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Abstract

Natural pyrochlore and zirconolite undergo a crystalline-aperiodic transformation caused by alpha-decay of ^{232}Th and ^{238}U at dose levels between 2×10^{14} and 3×10^{17} a/mg. The principal effects of the transformation are volume expansion and microfracturing, providing potential pathways for fluids. Geochemical alteration of the minerals may occur under hydrothermal conditions or in low temperature, near surface environments, but Th and U usually remain immobile and can be retained for time scales up to 10⁹ years. However, the Th-U isotope systematics of a zirconolite-bearing vein and dolomite host rock may provide evidence for disequilibrium between ^{230}Th , ^{234}U and ^{238}U .

Disciplines

Earth Sciences | Environmental Sciences | Physical Sciences and Mathematics

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Retention of Actinides in Natural Pyrochlores and Zirconolites

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*Actinides / Geochemical alteration / Lead loss /
Pyrochlore / Radiation damage / Zirconolite*

Summary

Natural pyrochlore and zirconolite undergo a crystalline-aperiodic transformation caused by alpha-decay of ^{232}Th and ^{238}U at dose levels between 2×10^{14} and 3×10^{17} α/mg . The principal effects of the transformation are volume expansion and microfracturing, providing potential pathways for fluids. Geochemical alteration of the minerals may occur under hydrothermal conditions or in low temperature, near surface environments, but Th and U usually remain immobile and can be retained for time scales up to 10^9 years. However, the Th-U isotope systematics of a zirconolite-bearing vein and dolomite host rock may provide evidence for disequilibrium between ^{230}Th , ^{234}U and ^{238}U .

1. Introduction

Natural analogue minerals provide a means of assessing the *long-term* performance of actinide host phases in high-level nuclear waste forms including Synroc and tailored ceramics [1, 2]. Mineral analogues are available that range in age from less than 10^6 to greater than 10^9 years and contain U and Th in trace to major proportions, resulting in alpha-decay doses of 10^{13} to 10^{18} α/mg . After crystallization in their host rocks, actinide-bearing minerals may be exposed to hydrothermal fluids at elevated temperature and pressure or relatively low temperature ground waters in near surface environments [3, 4]. Natural analogue mineral phases are suitable for the study of crystal chemistry, radiation damage effects caused by alpha-decay of ^{232}Th and ^{238}U , and geochemical alteration mechanisms.

Research conducted using natural samples provides an effective complement to laboratory-based studies of radiation damage and short-term studies of durability in aqueous solutions. In this paper, we illustrate the use of natural analogues through an investigation of radiation damage and geochemical alteration effects in the minerals pyrochlore (ideally $\text{NaCaNb}_2\text{O}_6\text{F}$) and zirconolite (ideally $\text{CaZrTi}_2\text{O}_7$) with particular reference to the behavior of actinides

and their daughter products. This work is part of a multidisciplinary study of mineral analogues and incorporates data from several analytical techniques including alpha spectrometry, analytical electron microscopy (AEM), electron probe microanalysis (EPMA), inductively coupled plasma mass spectroscopy (ICP/MS), and scanning electron microscopy and microanalysis (SEM-EDS).

2. Experimental

Small chips of zirconolite and pyrochlore were ground in acetone and deposited onto holey-carbon filmed, 3 mm copper grids for AEM work. Two additional crystals of zirconolite from Adamello, Italy, were prepared by ion beam thinning with Ar^+ at 4 keV. Samples were examined using a JEOL 2000FX transmission electron microscope operated at 200 keV. Analytical data for 25 elements were collected using a Tracor-Northern 5450 EDS system equipped with a beryllium window detector following recently developed procedures [5].

Secondary and backscattered electron images were obtained from polished sections using a JEOL 840 SEM operated at 15 keV. Selected points of interest were analyzed using a Tracor-Northern 5450 EDS system equipped with a standard beryllium window detector. Quantitative chemical analyses for up to 31 elements were performed using JEOL 733, Cambridge Microscan 9, and Cameca SX-50 microanalyzers according to established procedures [4, 6].

