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STUDIES ON THE LEAD METHOD OF AGE DETERMINATION, PART I

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STUDIES ON THE LEAD METHOD OF AGE DETERMINATION I.

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ABSTRACT

Ages of a number of radioactive minerals have been determined from Pb^{207}/Pb^{206}, Pb^{206}/U^{238}, Pb^{207}/U^{235} and Pb^{206}/Pb^{210} ratios. Values obtained for minerals from classic localities agree well with those reported by other investigators. Major attention has been given to the anomalies of the ages of a given mineral computed from the various possible isotope ratios. The development of the Pb^{210} method adds greatly to the fund of data required to obtain accurate ages. The 206/210 age is essentially independent of uranium leaching or radon leakage. The latter is a significant factor in 206/238 and 207/206 ratios and must be measured experimentally to evaluate ages from these ratios. It appears that throughout most of the span of geologic time the 207/235 and 206/210 ages are the most reliable. The 206/238 supersedes the 207/235 age in accuracy for very young minerals. The 207/206 age does not merit the reliability ascribed to it by earlier investigators.

INTRODUCTION

The lead method of age determination was put on a quantitative basis by the classic work of Nier (1, 2) around 1940 when he performed the necessary lead isotope analyses of radiogenic leads by mass spectrometric means and corrected for common lead contamination. Subsequent developments and an analysis of the errors involved in the method as currently used are reviewed by the authors in another publication (3).

In order to obtain a closer approximation to the true age of a mineral by the lead method, additional quantitative tests have been applied in the present research. These refinements may be enumerated as follows: (a) The Pb^{210} concentration in a mineral has been experimentally measured which together with the Pb^{206} analysis gives an additional independent age of the sample. Specifically this age is independent of recent leaching of uranium. (b) The amount of radon emanation from some samples under laboratory conditions was measured. This measurement provides an index of the errors of the Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages due to radon leakage. (c) In samples containing common lead, choice of the proper common lead composition to use for the correction was based on availability of analyses of common lead from the same metallogenic province. (d) The errors in the Pb^{207}/Pb^{206} ages arising from uncertainties in the U^{235} half-life and in the present ratio of U^{235}/U^{238} have been found to be of considerable magnitude for all but the oldest minerals.

APPARATUS AND METHODS

The isotopic analyses of lead were made with a 6-inch, 60-degree, direction-focussing spectrometer of glass-metal construction. A single collector was used to receive the ion currents which were then amplified by a vibrating reed electrometer and displayed on a speedomax recorder. The ion accelerating potential was held constant at approximately 2500 volts while the magnetic field was varied to provide the desired scan. The resolution of the instrument was approximately one part in two hundred and fifty. The sample was introduced into the instrument as $Pb(CH_3)_4$ which has sufficient vapor pressure at room temperature to be used directly without heating the all-metal sample manifold, as was demonstrated by Collins (4). This procedure permitted a short pump-down time between runs with no memory effects.

The isotopic abundances were calculated from the Pb^+ spectrum with suitable corrections made for the mono-hydride PbH^+. This correction amounted to about 10 percent. The exact value was calculated from the peak at mass 209 for samples of high Pb^{208} content. A complete discussion of the mass spectra of group IV tetramethyl compounds may be found in the literature (5).

MATERIALS

The samples measured in this study were obtained from the Mineralogical Collection of Columbia University through the kindness of Prof. Paul F. Kerr, and from the Atomic Energy Commission through the cooperation of Mrs. M. Mathez. The chemical analyses were done by the A. E. C., New Brunswick Analytical Laboratory and Ledoux and Co., New York City. The lead tetramethyl preparation was carried out in this laboratory using a procedure modified after that of Collins (4). The isotopic analyses, Pb^{210} determinations, radon leakage measurements and the petrographic examinations were made in this laboratory.

