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Effect of ^{222}Rn emanation from crystals on their ^{206}Pb/^{238}U age dating

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ABSTRACT

The escape of radon from certain minerals with high uranium is of particular interest to those concerned with the determination of ages of rocks, minerals and tectonic events. To the extent that radon escapes, these minerals are not closed systems from the thermodynamic point of view and, more particularly, from the geochronological point of view. This investigation aimed to determine the radon escape from zircon crystals and how this fit into the severe isotopic constraints of the concordia dating model.
To evaluate the consequences of radon loss on ^{238}U/ ^{206}Pb age dating methods, 20 zircon concentrates were analyzed. The observed range of relative percentage of radon loss was of 0.2-12 % and correlations with (i) weathering of the crystals (ii) with natural alpha dose and (iii) with U-Pb age discordances were found.
These correlations indicate relationships between the amount of lattice damage by radiation, the radon leakage out of the crystal and Pb mobility. Some of the stochastic complexities in specific age determinations are also discussed.

1. INTRODUCTION

Radon escape from minerals and particularly from radioactive minerals was already known at the beginning of this century and the available literature on isotopic lead age dating has become quite extensive since the first data on the subject were published by Nier (1). Common to most of these studies on mineral dating is the lack of agreement between ^{206}Pb/^{238}U, ^{207}Pb/^{235}U and ^{207}Pb/^{206}Pb and ages for the same sample. In general the standard ordering of apparent ages with ^{206}Pb/^{238}U<^{207}Pb/^{235}U<^{207}Pb/^{206}Pb< “true” age and with the ^{208}Pb/^{232}Th age falling somewhat randomly between the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages. The accepted reason is loss of lead isotopes during geological time. However, mechanism for lead loss (or uranium gain) that produces these discordant ages is not well understood. Krishnaswami and Seidemann (2) measuring the leakage of radiogenic ^{222}Rn, ^{40}Ar and reactor-produced ^{39}Ar plus ^{37}Ar in samples of granites, plagioclase, orthoclase, cleavelandite and hornblende concluded that the leakage of all three Argon isotopes was barely measurable. In contrast, the leakage of ^{222}Rn ranged between 1.45-18.1% orders of magnitude higher than that of the Argon isotopes.

Systematics in the discordant lead ages of suites of monazite and uraninite were reported by Ahrens (3) and suggested non-random processes in the lead-loss history of the samples. Shortly thereafter Wetherill et al (4) proposed the detailed theoretical systematics, for a closed system, with respect to lead loss or uranium gain. He demonstrated that the data would lie along a curved line in a plot of the ratio ^{206}Pb/^{238}U versus ^{207}Pb/^{235}U, this line or concordia, representing the loci of points for which the ^{206}Pb/^{238}U ages are equal to the ^{207}Pb/^{235}U ages. Further, he showed that if a system was subject to a short-duration (episodic) event, producing a change in lead or uranium concentration, the data would lie along a straight line between the two points on the concordia corresponding to age of the system and the time of the episodic event.

Doe (5) pointed out that while the mechanism producing the normally discordant ages in zircons is not well known, there is evidence for some zircons (6,7,8) to show a correlation between uranium content and $^{206}Pb/^{238}U$ ages, with those zircons of greatest uranium concentration having the greatest degree of discordance. This relation seems to suggest that radiation damage and a resulting time-dependent diffusion coefficient are significant for, at least, some zircons.

Other effects that can alter apparent lead ages and perhaps affect linearity are weathering and leaching by ground water (9) with the loss of intermediate radioactive daughters in the uranium-lead system. Whereas disequilibria resulting from the movement of other daughters such as ^{234}U or ^{226}Ra is expected to be of short duration or of minor importance, the emanation of ^{222}Rn might occur continuously over long time. If this were the case, ages could be significantly altered with a preferential loss of Pb due to the relatively long half life of ^{222}Rn (3.85 days) compared to that of the ^{219}Rn (4.0 sec) from the ^{235}U chain. The major effect of radon loss, therefore, should be to shift the data on a concordia plot downward (vertically in the standard plot) toward lower $^{206}Pb/^{238}U$ ratios and thus increase the $^{207}Pb/^{206}Pb$ ages.

To evaluate such impact and possible correction for uranium-lead age determinations, the ^{222}Rn loss was analyzed in twenty zircon concentrates of known U and Pb isotopic data and well documented geologic history.

2. TECHNIQUE AND SAMPLE DESCRIPTION

Laboratory Technique

To measure the naturally escaping fraction of gas produced within the crystals, it should be disturbed as little as possible; thus, any chemical treatment or gas sweeping type of radon collection could not be used. To avoid this an innovative technique of volume sharing was used for direct transfer of radon from the sealed sample container to the detector .The technique is described in detail by Barretto et al (10) and will be only briefly summarized here. Initially a sample was sealed at atmospheric pressure in a glass flask and allowed to de-emanate for approximately 8-10 days. The flask was then connected to a ZnS alpha counting scintillation chamber, which had been previously evacuated to approximately 100 microns, and the gas containing the accumulated radon allowed reaching equilibrium within the system for about 2 minutes. This volume sharing technique is based on the following relation:

$$\mathbf{N_o} = \mathbf{N} \times \mathbf{V_c} / \mathbf{V_s} \qquad \text{for} \qquad \mathbf{t} = 0$$

where $\mathbf{N_o}$ = radon atoms at transfer in the alpha chamber

$\mathbf{N}$ = total radon atoms in the system

$\mathbf{V_c}$ and $\mathbf{V_s}$ = chamber and system volumes.

