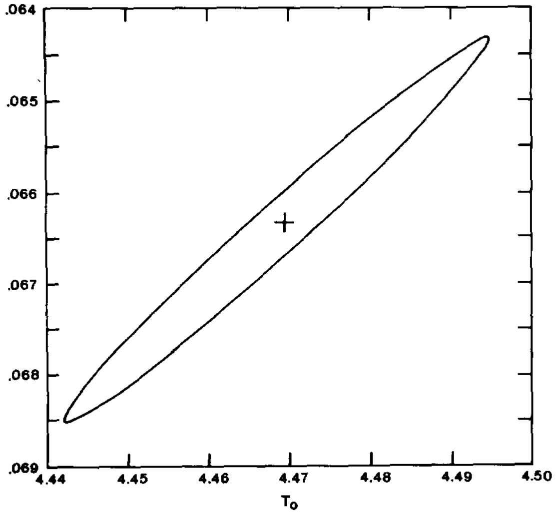

Fig. 4. Residual field for single-stage Model II. Cross indicates location of $r_{\min}$; contour shown for $r = 2r_{\min}$. Note that correlation between V and t_0 is large and negative. (t_0 measured in 10^9 years).

$V = 0.06633 \pm 0.00051$ ($\alpha V \equiv \mu = 9.145$)

$t_0 = 4470 \pm 6$ m.y.

following the error estimation procedure of Ostic et al. [46]. For example the σ_V is obtained by dividing the half-width of the twice-minimum ellipse by $\sqrt{N-2}$, where N is the number of degrees of freedom. This method does not allow for the possibility of correlation of errors when two or more variables are involved and another approach is possible.

5.3. Revised method of error estimation

With the squared residuals in the form of eq. 4 we may obtain the expected values of the second derivatives and by inverting the resulting matrix, obtain σ_V and σ_{t_0} directly. This method permits calculation of the correlation coefficient between V and t_0. Fig. 4 indicates that this coefficient is very large and negative. Using this method of calculation we obtain:

$\sigma_V = 0.00012 \quad \sigma_{t_0} = 2.6$ m.y. $\quad \rho = -0.88$

Hence it appears that the method of Ostic et al. [46] greatly overestimates the values of σ in this case, although it yields a good approximation to the correct value for a function of one variable.

The above values for V and t_0 yield present-day ratios:

$a = 18.454 \pm 0.011 \quad b = 15.640 \pm 0.007$

We have also applied the second derivative method to re-calculate the error estimates for the preceding Model I curve-fitting, and obtain for Model I:

$\sigma_a = 0.011 \quad \sigma_b = 0.008 \quad \sigma_V = 0.00019$

$\rho_{ab} = 0.166 \quad \rho_{aV} = 0.725 \quad \rho_{bV} = 0.229$

Again errors are highly correlated, particularly between a and V, and the estimates are substantially less than those obtained by the Ostic et al. [46] approximation.

5.4. Assessment of Models I and II

The constants and their associated errors obtained for the simple single-stage model by the two methods of curve fitting are the same within the error estimates. If we convert these errors into uncertainties in time

TABLE 3

Geologic and model ages

Sample	Geologic** Age (M.Y.)	Model I Age (M.Y.)	Linear model ages (M.Y.)		
			isochron	t_{206}	t_{208}
Daylight	3000-3200	3270	3227	3235	3189
French Bob's	3000-3200	3250	3207	3222	3182
Geneva Lake	> 2500	2549	2523	2532	2501
Cobalt	2120	2130	2122	2127	2169
Sudbury	1900	1806	1817	1818	1725
S.W. Finland	~ 1700	1695	1713	1724	1775
Broken Hill	~ 1660	1519	1549	1559	1570
Stacey et al.		1522	1553	1557	1563
Mount Isa	1500-1700	1504	1536	1505	1486
Richards		1496	1528	1499	1478
McArthur River	~ 1500	1489	1522	1480	1461
Sullivan	>1300	1258	1310	1288	1312
Balmat	1080	1010	1085	1086	1189
Stacey et al.		968	1048	1071	1202
Captains Flat	425	266	429*	445	360
Cobar, CSA Mine	410-420	251	416	422	358
Bathurst	450	200	372	380	379
Stacey et al.		213	384	365	377
Halls Peak	240-280	14	213	264	260
White Island	0	-300	-51	31	113
End of single stage model I	-	0	201	213	189