RESULTS

The chemical analysis data are given in Table 1. The isotopic compositions of the lead extracted from the radioactive minerals are listed in Table 2. In order to obtain the most precise correction for common lead, care was taken to choose the best available common lead data for sites as close as possible to the deposit which produced the radioactive mineral. The locality of the common lead used and the final percentages of radiogenic 206, 207, and 208 are given in Table 3. The ages for the ratios 206/238, 207/235, 208/232, 207/206 were computed with the aid of simplified nomographs published elsewhere (3). These results are listed in Table 4 along with the 206/210 ages. The latter are measured by alpha counting the

Po^{210} daughter of Pb^{210}. The Pb^{206} concentration is determined by mass spectrometric analysis. The theory and technique used in the Pb^{210} method is described in detail in another paper (6). It suffices here to point out that since Pb^{210} is below radon in the U^{238} decay chain, the ratio 206/210 will be independent of radon leakage if the leakage has been reasonably constant throughout the age of the mineral. Further, if uranium leaching takes place late in the history of the mineral, the lead will be essentially unaltered and the 206/210 age will be unaffected. Not only is the 206/210 age easiest to measure but it is very insensitive to changes in external conditions.

In addition to the samples studied in this laboratory, those of other workers for which isotopic data are available are also listed for purposes of comparison. Finally, Table 5 compares the ages of six representative samples with and without the correction for the experimentally measured radon leakage at room temperature. A recent study of the radon leakage of radioactive minerals (7) shows that the radon leakage increases with temperature. Therefore the integrated radon leakage must in all cases be greater than that shown in Table 5.

It should be observed from Table 4 that the agreement between different laboratories on different specimens from the same localities is quite good, indicating that the anomalies are not derived from errors in the isotopic or chemical measurements.

DISCUSSION

With reference to the Spruce Pine samarskite(K-4), it is seen that the internal agreement of all of the ages is good except for the 207/206 age which is usually unreasonably high for post-Cambrian minerals. It is known (13) that the Spruce Pine district was subjected to a second regional metamorphism about 100 m. y. after these radioactive minerals were formed. Although the radon leakage of this samarskite at room temperature proved to be less than 0. 1%, the large increase in temperature over a considerable period of time may explain the spread in the ages. If there is an integrated radon leakage of about 14% the 206/238 age would be brought up to about 350 m. y. and the 207/206 would be reduced to about 350 m. y. The most probable age for the first major regional metamorphism in the Spruce Pine District is 345±10 m. y. which produced the pegmatites and the uranium minerals. This would date the climax of this regional metamorphic cycle in the southern Appalachian at approximately the Ordovician-Silurian boundary.

The samples from the Central City district, Gilpin County, Colorado, are all in excellent agreement. As usual, the 206/238 age is low and the error in the 207/206 is too large to obtain a usable age from this ratio. Of particular interest is the agreement of the 207/235 and 206/210 ages. Note that the 206/210 error is small even at these recent ages. The best age for this deposit would now appear to be 59±2 m. y.

The Belgian Congo specimens are also in broad agreement. The radon leakage was apparently low in these specimens since the 207/206 ages are not exhorbitantly high. The three samples K-9, 10, 11 provide an interesting study. K-9 was an excellent sample. K-10 showed minor alteration with evidence of minor uranium leaching. K-11 was leached with concentrated HCl for 15 minutes until all of the yellow alteration products were removed. This clearly removed uranium from the mineral. The trend of the 207/235 and 206/238 ages from K-9 to K-10 to K-11 show the likely effects of leaching. Since the violent acid treatment only increased the 206/238 by a few percent it appears that this effect on age determinations has been greatly over-rated. This erroneous concept has made many workers regard the 207/206 ratio as being more reliable than it actually is, although it is true that the lead-lead ratios will not be appreciably affected by leaching. Note the striking constancy of the 206/210 ages for K-9, K-10, K-11. Further work is being done on the absolute calibration of the alpha counters for the Po^{210} measurement which may cause revision of 5-10% in absolute ages derived from the 206/210 ratios.

The agreement between the new data and that of Nier on the Joachimsthal locality is quite good. Again note the excellent correlation of the 207/235 and 206/210 ages. The most probable age for this deposit appears now to be 210±10.

Similar agreement is obtained for the Great Bear Lake samples K-16 and N-10. The K-18 sample appears to be different in age by about 150 m. y. Further study is required on this problem.