Two volume ratios were used according to the sample weight or activity, transferring approximately 38 or 65% of the emanated radon to the alpha counter. The intrinsic alpha counting efficiency of the detector known as "Lucas cell" was 84%. For such low level counting, a precise determination of the system background counting- rate is required. Thus, the background was monitored extensively for a long periods (sometimes over a week) depending on the uranium concentration in the sample.

Depending on the detector used this background varied from 4 to 19 cph. The alpha counting was done at room temperature and four hours after the transfer when the radon had reached transient equilibrium with its descendents.

Sample description

Sawatch Range, Colorado: Samples C-2, C-3 and HWDT are from the St. Kevin Granite, Sawatch Range, west of Leadville. Doe and Pearson (11) give a detailed sample description including isotopic composition of lead and other analytical data. HWDT is a mixture of hycinth and milkwhite zircon from the normal facies of the St. Kevin Granite and was collected in an area where "contaminated" granite and metasomatized metamorphic rocks are interlayered with compositionally uniform granite.

Central Arizona: Samples CAA-15 and CAA-17 (T.W. Stern, personal communication). No description or geological information was available.

Appalaches: Sample WSE-70-13. Radiometric studies of upper Precambrian zircons of the Blue Ridge in the Appalachian Mountains (12) indicate an age of 820 my and a disturbance about 240 my ago. In addition, the morphology of the zircons of that area suggested that it consist of a single unmixed population.

Minnesota: Sample 373 is from residual clay developed on the Morton Gneiss near Redwood Falls, Minnesota (9). It consists of a highly discordant, weathered zircon with much of the lead loss apparently due to ground water leaching when the Minnesota River Valley rocks were exposed and weathered during the Cretaceous.

SW Minnesota: Sample 346 is from the garnetiferous quartz diorite gneiss of the Granite Falls, Montevideo region (13, 14). It corresponds to the most nearly concordant isotopic ratios found in the Minnesota River Valley. Radiometric studies in the neighboring gneisses indicate, according to the above authors, an episodic lead-loss event 1850 my ago which did not affect the area of sample 346. These almost concordant ages date an older metamorphism 2650 my ago which reset the uranium-lead system. Based on rubidium-strontium and uranium-lead data they assign an age of 3550 my to the gneisses of the region. Samples CAA-15, CAA-17, 373, 346, WSE-70-13 were obtained on loan from T.W. Stern of the U.S. Geological Survey.

Finland: They were obtained on loan from O. Kouvo of the Geological Survey of Finland. According to Kouvo (15), Wetheril et al (4), Kouvo and Tilton (16) and Nevuonen (17), the Finnish basement complex crystallized 2600-2800 my ago (samples A-362, A-357, A-6b, A-176, A-416 of tables 5 and 7). There are two PreCambrian orogenic belts, Karelian (thick quartzites, carbonates and serpentinites) and Svecofennian (graywackes, carbonates and few quartzites). Samples A-24, A-25, A-229, A-240 are svecokarelian synkinematic zircons. Karelian regional metamorphism occurred about 1800 my ago. Within the belt of Karelian schist occur several domes of granite gneiss (samples A-362, A-357) mantled probably during the Karelian orogeny 1800 my ago. Sediments in both belts were intruded by granites of the anarogenic rapakivi series 1650 my ago (sample A-255).

3. RESULTS

A - Emanation

The radon emanation characteristics for the 20 zircons concentrates are shown in Table 1 (zircons from the USA) and Table 2 (zircons from Finland). All data correspond to leached aliquots of the material used in the U-Pb age determination. The only exception is HWDT, which is an unleached concentrate. In this case, the radioactive isotopic data used were obtained from published results for the leached experiments (9) on an aliquot of the same sample.

The errors for the radon escape-to-production rate include the following experimental uncertainties: statistical errors in the observed counting rate, variance in the number of counts resulting from the decay of a single radioactive family, accuracy of the absolute calibration and relative reproducibility. Radioactive equilibrium is assumed between ^{238}U and its progeny ^{226}Ra. For many of the samples, this assumption was experimentally confirmed by acceptable agreement between ^{238}U concentrations determined indirectly by gamma spectrometric counting of the ^{214}Bi. Each concentrate was analyzed t least twice for radon loss and for most of them three analyses were performed. The data displayed in the tables 4 to 7 correspond to the arithmetic average. A number of blanks were run at different times during the experiments.