Samples of a zirconolite-bearing vein and dolomite host rock from Adamello, Italy, were ground to a fine powder then successively leached with 0.3 M HCl and 9 M HCl [7, 8]. The treatment with 0.3 M HCl was carried out at 80°C for 30 minutes. The sample was then treated with 9 M HCl for 6 hours at room temperature. Finally, the residue was digested using aqua-regia followed by HF/HClO_4 . The vein sample required chemical fusion in a mixture of borax and sodium carbonate for complete dissolution. The three fractions (0.3 M HCl, 9 M HCl, and residue) and bulk sample were analyzed by alpha spectrometry for their

uranium and thorium content after the addition of ^{236}U and ^{229}Th tracers.

3. Radiation damage effects

The combined analytical data of this study give maximum concentrations of 9 wt% ThO_2 and 26 wt% UO_2 in the pyrochlore samples and 22 wt% ThO_2 and 9 wt% UO_2 in the zirconolites. The alpha-decay dose of both minerals can be calculated from the Th and U contents determined by AEM using the equation

$$D = 8 N_{238} (e^{\lambda_{238}t} - 1) + 6 N_{232} (e^{\lambda_{232}t} - 1) \quad (1)$$

where D is the dose in α/mg , t is the geologic age, N_{238} and N_{232} are the present number of atoms per mg of ^{238}U and ^{232}Th , and λ_{238} and λ_{232} are the decay constants [9]. Using Equation (1), alpha-decay doses of 5×10^{13} to 8×10^{17} α/mg and 1×10^{14} to 3×10^{17} α/mg were obtained for the pyrochlores and zirconolites, respectively.

AEM results show that pyrochlore and zirconolite undergo systematic structural changes at dose levels between 2×10^{14} and 3×10^{17} α/mg . Electron diffraction patterns, bright field, dark field, and high resolution images are consistent with a model of radiation damage involving accumulation and overlap of alpha-recoil collision cascades to produce aperiodic (amorphous) domains. Aperiodic domains continue to accumulate as a function of dose until all crystallinity is lost. An important physical result of the radiation damage process is volume expansion, causing microfracturing in coarse grained ($>100 \mu\text{m}$) samples.

Figure 1 shows that the crystalline-aperiodic transformation increases as a function of age, providing evidence for annealing of alpha-recoil collision cascades back to the original crystalline structure [9]. The data were analyzed using the equation

$$D_i, D_f = D_0 e^{tB} \quad (2)$$

where D_i is the initial dose defined by the first appearance of aperiodic domains, D_f is the final dose defined by loss of all crystallinity, D_0 is the intercept dose at $t = 0$, t is the geologic age, and B is a dose rate constant. The results yielded rate constants of 1.7 – $1.8 \times 10^{-9} \text{ yr}^{-1}$ for pyrochlore (Fig. 1 a) and 0.97 – $1.0 \times 10^{-9} \text{ yr}^{-1}$ for zirconolite (Fig. 1 b). If we include an additional data point for D_f derived from EPMA analyses of Lunar zirconolite [10], a value of $B = 0.38 \times 10^{-9} \text{ yr}^{-1}$ is obtained. Calculated D_0 values indicate that the critical dose for amorphization given by D_f is close to 10^{16} α/mg for both minerals.

4. Geochemical alteration effects

Examples of the geochemical alteration of pyrochlore and zirconolite are shown in Figure 2. Both specimens are heavily radiation damaged and microfractured, having sustained alpha-decay doses in excess of 10^{17} α/mg . The backscattered electron images reveal