Uranium mineralization in the Upper Huronian of Michigan appears to have taken place about 400±20 m. y. ago, while that from the Sofia Mine, Baden, Germany is close to 100±10 m. y.

The Athabasca area samples showed considerable spread in ages although individual deposits are self-consistent. Note the excellent agreement again between the 207/235 and 206/210 ages for K-14. The radon leakage at room temperature (Table 5) is inadequate to change the ages noticeably but increased temperature may provide an integrated leakage correction of a few percent which could account for the observed discrepancies. The K-19 ages show a much wider spread but it also has a much larger radon leakage at room temperature (Table 5). If the integrated leakage approaches 10% the agreement would be complete. Similar remarks apply to K-7. It is noteworthy that in no case does the measured radon leakage cause an "overcorrection" for the 206/238 age. Furthermore, the samples showing the greatest percentage of discrepancy in the 206/238 age have the largest radon leakage at room temperature.

The Marysvale, Utah, sample was so small that it had to be diluted with a known quantity of radiogenic lead of known isotopic composition in order to prepare the $Pb(CH_3)_4$. K-14 was chosen because of its very low common lead content. The total lead present in the sample was very small and the common lead was about 60% so that the net 207 content was small and involved a large error. The result is that the 207/235 age was almost useless. In this case the 206/238 age is the most reliable. The Marysvale ore is very fine and has a radon leakage at room temperature of 7.6%.

Since this mineral was emplaced very recently under epithermal conditions it probably has not existed for an appreciable part of its history above room temperature. Further measurements must be made in this interesting occurrence which records the youngest known uranium mineralization. The best age at present is 10±2 m. y. taking into account the radon leakage.

The last sample is uraninite associated with the gold ore of the Witwatersrand, South Africa. The isotopic analysis of galena from the same mine provided an excellent base for the common lead correction. Although the 207/206 age agrees with that of Collins, this is clearly not the age of the mineralization which must be closer to 1300 m. y. The 207/235 age in this case appears anomalously high. Further study on this locality is required.

CONCLUSIONS

Sixteen new age determinations by the various isotopic ratios of the lead method have been made. The development of the Pb^{210} method is a major advance in the program of absolute age determination. It appears highly desirable to measure the radon leakage from radioactive minerals subject to age determination by the lead method. The most reliable ages are given by the 206/210 and 207/235 ratios. 207/206 ratios give the least reliable ages and 206/238 ratios are of greatest value for very young minerals.

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Table 1

Chemical Analysis Data

Sample No.	Mineral & Locality	%Pb	%U	%Th
K-4	Wiseman Mine, Spruce Pine, No. Carolina Samarskite	0.60±.01	13.06±.02	1.11±.03
K-6	Rickards Mine, Gilpin Co., Colorado Uraninite	1.34±.01	47.88±.01	0.10±.01
K-7	Contact Lake, Saskatchewan Uraninite	2.51±.01	19.46±.03	0.22±.02
K-8	Gorman & Belchin Mine, Central City, Colo. Uraninite	0.79±.01	64.66±.05	0.18±.01
K-9	Belgian Congo Uraninite	6.273±.04	73.78±.02	0.016±.005
K-10	Belgian Congo Uraninite (Minor Alteration)	6.62±.02	72.51±.02	0.008±.001
K-11	Belgian Congo (Crushed & leached) Uraninite	7.52±.05	76.00±.03	0.01
K-12	Marysvale, Utah Uraninite Concentrate	0.0233±.001	6.35±.05	
K-13	Marysvale, Utah Uraninite Concentrate	0.0267±.005	7.70±.02	
K-14	Eagle Mine, Lake Athabasca, Canada Uraninite Ore	6.43±.03	27.95±.04	0.0045
K-15	Joachimsthal, Bohemia Uraninite	2.74±.01	55.97±.02	
K-16	Eldorado Mine Uraninite	1.40±.01	6.60±.01	
K-18	Eldorado Mine Uraninite	8.39±.05	45.85±.01	

Table 1 (Cont.)