Table 1. Radon Emanation Characteristics
Zircons from the USA

SAMPLE	WEIGHT (g)	CONCENTRATIONS (ppm) ^{238}U	^{232}Th	ACTIVITY (dph)	EMANATION RATE (atoms/h/g)	ESCAPE-TO-PRODUCTION-RATIO (%)
C-2	1.054	570.1	284.2	2.68x10^{4}	2.08x10^{2}	0.8 ± 0.2
C-3	0.866	867.6	404.2	3.38x10^{4}	0.65x10^{2}	0.2 ± 0.1
HWDT*	1.482	2660.1	1549.3	1.75x10^{5}	5.51x10^{3}	4.5 ± 0.4
CAA-15	0.511	757.6	373.9	1.72x10^{4}	3.16x10^{2}	0.9 ± 0.2
CAA-17	0.796	504.7	180.9	1.78x10^{4}	3.42x10^{2}	1.9 ± 0.3
373	0.735	505.8	127.5	1.32x10^{4}	2.21x10^{3}	12.1 ± 0.6
WSE-13	1.254	416.4	154.2	2.36x10^{4}	1.40x10^{2}	0.8 ± 0.1
346	0.043	601.9	159.1	1.15x10^{3}	0.84x10^{2}	0.3 ± 0.2

*Unleached dph = disintegration per hour

Due to the high uranium concentration characteristic of the zircons, their emanation rate in general is large (100 - 2000 atoms h-1 g-1), which allows the detection of even a small percent of radon loss (as sample C-2 with 0.2%) without much difficulty. The radon losses for the zircons vary from 0.07 to 4.5%, with one exceptional high value (12.6%) for sample 373, obtained from residual clay. This high percentage of radon loss is probably related to the weathering of the sample.

Table 2. Radon Emanation Characteristics
Zircons from Finland

SAMPLE	WEIGHT (g)	CONCENTRATIONS (ppm)		ACTIVITY (dph)	EMANATION RATE (atoms/h/g)	ESCAPE-TO-PRODUCTION-RATIO (%)
		^{238}U	^{232}Th			
A-66	0.705	711	645	2.21×10^4	485	1.54 ± 0.04
A-24	0.13	848.7	132	4.87×10^3	517	1.38 ± 0.07
A-25	0.574	1123.8	141	2.8×10^4	1025	2.06 ± 0.08
A-73	0.922	657.3	243	2.67×10^4	631	2.18 ± 0.08
A169	0.757	1053.3	445	3.52×10^4	2220	4.78 ± 0.10
A-176	0.283	1174.4	549	1.46×10^4	2310	4.45 ± 0.14
A-229	0.363	415.2	177	6.60×10^3	282	1.53 ± 0.06
A-240	0.279	313.5	187	3.83×10^3	23	0.17 ± 0.03
A-255	0.388	122	102	2.09×10^3	45	0.83 ± 0.06
A-334	0.219	216.7	271	1.97×10^3	65	0.68 ± 0.07
A-335	0.646	428.6	178	1.22×10^4	244	1.28 ± 0.06
A-362	1.04	552.2	190	2.52×10^4	235	0.96 ± 0.04

A close examination of tables 4 to 7 suggests that the radon loss in zircon is generally greater for samples with high uranium concentration. For example, in table 4, sample HWDT is the largest emanator (relative to its cogenetic C-2 and C-3) and shows high uranium concentration; in table 5, the zircons A-169 and A-176, the highest emanators, have more than 1000 ppm uranium; sample DKL-2B also corresponds to high uranium and high emanation. These findings led to the investigation of the possibility that radon emanation from fresh minerals is related to the total a-dosage received by the crystal since its formation.

B. Total Alpha-Dose and Emanation

The evaluation of the natural radiation damage, which may be present in a crystal, is directly proportional to the total alpha-dose received by the sample. Thus, the importance of a precise determination of the uranium and thorium concentrations present in each sample. Both the uranium and thorium concentrations in the samples were determined by thermal ionization procedures on a mass spectrometer (1%. uncertainty) and by gamma-ray spectrometric analyses utilizing the low level counting facilities described by Adams (18) The calibration was done by using samples C-2 and C-3 as internal standards.

The activities and dosages received by the samples were calculated with the equation given by Holland and Gottfried (19) for the total disintegration per milligram as follows:

$$D = \alpha \frac{8\,(e^{\lambda 8 t} - 1) + 7/139\,(e^{\lambda 5 t} - 1) + 6\varphi\,(e^{\lambda 2 t} - 1)}{8\,\lambda 8 + 7/139\,\lambda 5 + 6\varphi\,\lambda 2} \tag{1}$$

Where:

D = Total number of disintegrations per milligram of sample since the time of formation

α = present alpha activity in alphas mg-1 year-1

λ8, λ5 and **λ2** = decay constant in years-1 of ^{238}U, ^{235}U and ^{232}Th, respectively

t = sample age in years

φ = present ^{232}Th/^{238} U ratio

In table 1, it may be observed that the alpha activities are practically the same for the zircons with the exception of sample HWDT that has a high uranium and thorium content. Sample 373 is weathered and has 55% apparent lead loss with the actual loss greater if alpha was leached out as suggested by the average uranium content of fresh zircons in the same rock (9). Then, assuming a pre-weathered and leached uranium concentration equal to twice the present value, the second values for this sample were obtained.