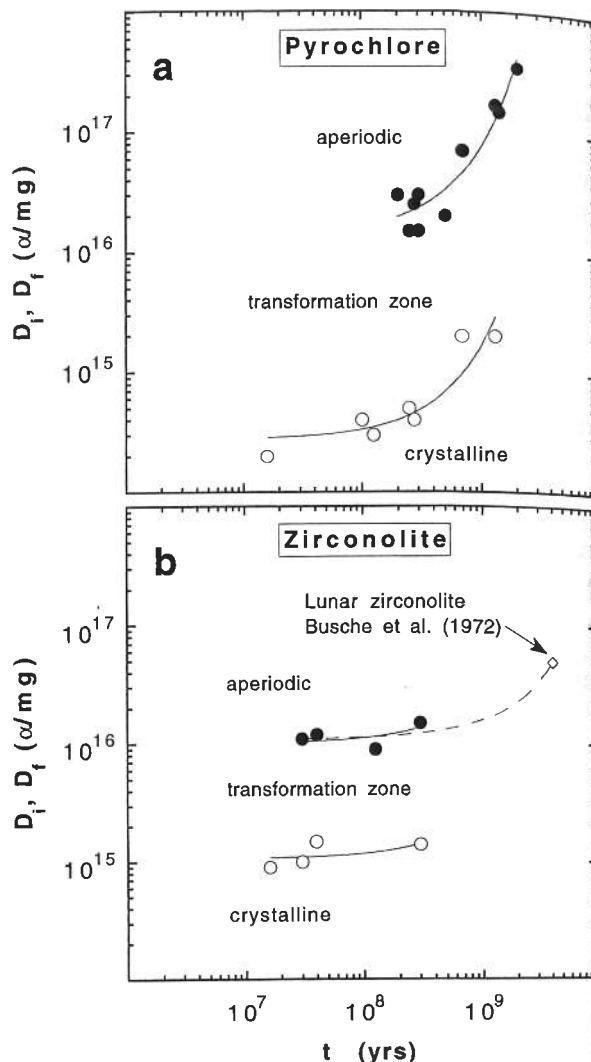


Fig. 1. Plots of alpha-decay dose in α/mg versus geologic age showing data which define the beginning (initial dose, D_i) and end (final dose, D_f) of the crystalline-aperiodic transformation for a) pyrochlore and b) zirconolite.

chemical alteration as areas of darker gray contrast, indicating a lower average atomic number than the associated unaltered areas. Chemical alteration typically follows available pathways such as fractures and voids, but may be strongly diffusion controlled at elevated temperature and pressure [4].

Table 1 gives a summary of the geochemical alteration characterized by EPMA and SEM-EDS in crystalline, partially damaged, and aperiodic pyrochlores under conditions ranging from hydrothermal systems at elevated pressure and temperature to low temperature, near surface environments. The alteration is broadly classified as Na-Ca ion exchange, Na leaching, and Ca leaching. The two latter mechanisms involve hydration (up to 10–15 wt% H_2O) and in specific cases may be accompanied by ion exchange for K, Sr, and Ba. Most importantly, the amounts of Th and U remain relatively constant in all three types of alteration, as do the major framework cations of the pyrochlore structure, Nb, Ta, and Ti.

