

October 1, 1985

#10

DOE/ER/45099-T1

**THERMAL RECRYSTALLIZATION OF
ALPHA-RECOIL DAMAGED MINERALS OF THE PYROCHLORE
STRUCTURE TYPE**

By

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ABSTRACT

Thermal recrystallization effects (heat of recrystallization and identification of phases formed), have been determined for naturally occurring members of the pyrochlore group which have received alpha doses of up to 4×10^{16} alphas/mg. The heats of recrystallization, E_r , range from 125 to 210 J/g. Release of energy decreases as a function of crystallinity (estimated on the basis of the intensity of x-ray diffraction maxima), with the fully-metamict samples approaching 210 J/g. Lower measured values (40-125 J/g) are the result of alteration of the pyrochlores. Other metamict, complex oxides with stoichiometries of ABO_4 and AB_2O_6 have lower heats of recrystallization (40-85 J/g), and are easily distinguished from pyrochlore group minerals. Activation energies of recrystallization, E_a , range between values of 0.29 to 0.97 eV, less than those measured for Pu-doped, synthetic zirconolites.

1. INTRODUCTION

Important among the potential host phases for actinides in polycrystalline nuclear waste forms are pyrochlore structure types [1-3] and the structural derivatives, e.g. zirconolite in SYNROC [4-7]. The long-term response of these crystalline phases to alpha and alpha-recoil damage (i.e. degradation of mechanical properties, increased leach rates and stored energy) are among the principal criteria in the evaluation of waste forms. Radiation effects have been studied in accelerated experiments in which synthetic pyrochlore and zirconolite have been doped

with short-lived radionuclides (^{238}Pu and ^{244}Cm) and have experienced alpha-event doses of up to 10^{16} alphas/mg ($= 10^{26}$ alphas/m 3) [8-11]. We present the results of a study of the recrystallization of alpha-recoil damaged minerals of the pyrochlore group which have experienced doses of up to 4×10^{16} alphas/mg ($= 10^{26}$ alphas/m 3) due to the decay of constituent ^{238}U , ^{235}U , ^{232}Th and radionuclides in their decay series. We should emphasize that in the case of fully-damaged, aperiodic ("metamict") materials, the energy released on heating is due to recrystallization, and not due to the thermal annealing of isolated defects or defect aggregates in an otherwise periodic structure. Comparison of these natural analogues to synthetic waste form phases can be used to evaluate dose rate effects (which vary by as much seven orders of magnitude) and to confirm the long-term extrapolation of the behaviour of the synthetic phases.

Pyrochlore group minerals have the general formula $A_{2-2m}B_2X_6Y_{1-n}p\text{H}_2\text{O}$, where $m = 0.0-1.7$, $n = 0.0-1.0$, and $p = 0.0-2.5$. The A-site contains Ca, Na, U, Th, and rare earth elements as major cations and minor Y, Ba, Sr, Pb, Bi, Sb, Mn, and Fe^{2+} . The major B-site cations include Nb, Ta, and Ti which are used to define the mineralogical subgroups: pyrochlore, Nb-rich; microlite, Ta-rich; betafite, Ti-rich [12]. Minor B-site cations include Zr, Sn, and Fe^{3+} . This study presents data for members of all three mineralogical subgroups. The principal anions are $X = \text{oxygen}$ and $Y = \text{O, OH, F}$. Minerals of the pyrochlore group occur as primary phases in carbonatites and granitic pegmatites. They are often subjected to hydrothermal (ca. 250-500°C) or weathering (surface temperatures) alteration. The timing of alteration relative to radiation effects is based

on textural observations [13]. Annealing studies require careful selection of well-characterized material with minimum evidence for alteration.

2. EXPERIMENTAL TECHNIQUES

2.1. Differential Thermal Analysis (DTA)

A Perkin-Elmer DTA-1700 was used to analyze samples weighing from 60 to 140 mg. Samples were heated to 1200°C at a rate of 10°C per minute. All runs were completed in an atmosphere of argon flowing at a rate of 40 ml per minute. The instrument was operated in the differential scanning calorimetry (DSC) mode and calibrated with pure metal standards. In order to evaluate stored energy and activation energy, the exothermic peak areas for three samples (*153, *168 and *204) were integrated using a planimeter at intervals ranging from 15° to 80°C.

2.2. Thermogravimetric Analysis (TGA)

A DuPont 951 TGA and 990 recorder were used to monitor weight change as a function of temperature. Samples weighing from 10 to 20 mg were heated in air to 1000°C at a rate of 10°C per minute. The instrument was calibrated using calcium oxalate. The calibration was checked by reweighing each sample after cooling to room temperature and calculating the percentage of weight loss. The calculated and measured values of weight loss agreed to within ± 5 percent.