In the case of samples C-2, C-3, CAA-15, CAA-17 and WSE-70 have approximately the same relatively low a dosage, about 1-5 x 10^{15} alpha/mg and correspondingly low percent of radon loss. Sample HWDT was subjected to a higher dose and presents higher radon escape. Sample 373 consists of recently weathered zircon (9) and this weathering could leach out a significant fraction of ^{226}Ra and other intermediate daughters thereby producing an underestimated emanation rate because the assumed secular equilibrium does not really exist. However, a compensating effect is at work. The weathering may increase the permeability of the material for direct radon diffusion thereby raising the present percentage of radon escape above that applicable to most of the sample history. This probably explains the anomalous high 12% radon escape for the sample~~.~~

Table 2 displays 12 zircon concentrates from Finland. These samples, collected in different areas and from different rock types, very clearly show a trend by which samples that received high alpha doses indicate larger percentage of radon loss. Zircons A-176, A-169, A-25, A-73 received the highest doses and display, as a direct systematic consequence, higher and higher radon losses. The interpretation of these results must be done carefully taking in account the sample's geological history.

4. RADON CONTRIBUTION TO THE ^{206}Pb/^{238}U DISCORDANCE

The effect of ^{222}Rn loss on the ^{206}Pb/^{238}U isotopic ratios is summarized in Tables 3 and 4 showing the direct contribution of radon loss to the discordance for the different samples.

Table 3. Emanation Contribution to Discordance
Zircons from Finland

SAMPLE	AGE ^{207}Pb/Pb^{206} (in my)	ASSUMED AGE (my)	PRESENT ATOMIC RATIOS		CONCORDANT ATOMIC RATIOS		DISCORDANCE (%)		RADON CONTRIBUTION TO ^{206}Pb/^{238}U	
			^{206}Pb/^{238}U	^{207}Pb/^{235}U	^{206}Pb/^{238}U	^{207}Pb/^{235}U	^{206}Pb/^{238}U	^{207}Pb/^{235}U	relative to concordance Ratios(%)	relative to discordance (%)
A-6b	2150	2160	0.2819	5.003	0.3952	7.153	28.6	30.0	1.54	5.4
A-24	1900	1900	0.2817	4.235	0.3399	5.327	20.1	20.5	1.38	6.8
A-25	1900	1900	0.2195	3.412	0.3399	5.327	35.4	35.9	2.06	5.8
A-73	2600	2620	0.3683	8.781	0.4930	11.536	25.3	23.9	2.18	8.6
A-169	1800	1810	0.1403	1.806	0.3215	4.800	56.4	62.4	4.78	8.5
A-176	2150	2160	0.1129	2.060	0.3952	7.153	71.4	71.2	4.45	6.2
A-229	1900	1900	0.2880	4.557	0.3399	5.327	15.2	14.4	1.53	10.1
A-240	1915	1920	0.3339	5.294	0.3430	5.436	2.6	2.6	0.17	6.5
A-255	1700	1700	0.2647	3.706	0.2992	4.211	11.5	11.9	0.83	7.2
A-2334	1850	1860	0.2935	4.440	0.3321	5.093	11.6	12.8	0.68	5.8
A-335	1850	1860	0.2382	3.531	0.3321	5.093	28.3	30.6	1.28	4.5
A-362	2400	2420	0.3946	8.357	0.4516	9.390	12.6	11.0	0.96	7.6

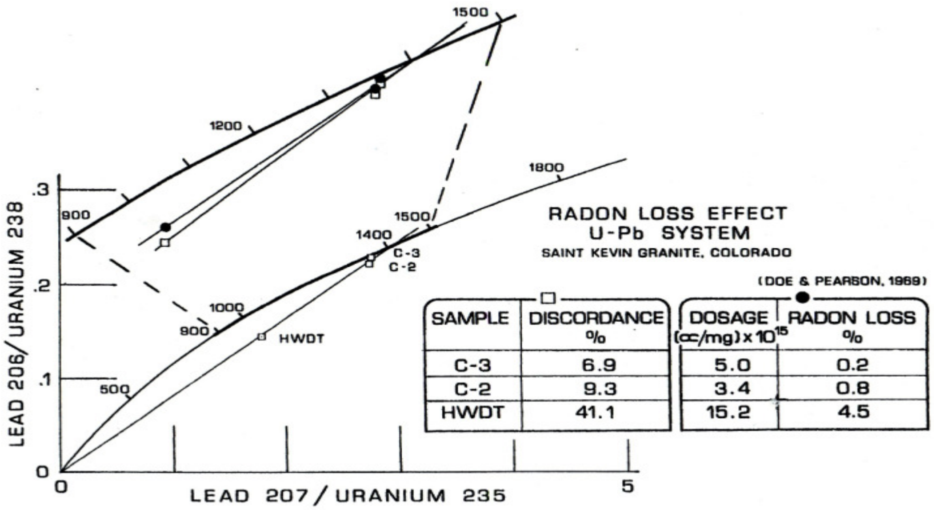
Table 4. Emanation Contribution to Discordance
Zircons from the USA