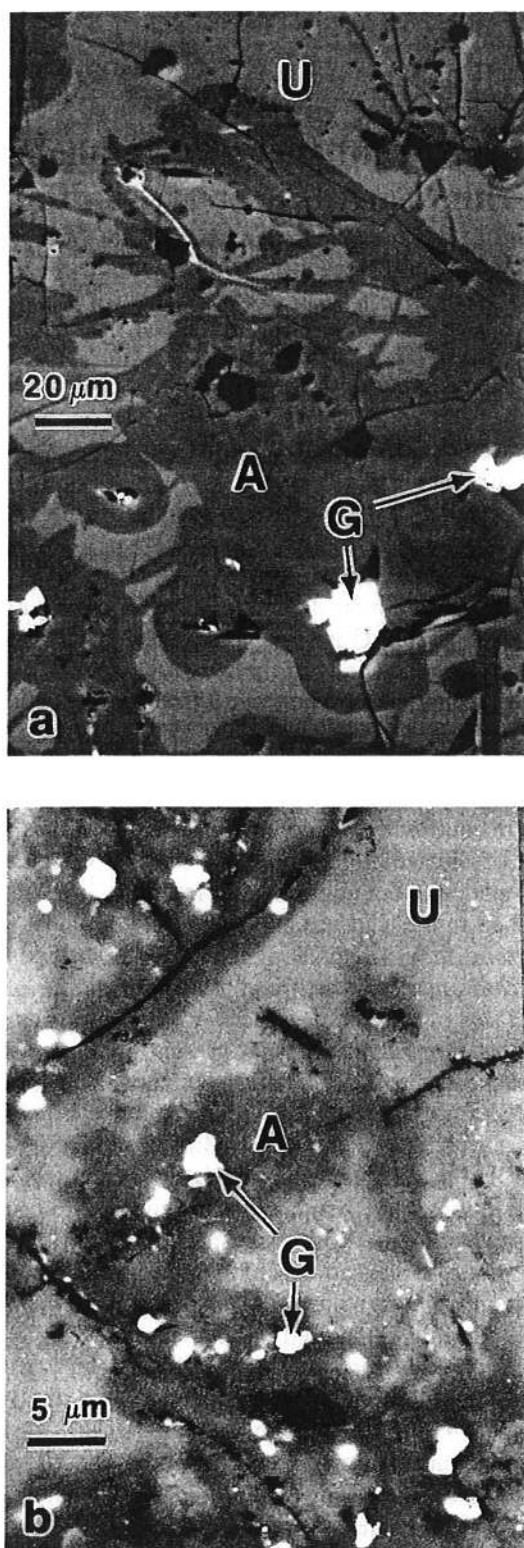


Fig. 2. Backscattered SEM images showing alteration of radiation damaged samples of a) pyrochlore from Bancroft, Ontario, Canada (age = 1.0×10^9 yr, dose = 8×10^{17} α /mg) and b) zirconolite from Phalaborwa, South Africa (age = 2.5×10^9 yr, dose = 3×10^{17} α /mg). U = unaltered area, A = altered area, and G = galena precipitate.

Apart from one example showing corrosion at high temperature (Table 1), alteration of zirconolite was found only in 2.5×10^9 year old specimens from Phal-

aborwa, South Africa. AEM work on the sample shown in Figure 2 b indicates that most of the zirconolite has been rendered aperiodic by alpha-recoil damage at a dose level of $2-3 \times 10^{17}$ α /mg. EPMA analyses demonstrate that the major chemical effects of alteration are substitution of Si for Ti and Fe coupled with leaching of Ca producing vacancies at the Ca-site. Minor increases in Zr and Ce were also observed in the altered areas, together with low analytical totals suggesting the presence of 6–12 wt% H₂O. The analyses also show that Th and U remained relatively immobile during alteration, similar to the results found for pyrochlore.

The behavior of Pb was investigated by comparing the Pb content measured by EPMA with the expected amount of radiogenic Pb* from the decay of ^{238}U and ^{232}Th calculated from the equation

$$\text{Pb}^* = \text{U} (e^{\lambda_{238}t} - 1) + \text{Th} (e^{\lambda_{232}t} - 1) \quad (3)$$

using the measured amounts of Th and U. In most pyrochlores with detectable quantities of Pb the amount is sufficient to account for all of the Pb* calculated from Equation (3). In a few cases, minor losses or gains in Pb occur as a direct result of alteration (Table 1). In some of the older radiation damaged and microfractured samples, the behavior of Pb is unrelated to the observed alteration. Data for a suite of 1×10^9 year old pyrochlores from Canada are shown in Figure 3 a. The results indicate that major amounts of radiogenic Pb have been lost from *both unaltered and altered areas* of the samples, consistent with a model of long-term Pb diffusion assisted by radiation damage and microfracturing [4, 11]. Part of the radiogenic Pb may be stored in galena (PbS) precipitates which formed in the presence of a S-rich fluid phase (Fig. 2 a).

Similar data shown in Figure 3 b indicate loss of radiogenic Pb from the unaltered and altered areas of zirconolite from Phalaborwa. ICP/MS analyses of the sample give bulk Th and U contents equivalent to 5.5 wt% ThO₂ and 1.9 wt% UO₂, in excellent agreement with EPMA. A bulk PbO content of 2.2 wt% was also determined, whereas only 1.34 wt% PbO is expected from the decay of Th and U, suggesting that some Pb may have been added to the system via transport in a Si- and S-rich ground water or fluid phase and precipitated as galena (Fig. 2 b).