2.3. Electron Microprobe Analysis (EMPA)

Chemical analyses were obtained using an automated JEOL 733 electron microprobe operated at an accelerating voltage of 15 keV and a sample current of 20 nA. Standards included natural samples of microlite (F, Na, Ca, Nb, Ta), manganotantalite (Mn), stibiotantalite (Sb, Bi), benitoite (Ti, Ba), olivine (Fe), cerussite (Pb), pollucite (Cs) and cassiterite (Sn). Synthetic crystals of SrMoO_4 , ZrSiO_4 , CaWO_4 , YPO_4 , REEPO_4 , ThSiO_4 , and UO_2 were used for Sr, Zr, W, Y, REE, Th and U. Each element was counted until a standard deviation of 1.0 percent was reached, up to a maximum counting time of 30 seconds. To minimize volatilization induced by electron beam heating, all analyses were performed with a beam diameter of 10 μm . The data were corrected for drift, deadtime, absorption, fluorescence and atomic number effects using a theoretical (ZAF) procedure based on the program MAGIC IV [14].

2.4. X-Ray Diffraction (XRD)

Samples were scanned from 20° to 80° two-theta at a rate of 2° two-theta per minute using an Scintag automated diffractometer and CuK_{α} radiation ($\lambda = 0.5418 \text{ nm}$). The degree of crystallinity was judged by reference to highly crystalline pyrochlore reference samples. Samples were run again following TGA/DTA runs in order to identify recrystallization products. Lattice constants were refined using the least squares program CELLREF [15].

3. SAMPLE DESCRIPTION

Most of the specimens examined are metamict. Their x-ray diffraction patterns display two diffuse bands corresponding to "equivalent" d-spacings of 0.30 and 0.18 nm [21]. Pyrochlore #230 was found to be moderately crystalline with $a_0 = 1.0419(1)$ nm (standard deviation in parentheses refers to the last decimal place). Microlites #147 and #201 are highly crystalline with cell edges of 1.0429(1) and 1.0428(1) nm, respectively. Betafite #155 is the most severely altered sample. Virtually no Ca, Na or F are present. Areas of relict betafite are surrounded by patches and spherulites of a Ti-rich phase and a U-rich phase. Both phases also occur in veinlets which crosscut the sample [13]. Sample #186 has broken down into a fine-grained assemblage of betafite plus a Nb-Ti-Fe rich oxide (rutile-like phase), probably as a result of alteration. Alteration in microlite #080 is confined to microfractures where leaching of Ca, Na, and F took place. Microscopic observations indicate that pyrochlores #214 and #251 also show significant alteration effects, mainly along narrow fractures. Samples #153, #168, and #204 were selected for stored energy and activation energy measurements. They are described in further detail below and electron microprobe analyses are given in Table 1.

Microlite #153 is from the microcline-spodumene zone of the Harding pegmatite, Taos Co., New Mexico [16]. The average composition given in Table 1 is close to that for unaltered material. Both primary (hydrothermal) and secondary (weathering) types of alteration are present [13,16]. Marginal primary alteration is characterized by increased Ca, Mn,

and Fe and decreased Na at the A-site. Rare secondary alteration is confined to microfractures. Leaching of Ca, Na, and F and extensive hydration (up to ~12 wt. % H₂O) are characteristic of these areas. X-ray diffraction work and transmission electron microscopy show that the sample is metamict [16].

Microlite *168 is from the blocky-albite unit of the Rutherford pegmatite, Amelia Co., Virginia. This specimen appears to be relatively unaltered, although secondary alteration has been reported in another sample (*080) from this locality [13]. The x-ray diffraction pattern shows weak (222), (440) and (622) reflections indicative of slight crystallinity.

Betafite *204 is from the Silver Crater mine near Bancroft, Ontario, Canada. The specimen is metamict, consisting of relatively unaltered betafite (3-4 wt. % H₂O) with increased hydration along fractures and voids (10-12 wt. % H₂O). The average composition and alteration effects are similar to sample *083 from the same locality [13,17].

4. EXPERIMENTAL RESULTS

Results of DTA and TGA on the pyrochlore group minerals are given in Table 2. One sample of AB₂O₆ and five samples of AB₂O₆ type, metamict, complex, Nb-Ta-Ti oxides are included for comparison. The metamict betafites and pyrochlores show exotherms ranging from 650° to 700°C, often accompanied by a smaller exotherm near 425°C. An exception is pyrochlore *214, which shows a strong exotherm at 410°C and a weaker peak at 620°C. Moderately crystalline pyrochlore *230 has weak

exotherms at 430° and 570°C. Metamict and slightly crystalline microlites have their most intense exotherms at 460°-570°C, with weaker peaks near 600° and 740°C. Crystalline microlites #147 and #201 show weak exotherms at 545°C and 425°C, respectively. In general, the results are consistent with previous work [17,18]. With the exception of samarskite #250, the pyrochlore group minerals can be distinguished from metamict ABO_4 and AB_2O_6 oxides using DTA.