SAMPLE	AGE $^{207}Pb/Pb^{206}$ (in my)	ASSUMED AGE (my)	PRESENT ATOMIC RATIOS		CONCORDANT ATOMIC RATIOS		DISCORDANCE (%)		RADON CONTRIBUTION TO $^{206}Pb/^{238}U$	
			$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	relative to concordance Ratios(%)	relative to discordance (%)
C-2	1444 ± 15	1450	0.223	2.75	0.250	3.09	10.7	11.0	0.8	7.5
C-3	1416 ± 15		0.229	2.76			8.4	10.7	0.2	2.4
HWDT	1338 ± 15		0.145	1.80			42.0	41.7	4.5	10.7
CAA-15	1456	1700	0.218	3.11	0.299	4.21	27.1	26.1	1.0	3.7
CAA-17	1640		0.170	2.33			43.1	44.8	1.9	4.4
373	3380	3540	0.275	10.33	0.725	30.10	62.1	65.7	12.1	19.5
WSE-70	804	800	0.115	1.04	0.131	1.16	12.2	10.5	0.8	7.3
346	2640	2650	0.486	11.75	0.503	12.11	3.4	2.9	0.3	8.2

The assumed “true ages” used in the computations of the concordant atomic ratios were obtained from the intersection point of the concordia and the straight-line Discordia drawn through data plots for samples from the same geological provenance. This is the case for /samples C-2, C-3, HWDT, CAA-15, CAA-17 (Figures 1 and 2). In the case of the zircons from Finland, the assumed age was obtained for every individual sample by connecting each of the actual sample plots on the concordia diagram to the origin of the coordinates (zero isotopic ratios) and reading directly the age in the concordia intersection.

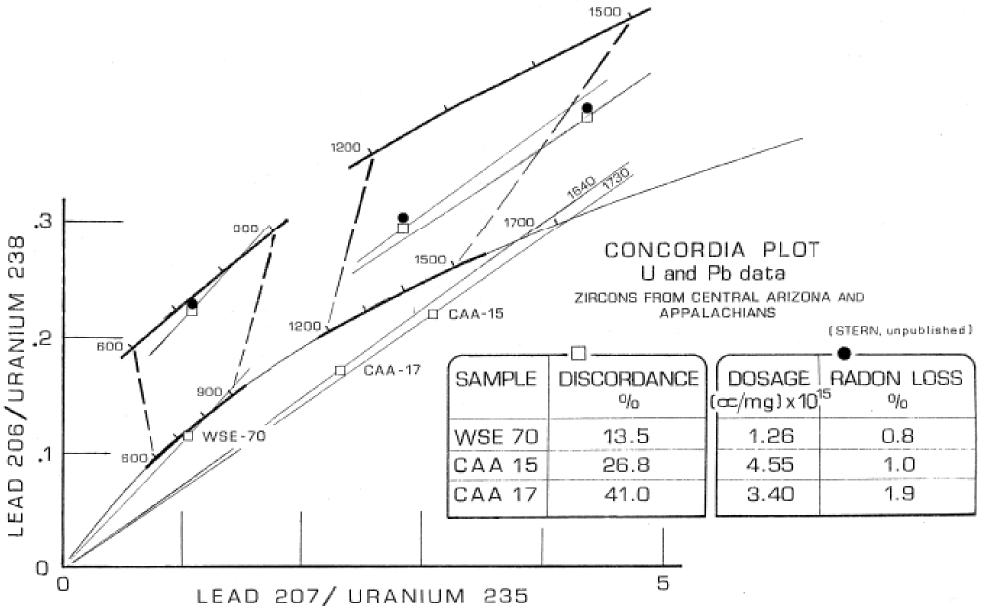
In Figure 1 are plotted the three samples from St. Kevin Granite, C-2, C-3 and HWDT. The latter is very discordant whereas C-2 and C-3 have ratios that are more concordant. In the inset enlargement of the concordia, the solid dots correspond to the plot of the measured isotopic $^{206}Pb/^{238}U$ ratios corrected for the respective percentage of radon loss (Table 4). An inspection of the data shown in this figure reveals a correlation between discordance, alpha dose, and emanation. Samples C-2 and C-3 have approximately the same relatively low alpha dose and their percentage of radon loss is relatively small. Their plot fall close to the Concordia. HWDT is highly discordant, was subjected to higher dose and presents a high percentage of radon loss and it plot is well off from the concordia.

If the radon leakage has remained constant for a long period of geologic time, the ^{222}Rn contribution to the $^{206}Pb/^{238}U$ would be the present percentage of emanation as shown in the last two columns in these tables. This contribution ranges from 2.4% to 10.7% (with the exception of the weathered zircon #373).