5. Th-U isotope systematics

Alpha spectrometry results for the zirconolite-bearing vein sample from Adamello, Italy give total concentrations of 95 ppm Th and 36 ppm U. The bulk Th/U ratio of 2.6 is in good agreement with the compositions of the vein minerals. Zirconolite is a trace mineral in the vein sample, but AEM and EPMA analyses demonstrate that it contains up to 22 wt% ThO₂ and 9 wt% UO₂. Traces of Th and U are also found in apatite (122 ppm Th, 30 ppm U) and titanite (418 ppm Th,

Table 1. Summary of geochemical alteration effects in natural pyrochlore and zirconolite

Estimated conditions	Mechanism	Elements lost*	Elements gained*
250–550°C, 1–4 kb <300°C, <2 kb? <150°C, <1 kb?	Na-Ca exchange	Pyrochlore Fa, F, (OH, Pb)	Ca, O, (Sr, Mn, Fe)
	Na leaching	Na, F, (Ca, O)	H ₂ O, Fe, Sr, (Mn, REEs, Ba, Pb)
	Ca leaching	Ca, O, (Na, F)	H ₂ O, K, Sr, Ba, Pb, (Mn, Fe, REEs, OH)
unknown 500–600°C, 2 kb [12]	Ti-Si exchange dissolution-reprecipitation	Zirconolite Ti, Fe, Ca Th, U, Mg, Fe	Si, (Zr, REEs) Ca, Ti

* Elements in parentheses exhibit minor changes in some samples.

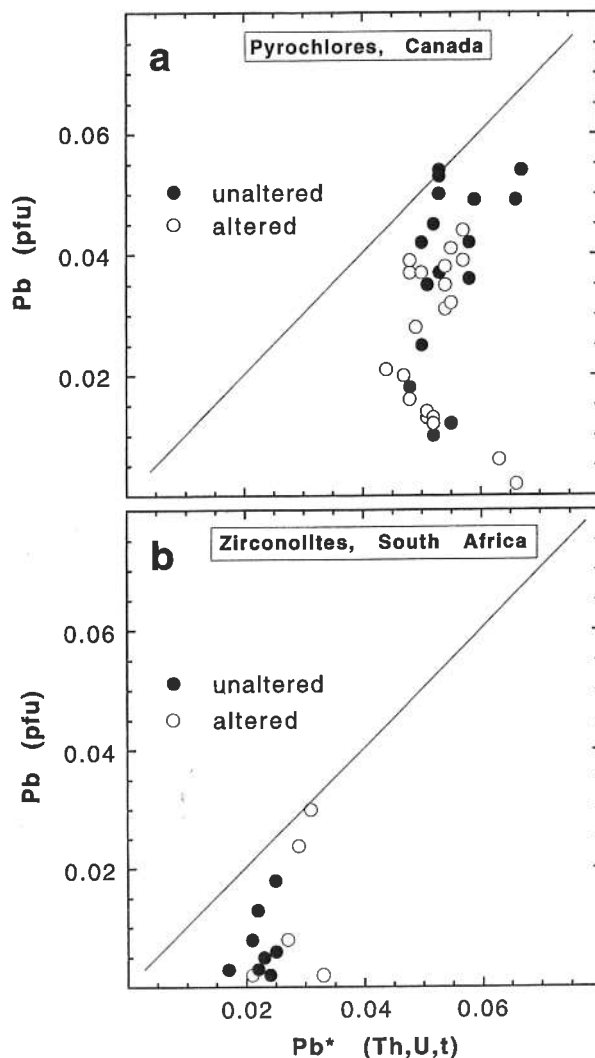


Fig. 3. EPMA data showing the measured Pb content plotted versus Pb*, the expected amount of radiogenic Pb from the decay of Th and U over time, for radiation damaged samples of a) pyrochlore from Canada (age = 1.0×10^9 yr, dose = $5-8 \times 10^{17}$ a/mg) and b) zirconolite from South Africa (age = 2.5×10^9 yr, dose = $2-3 \times 10^{17}$ a/mg).

183 ppm U) which occur as accessory minerals in the sample [12]. AEM results also show that the zirconolite crystals range from partially damaged to fully aperiodic at alpha-decay doses of $0.3-1.1 \times 10^{16}$ a/mg. The dolomite host rock was found to contain only

0.5 ppm Th and 3.2 ppm U, values typical of sedimentary carbonate rocks.