Sample No.	Mineral & Locality	%Pb	%U	%Th
K-19	Nicholson Mine, Gold-fields Uraninite Ore	4.91±.02	44.31±.02	
K-20	Witwatersrand, South Africa Uraninite Concentrate	14.36±.11	62.025±.01	
K-21	Upper Huronian Iron Formation Pitchblende Concentrate	3.903±.03	70.21±.07	
K-23	Sofia Mine, Baden Germany Pitchblende Ore	0.96±.01	32.97±.11	

Table 2

Isotopic Data

Sample No.	Locality	204	206	207	208	Mineral
K-4	Wiseman Mine Spruce Pine, N. C.	<0. 02	91. 2±. 2	5. 60±. 08	3. 18±. 07	Samarskite
K-6	Rickards Mine Gilpin Co., Colo.	0. 97±. 01	44. 88±. 20	16. 63±. 05	37. 52±. 10	Pitchblende
K-8	German Belchin Mine Central City, Colo.	0. 57±. 01	65. 7±. 1	11. 78±. 04	21. 97±. 20	Pitchblende
K-9	Katanga, Belgian Congo	<0. 01	93. 6±. 03	5. 79±. 08	0. 32±. 02	Uraninite (hard and shiny)
K-10	Katanga, Belgian Congo	<0. 01	94. 0±. 05	5. 90±. 09	0. 06±. 02	Uraninite (minor alteration)
K-11	Katanga, Belgian Congo	<0. 01	94. 0±. 03	5. 93±. 07	0. 07±. 02	Uraninite (acid leached)
K-7	Contact Lake, N. W. T.	<0. 01	92. 3±. 2	7. 50±. 20	0. 27±. 03	Pitchblende
K-14	Eagle Mine (200-300') Lake Athabasca	<0. 01	91. 20±. 15	8. 61±. 20	0. 18±. 06	Pitchblende
K-16	Eldorado Mine (151 Stope) Great Bear Lake	0. 12±. 01	86. 4±. 1	9. 27±. 15	4. 26±. 10	Pitchblende Ore
K-18	Eldorado Mine (913 Stope) Great Bear Lake	0. 24±. 01	82. 6±. 1	9. 66±. 05	7. 52±. 04	Pitchblende
K-19	Nicholson Mine (No. 2 shaft) Coldfields (dump)	<0. 02	92. 44±. 03	7. 25±. 10	0. 32±. 02	Pitchblende Ore

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Table 2 (Cont.)

Sample No.	Locality	204	206	207	208	Mineral
K-15	Joachimsthal	0.62±.02	60.81±.06	13.10±.04	25.45±.04	Pitchblende (clean)
K-20	Witwatersrand	< 0.1	85.4±.2	11.38±.06	3.15±.10	Pitchblende concentrate
K-21	Upper Huronian Iron Formation Michigan	< 0.05	93.25±.05	6.00±.08	0.75±.05	Pitchblende concentrate
K-23	Sofia Mine Baden, Germany	0.71±.02	61.2±.4	12.64±.15	25.4±.2	Pitchblende Ore
K-12, 13, 14 (Mixture) Marysvale, Utah K-12, 13 - 13.6% Athabasca K-14 86.4%		0.105±.03	85.89±.08	9.76±.08	4.36±.04	Pitchblende concentrate

Table 3

Corrected % Radiogenic Lead

Sample	Common Lead Locality	% Radiogenic Lead 206	207	208
K-4	----	91.2±.2	5.60±.08	3.18±.07
K-6	[1]Av. Colo. Plateau	26.1±.5	1.30±.33	---
K-8	Av. Colo. Plateau	54.6±.3	2.84±.20	---
K-9	[2]Kengere, Belgian Congo	93.6±.03	5.79±.08	---
K-10	Kengere, Belgian Congo	94.0±.05	5.88±.09	---
K-11	Kengere, Belgian Congo	94.0±.03	5.90±.07	---
K-7	[3]Great Bear Lake	92.2±.2	7.36±.20	---
K-14	Great Bear Lake	91.2±.2	8.53±.20	---
K-16	Great Bear Lake	84.5±.2	7.4±.2	---
K-18	Great Bear Lake	79.2±.2	6.4±.1	---
K-19	Great Bear Lake	92.3±.1	7.1±.1	---
K-15	[4]Av. Southern Germany	48.7±.2	2.6±.2	---
K-20	[5]Witwatersrand	80.7±.2	9.48±.07	---
K-21	[5]Michigan	92.9±.2	5.67±.12	---
K-23	[4]Av. Southern Germany	50.8±.5	2.15±.20	---
K-12, 13, 14	[5]Marysvale, Utah	37.2±.11*	4.3±1.6*	---