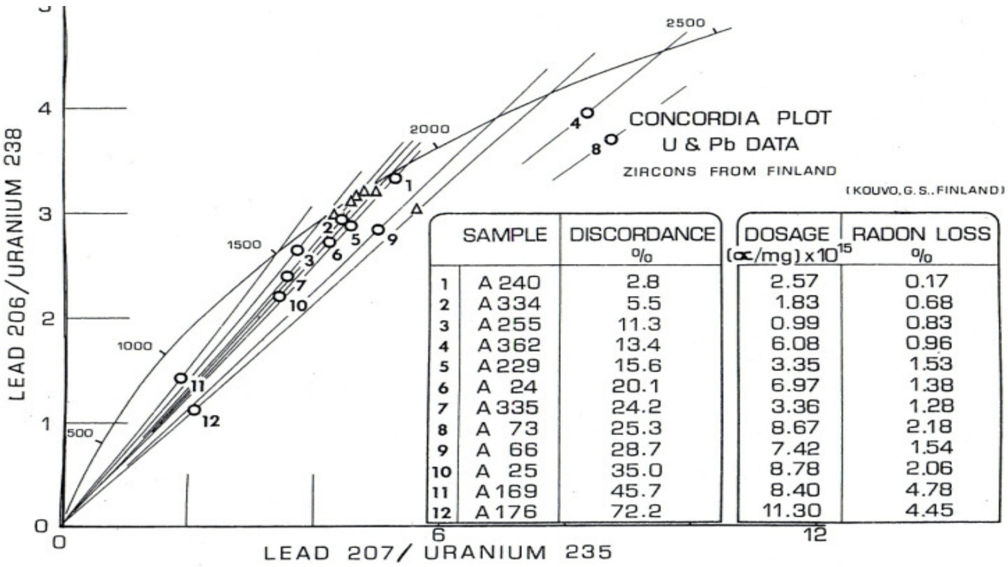
SAMPLE	□ DISCORDANCE %	DOSAGE (cc/mg) x 10^{15}	● RADON LOSS %
C-3	6.9	5.0	0.2
C-2	9.3	3.4	0.8
HWDT	41.1	15.2	4.5

Figure 1. Daughter-parent diagram (Concordia) for the zircons concentrates from the Saint Kevin granite, Colorado. The open square represent the present measured values for the lead/uranium ratios. The solid dots represent the ratios that would be found if there were no radon leakages (assuming ^{219}Rn loss is negligible). The straight lines are only to indicate the direction and size of the shift in the Discordia chords necessary to correct for the ^{222}Rn loss.



SAMPLE	□ DISCORDANCE %	DOSAGE (cc/mg) x 10^{15}	● RADON LOSS %
WSE 70	13.5	1.26	0.8
CAA 15	26.8	4.55	1.0
CAA 17	41.0	3.40	1.9

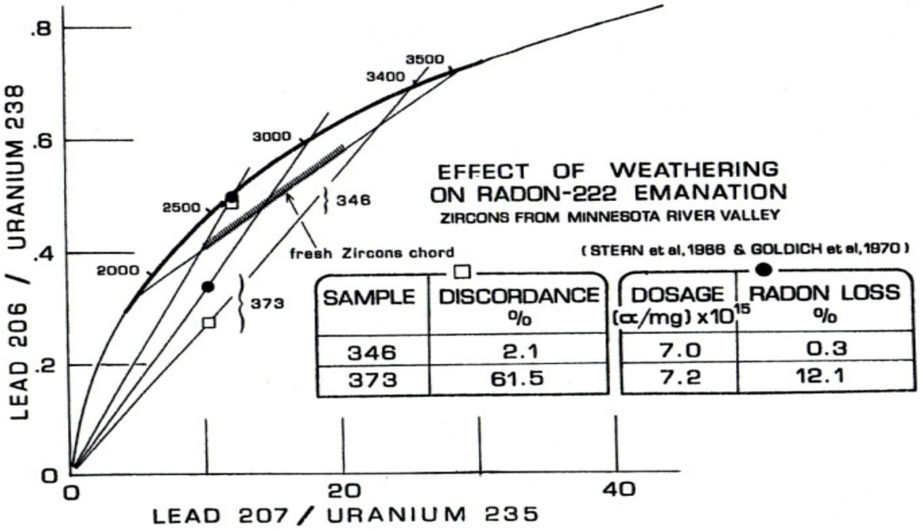
Figure 2. Concordia diagram for zircons from Central Arizona and the Appalachians. The open squares represent the measured values for the lead/uranium ratios. In the enlarged inset, the solid dots correspond to the plot of these ratios corrected for the percentage of radon loss. The data show a relationship between discordance and percentage of radon loss, where the increase in the discordance correspond to an increase in the ^{222}Rn emanation.



	SAMPLE	DISCORDANCE %	DOSAGE (α/mg) x10^{15}	RADON LOSS %
1	A 240	2.8	2.57	0.17
2	A 334	5.5	1.83	0.68
3	A 255	11.3	0.99	0.83
4	A 362	13.4	6.08	0.96
5	A 229	15.6	3.35	1.53
6	A 24	20.1	6.97	1.38
7	A 335	24.2	3.36	1.28
8	A 73	25.3	8.67	2.18
9	A 66	28.7	7.42	1.54
10	A 25	35.0	8.78	2.06
11	A 169	45.7	8.40	4.78
12	A 176	72.2	11.30	4.45

Figure 3. Concordia diagram for the zircon concentrates from Finland. The data shown for discordance, alpha dosage and percent of radon loss strongly suggest a relationship between these parameters. The most discordant zircons correspond to those receiving high dose and large percentage of ^{222}Rn loss.