The samples were treated sequentially with HCl in order to examine the distribution of Th and U isotopes between acid soluble and insoluble fractions. Results listed in Table 2 indicate a more or less uniform distribution of Th and U isotopes between the acid soluble and insoluble fractions of the zirconolite-bearing vein. There is a minor depletion of all isotopes in the 0.3 M HCl fraction, a minor enrichment in the 9 M HCl fraction, and only a slight enrichment in the residue. Approximately 83–91% of the Th and U occur in the acid residue which accounts for 79.4% of the total mass of the sample. In contrast, ^{230}Th , ^{234}U , and ^{238}U are depleted in both acid soluble fractions and strongly enriched in the acid residue of the dolomite host rock. Approximately 43–65% of the U-series isotopes occur in the residue which comprises only 0.8% of the total mass of the sample. Interestingly, the results suggest that most of the ^{232}Th is present as a trace component of the soluble carbonate minerals in the dolomite host rock.

Data in Table 3 show that all of the $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios in the bulk sample, acid soluble fractions, and residue of the zirconolite-bearing vein and dolomite host rock are significantly greater than unity. Enhanced leaching of ^{230}Th by the HCl treatments may represent a chemical effect; however, this is not fully supported by the data for $^{232}\text{Th}/^{238}\text{U}$ in the zirconolite-bearing vein for which values of 0.57 ± 0.07 and 1.26 ± 0.13 were obtained for the 0.3 M HCl and 9 M HCl treatments, respectively. Furthermore, the mass of material dissolved by the HCl treatments (see Table 2) indicates that the activity ratios relate mainly to the distribution of isotopes within the acid soluble and insoluble phases of the samples as opposed to a chemical effect arising from near surface sites.

All of the $^{234}\text{U}/^{238}\text{U}$ activity ratios listed in Table 3 are within two standard deviations of the secular equilibrium value of one except for the 0.3 M HCl treatment of the zirconolite-bearing vein for which a value of 1.59 ± 0.16 was obtained. This result could indicate a preferential leaching of ^{234}U relative to ^{238}U , but the percentage of the total activity of U in the acid soluble fractions are quite low and have relatively large errors

Table 2. Distribution of Th and U isotopes between the acid soluble and acid resistant fractions of a zirconolite-bearing vein and dolomite host rock from Adamello, Italy

Sample/treatment	Percentage of total mass	Percentage of total activity			
		^{230}Th	^{234}U	^{238}U	^{232}Th
Zirconolite-bearing vein					
0.3 M HCl	16.9	$4.7 \pm 0.3^*$	5.1 ± 0.3	3.1 ± 0.3	2.0 ± 0.2
9 M HCl	3.7	11.4 ± 0.7	5.8 ± 0.5	6.7 ± 0.5	9.6 ± 0.8
Residue	79.4	83.9 ± 3.0	89.1 ± 3.1	90.2 ± 3.0	88.4 ± 3.5
Dolomite host rock					
0.3 M HCl	35.0	23.6 ± 2.2	9.8 ± 1.4	11.8 ± 1.4	49.4 ± 11.4
9 M HCl	64.2	32.6 ± 1.9	28.5 ± 2.3	23.7 ± 2.4	38.0 ± 7.6
Residue	0.8	43.8 ± 1.1	61.7 ± 1.4	64.5 ± 1.4	12.6 ± 1.9

* 1 σ standard deviations.**Table 3.** Activity ratios of Th and U isotopes in bulk samples and sequential HCl treatments of a zirconolite-bearing vein and dolomite host rock from Adamello, Italy

Sample/treatment	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{232}\text{Th}/^{238}\text{U}$
Zirconolite-bearing vein				
Bulk sample	$1.36 \pm 0.08^*$	1.33 ± 0.08	0.98 ± 0.04	0.88 ± 0.06
0.3 M HCl	1.34 ± 0.11	2.14 ± 0.21	1.59 ± 0.16	0.57 ± 0.07
9 M HCl	2.86 ± 0.29	2.44 ± 0.24	0.86 ± 0.10	1.26 ± 0.13
Residue	1.38 ± 0.07	1.33 ± 0.07	0.97 ± 0.05	0.86 ± 0.04
Dolomite host rock				
Bulk sample	1.21 ± 0.08	1.22 ± 0.06	1.01 ± 0.04	0.05 ± 0.01
0.3 M HCl	4.14 ± 0.62	3.48 ± 0.53	0.84 ± 0.16	0.52 ± 0.14
9 M HCl	1.97 ± 0.23	2.40 ± 0.27	1.22 ± 0.16	0.20 ± 0.04
Residue	1.22 ± 0.04	1.18 ± 0.04	0.97 ± 0.03	0.024 ± 0.003

* 1 σ standard deviations.