* Model chosen on basis of this age

** See Text

we find that model age estimates based either on eqs. 1 or eqs. 3 would have 67% confidence limits always much less than 50 m.y. As may be seen from Table 3 the model ages depart from known geologic ages of young ore deposits by more than 200 m.y., and thus we must reject the single-stage model on the basis of the criterion indicated previously. It should be emphasized that we reject the single-stage model, not because we are dissatisfied with the implied "age of the Earth", but because the model does not fit the known ages of the ore deposits.

6. A "linear" increase in *V*: Model III

Stacy and Kramers [8] have shown that a two-stage model can be constructed which fits the data well and they dismiss a continuous change in *V* (and *W*) as being inconsistent with some whole-rock data. We are not entirely convinced since we feel that there is much not yet clear about the relationship of crustal rock systems to ores. Some type of model with continuously variable *V* is worth re-examination if only to provide a basis for comparison with other alternatives.

Besides, a succession of numerous small increments over the whole of Earth history (a not impossible mechanism) would appear on average to be very like such a model.

Many authors have either used or proposed linear or exponential variations in V to obtain a better fit to the ore lead data ([47–52] and others). There seems little to choose between these two alternatives. Either mathematical formulation may be considered as a reasonable approximation to the possible geological situation, and as long as the changes in the U/Pb ratio are reasonably small there is not likely to be any great difference between the two types of model.

For the linear case we may begin with the integral equation for evolution of the $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ ratio as expressed by Kanasewich [53]:

$$X = a_0 + \int_{t}^{t_0} U(t)\,\lambda \mathrm{e}^{\lambda t}\,\mathrm{d}t \tag{5}$$

with similar expressions for Y and Z. If we let $U(t) = \alpha V(t)$ = a constant, the usual single-stage equations result.

We have chosen to allow V to increase linearly over the history of the Earth, which appears to be geologically reasonable if we consider a regional average of crustal material to be the effective source of our ore leads. This appears to contrast with Gast [50], who was contemplating a mantle development. Following the Russell school by taking present day as origin, we write:

$$U(t) = \alpha V(t) = \alpha V_{\mathrm{p}}(1 - \epsilon t)$$

$$W(t) = W_{\mathrm{p}}(1 - \epsilon' t)$$

where V_{p} and W_{p} are the present-day $^{235}\mathrm{U}/^{204}\mathrm{Pb}$ and $^{232}\mathrm{Th}/^{204}\mathrm{Pb}$ ratios. $V(t)$ and $W(t)$ are the effective ratios at time t, corrected for radioactive decay to $t = 0$ and ϵ, ϵ' are rate factors (with dimensions of inverse time). Note that αV_{p} is equivalent to the μ_{p} which many other authors would employ in similar circumstances. In that the succeeding integration of eqs. 5 takes care of the time limits t_0 to t, we prefer this simpler formulation to the linear expression written by Sinha and Tilton [52] in whose derivation, moreover, we suspect an algebraic error.

After integration, we obtain:

$$X = a_0 + \alpha V_{\mathrm{p}} \left\{ \mathrm{e}^{\lambda t_0} \left[1 - \epsilon \left(t_0 - \frac{1}{\lambda} \right) \right] - \mathrm{e}^{\lambda t} \left[1 - \epsilon \left(t - \frac{1}{\lambda} \right) \right] \right\} \tag{6}$$

with similar equations for Y and Z.