1 - Stieff et al. (9)
2- Collins et al. (8)
3 - Nier (10)
4 - Nier (10) and Vinogradov et al. (11)
5 - Kulp et al. (12)

* - Percent radiogenic 206 and 207 from the K-12, 13 part of the sample only.

Table 4

Ages from Various Isotopic Ratios
(not corrected for radon leakage)

Sample**	Locality	Age in m. y. 208/232	207/206	206/238	207/235	206/210
K-4	Spruce Pine, N. C.	354±35	699±35	312±6	362±10	325±15
C*	Spruce Pine, N. C.	---	370±40	---	---	---
K-6	Gilpin Co., Colo.	---	220±300	55±2	58±10	61±3
K-8	Central City, Colo.	---	250±250	51±1	56±5	58±3
N-25	Gilpin Co., Colo.	---	280±350	59±1	64±10	---
N-24	Woods Mine, Colo.	---	183±300	56±1	59±11	---
K-9	Katanga (clean)	---	676±25	576±4	598±8	650±15
K-10	Katanga (minor alteration)	---	703±30	645±10	617±15	645±15
K-11	Katanga (acid leached)	---	705±30	668±7	677±7	650±15
N-2	Katanga	---	630±14	615±4	609±6	---
N-6	Katanga	---	632±13	567±5	577±8	---
C*	Katanga	---	612 to 655	---	---	---
K-15	Joachimsthal	---	425±200	179±3	197±15	206±10
N-1	Joachimsthal	---	165±180	226±5	221±22	---
K-16	Eldorado	---	1407±50	1230±10	1286±20	1208±40
K-18	Eldorado	---	1251±45	1015±5	1088±14	1105±30
N-10	Great Bear Lake	---	1397±20	1215±10	1271±15	---
C-1-4	Eldorado	---	1430-1330	---	---	---
K-21	Upper Huronian	---	650±35	384±5	421±6	---
K-23	Baden, Germany	---	---	111±2	97±13	---
K-14	Eagle Mine, Lake Athabasca	--	1523±50	1425±10	1450±20	1448±35
C*	Eagle Mine, Lake Athabasca	--	1100 to 1700	---	---	---
K-19	Nicholson Mine #2, Goldfields	---	1141±12	730±8	843±10	808±25
C*	Nicholson Mine #2, Goldfields	---	1160±30	---	---	---
K-7	Contact Lake(N. W. Terr.) Canada	---	1212±60	840±5	942±24	864±35
K-12, 13	Marysvale, Utah	---	---	9.8±1.2	24±10	---
K-20	Witwatersrand	---	1960±40	1282±15	1562±20	1290±40
C*	Witwatersrand	---	2070±100	---	---	---

** K-Determination made at the Lamont Geological Observatory
N-Nier (1, 2)
C-Collins (8)
C*- Collins unpublished data

Table 5

Room Temperature Radon Leakage on Selected Samples

Sample	% Radon Leakage Room Temp.	"Best Age" in m. y.	Age in m. y. Uncorrected 207/206	Uncorrected 206/238	Corrected 207/206	Corrected 206/238
K-6 Gilpin Co.	2.7±.1	59±2	220±300	55±2	165±300	56±2
K-8 Central City	8.6±.1	59±2	250±250	51±1	34±250	55±1
K-7 Contact Lake	7.4±.1	900±25	1212±60	840±5	1056±60	902±5
K-9 Katanga slightly altered	5.6±.4	600±10	676±25	576±4	542±25	608±4
unaltered	1.6±.1				638±25	585±4
K-13 Marysvale	7.6	10±2		9.8±1.2		10.5±1.2
K-14 Eagle Mine	.06	1450±20	1523±50	1425±10	1521±50	1426±10

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