Zircons concentrates from the Minnesota River Valley are plotted in Figure 4. In this figure the very high radon loss of sample 373 (12.1%) will have a contribution relative to the discordance of the ^{206}Pb/^{238}U ratios of 19.5 % (Table 4) which is the largest correction for radon for the analyzed samples. In the same figure, sample 346 (fresh material) has almost concordant isotopic ratios and indeed the percentage of radon escape is very small. The data displayed in this figure clearly show that the most discordant samples correspond to those with the largest percentage of radon loss. It also strongly suggests a positive relationship between discordance, a dosage and radon loss, in which the most discordant samples correspond to those with high dose and largest emanation.



SAMPLE	□ DISCORDANCE %	DOSAGE (α/mg) x10^{15}	● RADON LOSS %
346	2.1	7.0	0.3
373	61.5	7.2	12.1

Figure 4. Concordia diagram for zircons from the Minnesota River valley. It shows the strong effect of the weathering on ^{222}Rn loss due to the ground water leaching (sample 373).

For all the above figures, the data shows that applying the calculated corrections and analyzing the results, the overall contributions of the radon loss to the ^{206}Pb/^{238}U discordance are as follows:

- to lower the ^{206}Pb/^{207}Pb ages
- to increase the slope of the chords
- displace the ^{206}Pb/^{238}U ratios vertically toward the concordia.

5. DISCUSSION

Other evidence does exist to support the hypothesis of the movement of intermediate members of the uranium series within a crystal. For example, reports of pleochroic haloes with rings assignable to unsupported polonium isotopes (20) are consistent with the mobilization and movement of polonium parents, including radon. It seems probable that a radiation-damage model similar to that described by Wasserburg (21) for changes in lead diffusion coefficients could also apply to radon emanation rates. Grain size is another important aspect to consider as it is known that radon emanation is an inverse function of grain size for grains larger than 0.5 mm in diameter (22). However, in this case, most of the zircon grains were about the same size.

The important effect of temperature on radon emanation is one of the most difficult to evaluate and practically impossible to correct for or to establish any compensation when analyzing geological samples. Annealing of the nuclear tracks within a mineral significantly reduces the emanation rates of radon in these minerals, suggesting that the tracks created by decay events serve as conduit pathways for the release of ^{222}Rn (23, 24).

For that it would be necessary to know the temperature to which a rock has been subjected (usually determined with large approximation by some characteristic mineral assemblage), as well as, the duration of any heating event in order to evaluate the state of radiation damage that is present (unit cell dimensions and broadening of X-rays reflection peaks may be used for zircons subjected to high dosages (19). Consequently, the dosages figures given were obtained using the age of formation of the minerals without regard to any possible thermal event.

Finally, it is relevant to recall that the percentage of radon escape as measured represents a maximum value if the radiation damage model is assumed. Thus, one can argue that the value for the radon correction should be an average of the initial emanation, when the mineral was formed, and the present value. The emanation at time zero should be small and coming mostly from the mineral surface. For a precise correction, two other factors must also be considered: the possible removal of uranium and its daughters or gain of uranium as well as temperature variations during the sample’s history. These factors are difficult to evaluate but would tend to reduce the radon escape. Because of these difficulties and the existence of such compensating mechanisms, the corrections proposed are based on present day escape rates.

5. CONCLUSIONS

a) Natural alpha radiation dose: The percentage of radon loss in fresh minerals, which retain the radiation damage produced since its formation, increases with increasing doses. However, a strict one-to-one proportionality between dose and emanation was not observed nor was it expected because of the influence of geological phenomenon like metamorphic events (temperature), exposure of the mineral to weathering and other factors such as radioactive disequilibrium, uranium and thorium distribution within the grain, damage saturation effects, grain geometry, etc. Samples with low uranium content hence subjected to low a dose, like sphenes, showed nearly concordant ratios. Their characteristic low radiation damage and self-annealing character (being resistant to radiation damage) results in low radon and lead mobility. It is here proposed that the combination of a large a dose with a low percent of radon loss is indicative of a recent thermal event.

b) Self-annealing: Minerals possessing natural annealing rates larger than their damage rates should exhibit very low radon loss and emanation rate, e.g. uraninite.

c) Discordance. There is a clear correlation between discordance, radiation damage and percent of radon leakage. This correlation is in agreement with the hypothesis that the emanation is an increasing function of radiation damage. In this research radon leakage was shown to directly account for 2.5 - 17% of the total ^{206}Pb/^{238}U discordance.

d) The measurement of the radon emanation characteristics of zircon concentrates that will be used for ^{206}Pb/^{238}U dating seems to be a useful technique for a quick assessment if a sample will be discordant or not. This assessment should be done on the very aliquot reserved for the isotopic dilution analyses and the radon emanation evaluated before attempting the tedious isotopic determinations. Low emanation (0.1 - 1.0%) would indicate a nearly concordant age, whereas high percentage of radon loss (1.5 - 5%) would be indicative of major discordance.