In order to determine suitable values for t_0, V_{p} and ϵ, we have used the same technique as outlined previously; that is, find the sum of squared residuals for the ore leads of Table 1, forcing the growth curve through the Canyon Diablo values since we have shown that the single-stage equations justify this approach. The residuals are taken as the distance along an "isochron" as for Model II above, and V_{p} is chosen to make residuals a minimum for each (t_0, ϵ) pair. Contours of the sum of squared residuals, normalized to the value for the single-stage Model II found previously, are shown in Fig. 5. It may be seen that a reasonably well-defined minimum occurs in a region around $\epsilon = -0.01 \times 10^{-9}\ \mathrm{yr}^{-1}$, the minimum being slightly less than that for the single-stage model ($\epsilon = 0$). A moment's reflection will suggest that this is not a useful solution since it will produce a decrease in present-day Pb ratios and hence even younger apparent ages than the single-stage model. For positive values of ϵ the region of minimum residuals forms a narrow, roughly elliptical band and the sum of squared residuals only increases by 20% for the values $\epsilon = 0.050 \times 10^{-9}\ \mathrm{yr}^{-1}$ and $t_0 = 4509$ m.y.

Because we cannot use the actual values at the minimum we are impelled to impose one additional restraint on the equations. It would be convenient to use a value of the $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ ratio for modern lead but this is not well known (see for example the range of possible values given in [8]). Any choice of Precambrian lead is not particularly helpful because none of the ages is known precisely and the growth curve parameters are relatively insensitive to the age chosen for old leads. The data for White Island (Table 1) may not be typical of modern lead ores and there are only two values [39] so the point may be suspect. We have chosen to fit our calculated curves in such a way as to yield an age of about 430 m.y. for Captains Flat, since there are seven measurements on the lead to prove its homogeneity and we believe a Middle Silurian age can be defended for this locality about as well as can the age for any deposit which has been studied in detail

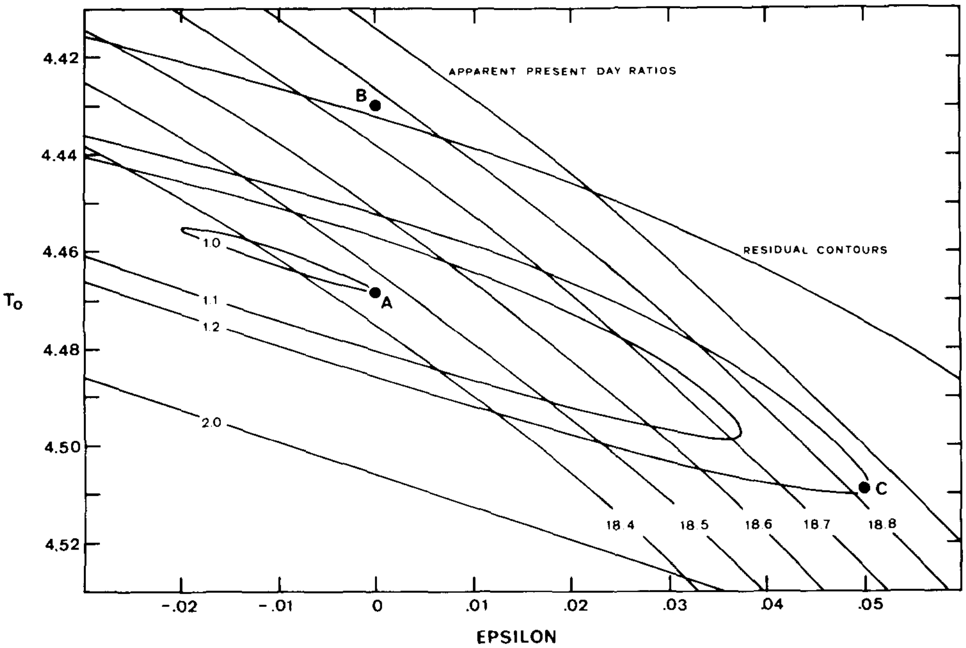

Fig. 5. Residual field for variable V model. Normalized to residual value at A (single-stage model). Present-day ratios a are also shown. The units of ϵ are 10^{-9} yr^{-1}.

(B.L. Gulson, personal communication). For parameter values $\epsilon = 0.050 \times 10^{-9}$ yr^{-1} and $t_0 = 4509$ m.y. there corresponds $V_p = 0.07797$ and the model age for Captains Flat becomes $t = 429$ m.y., which we take as an adequate fit to the geological age for that orebody.