(Table 2). Consequently, the $^{234}\text{U}/^{238}\text{U}$ ratios in the acid soluble fractions exhibit considerable variability above and below unity, suggesting that the above result could be a statistical anomaly.

6. Discussion

This investigation confirms that natural pyrochlore and zirconolite undergo a crystalline-aperiodic structural transformation resulting from the radioactive decay of Th and U [9, 13, 14]. For relatively young samples, the transformation occurs at alpha-decay doses between 10^{14} and 10^{16} α/mg , consistent with laboratory studies of synthetic pyrochlore and zirconolite doped with ^{238}Pu or ^{244}Cm [15, 16]. Dose rate effects are significant only for samples older than $\sim 10^8$ years, where there is evidence for annealing of alpha-recoil collision cascades back to the original crystalline mineral structure with estimated dose rate constants of $0.3 - 2 \times 10^{-9}$ yr^{-1} .

For time periods less than 10^8 years, the overall results indicate that pyrochlore and zirconolite in nuclear waste ceramics will be rendered aperiodic at an alpha-decay dose of $\sim 10^{16}$ α/mg at ambient temperatures. In Synroc, for example, we estimate that zirconolite will sustain this dose in $10^4 - 10^6$ years, de-

pending primarily on waste loading and actinide element partitioning. The principal effects of alpha-decay damage are volume expansion and microfracturing, providing potential pathways for fluids; however, the extent to which microfracturing occurs is a function of grain size. Fine-grained ($< 1 \mu\text{m}$) nuclear waste ceramics are designed to accommodate volume expansion without significant microfracturing.

Hydrothermal alteration of pyrochlore and zirconolite may occur at temperatures well above those expected for nuclear waste repositories, but may provide useful information on stability limits as a function of temperature and fluid composition. Furthermore, the fluid compositions can point to specific elements to include in laboratory dissolution studies, e. g., F and P [4, 12]. The near surface conditions represent temperatures below $\sim 150^\circ\text{C}$ and ground water compositions which are readily applicable to the prediction of waste form performance.

Natural pyrochlores are clearly susceptible to chemical alteration by ion exchange under hydrothermal conditions and by leaching and hydration in near surface environments. The effects of alteration have been observed in many crystalline, partially damaged, and aperiodic pyrochlore samples. Except for one example of corrosion at high temperature ($500 - 600^\circ\text{C}$),

alteration of zirconolite was observed only in 2.5×10^9 year old, radiation damaged samples from a single locality. The weight of evidence indicates that zirconolite is generally resistant to alteration, consistent with previous U-Th-Pb isotopic studies of natural samples [17] and laboratory dissolution experiments on Synroc and its constituent phases [18, 19]. Both pyrochlore and zirconolite are capable of immobilizing Th and U during specific alteration events and for time scales up to 10^9 years.

The Th and U isotope systematics of a zirconolite-bearing vein and dolomite host rock may provide evidence for isotopic disequilibrium between ^{230}Th , ^{234}U , and ^{238}U . Elevated $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios in bulk samples and acid residues possibly indicate a recent loss of U. A potential mechanism for U loss is partial oxidation of U^{4+} to the more soluble U^{6+} ion followed by leaching and removal from the system [20]. In this scenario, the abundance of dolomite and calcite in the rocks provides a readily available source of carbonate ions to aid in the leaching and transport of U.

Other possible mechanisms related to the alpha-decay process include ejection of the recoil atom into an adjacent phase of higher solubility [8] and location of the recoil nucleus within a damage "track" or interstitial site of higher chemical reactivity than the surrounding matrix [21–23]. These mechanisms are less consistent with the data in view of the failure to observe significantly elevated $^{234}\text{U}/^{238}\text{U}$ activity ratios. Additional potentially leachable sites for recoil nuclei largely overlooked in previous studies are microfractures and grain boundaries. A more comprehensive evaluation of the potential mechanisms for isotopic disequilibria in the Adamello rocks will be presented following the analysis and detailed mineralogical characterization of additional samples.

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