REFERENCES

1. Nier, H.O., "The isotopic constitution of radiogenic leads and the measurement of Geological Time", *Phys. Rev.*, **vol. 1,** p. 150-153, 1939.
2. Krishnaswami S. and Seidemann D. E. "Comparative study of ^{222}Rn, ^{40}Ar, ^{39}Ar and ^{37}Ar leakage from rocks and minerals: Implications for the role of nanopores in gas transport through natural silicates" Yale Univ., New Haven, CT, 1988
3. Ahrens, L. H., "The Convergent Lead Ages of the oldest Monazites and Uraninites (Rhodesia, Manitoba, Madagascar and Transvaal)", *Geoch. Cosm. Acta*, **vol. 7** p. 294 and **vol. 8**, p. 1-15, 1955
4 Wetheril, G.W., Kouvo, O., Tilton, G.R., and Gast, P.W.,"Age measurements on rocks from the Finnish pre-Cambrian", *Jour. Geol.*, **vol. 70**, no. 1, p. 74-88, 1962.
5. Doe, B.R., *Lead Isotopes*, Springer-Verlag, 1970.
6. Silver, L.T., "The use of cogenetic uranium lead isotope systems in zircons in geochronology". In Radioactive Dating, *Proceedings International Atomic Energy Agency Symposium*, Athens, p. 279-287, 1963 .

7. Silver, L.T., “The relation between radioactivity and discordance in zircons". *In Nuclear Geophysics*, Nat. Acad. Sciences - NRC publ. 1075, p. 34-42, 1963.

8. Silver, L.T. and Deutsch, S., “Uranium-lead isotopic variations in zircons, A case study”. *J. Geol*., **vol. 71**, no. 6, p. 721-758, 1963

9. Stern, T.W., Goldich, S.S., Newell, M.R, “Effects of weathering on the U-Pb ages of zircon from the Morton Gneiss, Minnesota”, *Earth, Plan. Sci. Let.,* 1, p. 369-371, 1966.

10 Barretto, P.M.C. “Emanation Characteristics of Terrestrial and Lunar Materials and the ^{222}Rn Loss Effect on the U-Pb System Discordance.” PhD Thesis, Rice University, 1973

11 Doe, B.R. and Pearson, R. D.,“U-Th-Pb Chronology of zircons from the St. Kevin Granite, Northern Sawatch Range, Colorado”. *Geol. Soc. Am. Bull*., 80, p. 2495, 1969.

12. Rankin, D.W., Stern, T.W., Reed, J.C., and Newell, M.F., “Zircon ages of felsic volcanic rocks in the upper Pre-Cambrian of the Blue Ridge”, *Appalachian Mountains. Science*, **vol. 166**, p. 741-744, 1969.

13. Goldich, S.S., Nier A.O., Baadsgaard, H., Hoffman, J.H. and Krueger, H., “The Precambrian Geology and Geochronology of Minnesota”. *Minnesota Geol. Survey Bull*., no. 41, p. 1961.

14. Goldich, S.S., Hedge, C.E., and Stern, T.W., “Age of Morton and Montevideo Gneisses and Related Rocks, Southwestern Minnesota”. *Geol. Soc. Am. Bull*., 81, p. 3671-3695, 1970

15. Kouvo, O., “Radioactive age of some Finnish preCambrian minerals”. *Comm. Geol. Finland Bull*. No. 182, p. 1-70, 1958.

16. Kouvo, O. and Tilton, G.R., “Mineral ages from the Finnish pre-Cambrian”. *Jour. Geol*., **vol. 74**, no. 4, p. 421-442, 1966.

17. Neuvonen, K.J., “Paleomagnetism of the dike systems in Finland v. remanent magnetization of the Ava intrusives”. *Geol. Soc. Finland Bull*. No. 42, p. 101-107, The addendum, 1970.

18. Adams, J.A.S., “Laboratory gamma-ray spectrometer for geochemical studies”. In Adams and Lowder, Editors: *The Natural Radiation Environment*, Chicago Press, p. 485-497, 1964.

19. Holland, H.D. and Gottfried, D., “The Effect of Nuclear Radiation on the Structure of Zircon”. *Acta Cryst*, 8, p. 291-300, 1955.

20. Gentry, R.V., “Radiohalos: Some unique lead isotope ratios and unknown alpha radioactivity”. *Science*, **vol. 173**, p. 727-730, 1971.

21. Wasserburg, G.J., "Diffusion processes in lead-uranium systems”, Jour. Goop. Res**., vol. 68,** no. 16, p. 4823-4846, 1963.

22. Markkanen M. and. Arvela H. “Radon Emanation from Soils” Radiation Protection Dosimetry", **Vol. 45,** p. 269-27, 1992)

23. Barretto P. M. C., Clark, R. B., Adams, J. A. S.: Physical characteristics of radon-222 emanation from rocks, soils and minerals: Its relation to temperature and alpha dose, "The Natural Radiation Environment" (II), CONF-720805 P1, 731 (1974).

24. .Graver E. and Baseman M. – “Effects of heating on the emanation rates of radon-222 from a suite of natural minerals”, *Appl. Radiation.* 61 (6), p.1477-85, 2004