In Fig. 5, point A corresponds to the parameters for the single-stage model reported above, point B to the parameters used by Doe and Stacey [7] and point C to the best fit subject to the age restraint imposed on Captains Flat. It may be seen that the Doe and Stacey parameters, while yielding reasonable ages, correspond to parameters where the sum of squared residuals is more than twice the minimum value. Contours of the present-day ^{206}Pb/^{204}Pb ratios are also shown. Our parameters imply substantial agreement with both Doe and Stacey and with Stacey and Kramers [8] on the value for this ratio; this is to be expected if we are to obtain reasonable ages for young leads. Indeed, we have about reached the limit of interpretation: any reasonable model will probably yield a similar result!

The ^{208}Pb/^{204}Pb ratios are treated in the same way as before, that is W_p and ϵ' are obtained by minimizing the residuals for the X–Z diagram subject to the values for t_0, V_p and ϵ found in Fig. 5. In summary the "linear" growth curve solution yields:

$t_0 = 4509$ m.y.

$V_p = 0.7797 \quad (\alpha V_p \equiv \mu_p = 10.75)$

$\epsilon = 0.050 \times 10^{-9}$ yr^{-1}

$W_p = 41.25(^{232}\text{Th}/^{238}\text{U})_p = 3.84$

$\epsilon' = 0.037 \times 10^{-9}$ yr^{-1}

and these parameters imply present-day ratios:

$a = 18.824 \quad b = 15.671 \quad c = 38.893$

We do not assign errors to these parameters at present because they are related (and correlated) in a rather complex fashion, and the age restraint imposed on the curves is somewhat artificial. If Captains Flat is really 10 m.y. younger, viz. 420 m.y., then t_0 becomes about 4506 m.y. and $a = 18.80$, with correspondingly small changes in the other parameters. The solution is thus relatively insensitive to small variations in the assigned age. In any case it is not clear to us how the error assessment should be done since the solution no longer corresponds to the minimum in the least-squares problem. Intuitively we suppose that the errors will not be substantially greater than for Model II, since the sum of squared residuals is only slightly greater.

7. Discussion

Two benefits of this very simple Model III are immediately apparent. We will proceed to show that the simple procedure of choosing ϵ to yield a reasonable age for Captains Flat produces model ages for the other ore leads which are as compatible with the available geological evidence as those produced by Stacey and Kramers [8] and this without having to call for a world-wide catastrophe. Model III also successfully removes the discrepancy with the meteorite data on the 208/204–206/204 diagram, first noticed by Kanasewich and Farquhar [22], which we have referred to under Model I.

The comparison of estimated geological ages with four of the new model ages is shown in Table 3. We show first the 207/206 isochron age for the single-stage Model I, then three different values based on the linear Model III of eq. 6: (1) the isochron age from equations for X and Y, (2) the age from the equation for X alone, and (3) the age from the Z equation. The variation amongst the three "linear" ages is a measure of the departure of the data from a single growth curve. (For a point above the curve, $t_{7/6} > t_{206}$; below it, $t_{7/6} < t_{206}$.) It should be noted that we now have a choice of parameters when calculating the "isochron" age for a point which does not fit the mean curve precisely. We may assume that any experimentally significant scatter of the data about the best-fitting curve is due either to variations in V or to variations in ϵ. The first alternative implies differing U/Pb ratios in the source from the beginning of geologic time and the second implies that the U/Pb ratio in the Earth is changing at different rates in different locations. Thus at least in principle we must have some geological criterion to determine which model is appropriate. Fig. 6 illustrates "isochrons" for variation in V compared with variation in ϵ and it may be seen that in practice the differences are quite small. Hence it is adequate to calculate ages by the usual isochron technique, i.e. variations in V only, even though it may seem geologically more reasonable to use the other alternative.

It is of interest that the values of ϵ and ϵ' are different, suggesting that U is accumulating in the "Pb-source region" faster than Th. This reinforces our wish to regard the crust as a dominant factor in the accretion of radiogenic Pb into the ore Pb stock, for most geochemical publications agree that U has migrated

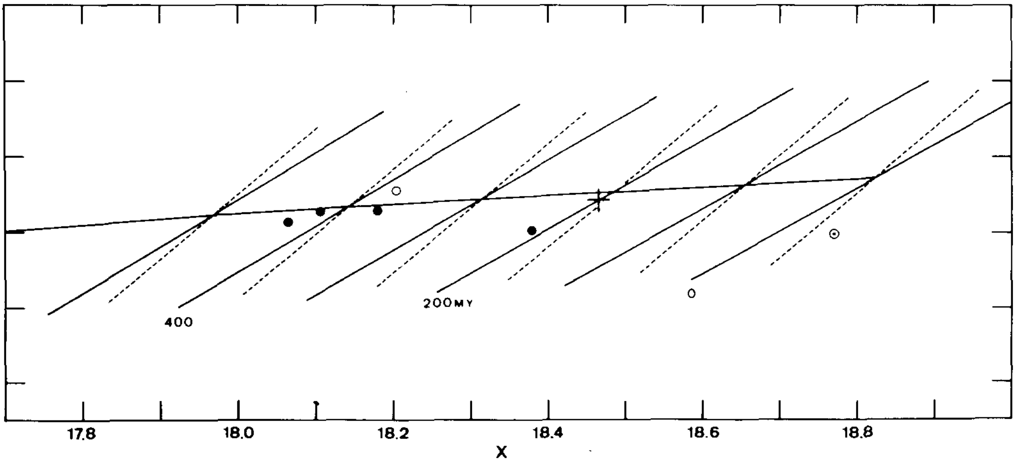

Fig. 6. Part of linear model growth curve. Fitted points for young leads are shown; symbols as in Fig. 1. Solid "isochrons" are for 2.5% variation in V_0; dashed isochrons for 10% variation in ϵ. Cross indicates end of best fitting single-stage growth curve.

TABLE 4
The "linear" Model III

t ($\times 10^9$ y)	X(t)	Y(t)	Z(t)	μ(t)	W(t)	^{232}Th/^{238}U(t)
				equivalent values extrapolated to t=0		
4.509	9.307	10.294	29.476	8.327	34.368	4.127
4.5	9.330	10.339	29.495	8.332	34.382	4.127
4.0	10.600	12.344	30.556	8.600	35.145	4.086
3.5	11.812	13.609	31.614	8.869	35.908	4.049
3.0	12.968	14.405	32.669	9.138	36.671	4.013
2.5	14.070	14.906	33.719	9.407	37.434	3.980
2.0	15.119	15.222	34.764	9.676	38.198	3.948
1.5	16.118	15.420	35.805	9.944	38.961	3.918
1.0	17.067	15.544	36.840	10.213	39.724	3.890
0.5	17.968	15.622	37.870	10.482	40.487	3.863
0.0	18.825	15.671	38.893	10.751	41.250	3.837

towards the upper crust faster than Th, and that both have moved in preference to Pb. The effect is shown in Table 4, which provides a selection of co-ordinates defining the Model III curves, together with corresponding values, corrected for radioactive decay to $t = 0$, of $\alpha V(t)$ [$\equiv \mu(t)$], $W(t)$, and the $^{232}\mathrm{Th}/^{238}\mathrm{U}(t)$ in the "Pb source region".

We are further encouraged to observe that the value of t_0 predicted by Model III is effectively the same as the average age of chondrites obtained by Huey and Kohman [43] whose data yield 4505 ± 8 m.y. This is distinctly less than the average age for several classes of meteorites as analyzed by Tatsumoto et al. [5] and also less than many Pb/Pb ages obtained for moon rocks. We are reluctant to attach particular significance, however, to our value for t_0, or for the time being indeed, to any of our calculated t values. We think the linear trend, for U/Pb and for Th/Pb, and its consequences is a reasonable average description of past Earth processes, even though it is undoubtedly not unique. It avowedly describes average behaviour, and hence we must not be surprised to find exceptions, both in age and in apparent source U/Pb and Th/Pb. But overall, it provides as good a geological fit as the two-stage model of Stacey and Kramers [8]. Other criteria will have to be used to distinguish between these and any other possible models in which the U/Pb ratios change with time. If the choice is ultimately between a catastrophic and a uniformitarian model we would be inclined to be on the side of Hutton.

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