Endotherms were consistently detected at 140°-190°C and 470°-510°C, corresponding to intervals of maximum weight loss recorded by TGA. Weight loss measurements indicate that H_2O content varies dramatically, ranging from 0.1 to 11.3 weight percent. The metamict and altered samples tend to have the highest H_2O contents. None of the pyrochlore group minerals showed a gain in weight which might be attributed to oxidation of Fe or U. The DTA traces of four samples are shown in Figure 1. The broad exotherm of microlite #153 (Fig. 1a) is unusual. Most of the pyrochlore group minerals give sharp exothermic peaks on heating (Fig. 1b,c,d). Multiple peaks are typical of the metamict and slightly crystalline microlites #168 (Fig. 1b) and #080 from Amelia, Virginia.

Exothermic peak areas were estimated for the full data set (Table 2) and converted to units of J/g based on sample weights. For the pyrochlore group, recrystallization energy values, E_r , ranged from 4 to 200 J/g. Crystalline microlites released 4 to 13 J/g. The moderately crystalline pyrochlore #230 had an energy release of 34 J/g. Metamict samples released from 20 to 200 J/g of energy. Values ranging from 20 to 60 J/g are suspect. For example betafite #155 and pyrochlore #186 are the most

severely altered samples examined. Heating products of *155 are pyrochlore, rutile, UNb_3O_8 , and $\text{UNb}_3\text{O}_{10}$. Sample *186 recrystallized to a mixture of pyrochlore and Nb-Ta-Fe-rutile. Samples *171 and *251 may actually be samarskite (an AB_2O_6 -oxide). Both recrystallize to pyrochlore + fergusonite + FeNbO_4 and have DTA patterns similar to samarskite (*250). All three have stored energies near 40 J/g. Taking these exceptions into account, stored energy values of metamict pyrochlore group minerals range from 120 to 200 J/g. Of the minerals included for comparison, only fergusonite (an ABO_4 oxide) approaches this range at 130 J/g (Table 2). However, this value could be as low as 70 J/g depending on the interpolation of background beneath three overlapping exotherms.

Samples *153, *168, and *204 were studied in greater detail. Activation energies were calculated using the relationship,

$$k_t = Ae^{-E_a/k_B T}$$

where k_t is the temperature dependent rate constant and k_B is Boltzmann's constant. A plot of $\ln(k_t)$ versus $1/T$ yields E_a/k_B as the slope and A for the y-intercept. Plots of the data are shown in Figure 2. Results of the calculations made from these plots are given in Table 3 with more precise values of E_a . Activation energies, E_a , range from 0.29 to 1.0 eV with betafite *204 having the highest value. For the microlites, additional determinations were made over an interval of 250°C below the exothermic maximum temperature. Similar results were obtained for microlite *153,

but lower values of E_a and A were obtained for *168.

5. DISCUSSION

The data in Table 2 suggest that there is a compositional control on the exothermic peak temperature of natural pyrochlores. Generally, the betafites recrystallize at higher temperatures (650°-700°C) than do the pyrochlores or microlites (400°-600°C). These differences appear to correlate with departures from ideal $A_2B_2X_6Y$ stoichiometry and with the degree of hydration. The betafites approximate AB_2O_6 stoichiometry (e.g. *204, Table 1) with 10-12 wt. percent total water. Pyrochlores and microlites tend to have less than 0.50 vacancies per formula unit at the A-site and Y-site (microlites *153 and *168, Table 1) and less than 4 wt. percent total water. Large amounts of H_2O , which in molecular form may help to stabilize the structure by filling large voids formed by vacancies, may act to delay the recrystallization of betafites to higher temperatures.

Release of energy decreases as a function of increased crystallinity, with the fully-metamict samples approaching 210 J/g. The lowest values (4-13 J/g) are found for crystalline microlites. The energy release probably corresponds to annealing of isolated defects and defect aggregates. For partially metamict samples, the double exothermic peaks may represent the annealing of crystalline areas which are rich in aggregated point defects, while the higher temperature exotherm represents the recrystallization of heavily-damaged, amorphous regions. This is consistent with the interpretation of the DTA and small-angle

x-ray scattering data for partially metamict titanites (CaTiSiO_5) [24] and transmission electron microscopy on partially-metamict zirconolites [21].

Most of the metamict specimens release 125-210 J/g with recrystallization. Lower values found for betafites #155 and #186 appear to be the result of severe alteration and breakdown into multiphase assemblages. These assemblages are reflected by the heating products of both samples (Table 4). Estimated E_t values of metamict pyrochlores are greater than those of samarskite (40-50 J/g) and other AB_2O_6 oxides (50-70 J/g). In addition, the pyrochlore derivative structures of zirconolite and zirkelite give lower E_t values of 40-50 J/g [19]. These differences are intriguing, considering the similar saturation dose levels of natural pyrochlores ($1-4 \times 10^{16}$ alphas/mg [16]) and zirconolites ($0.6-2.0 \times 10^{16}$ alphas/mg; $= 0.3 - 1.0 \times 10^{26}$ alphas/m³ [20]). Even the evolution of damage-microstructures, as observed by high resolution transmission electron microscopy, appear to be comparable [16,21].

In a systematic study of synthetic cubic zirconolite ($\text{CaPuTi}_2\text{O}_7$), Foltyn *et al.* [22] found that the stored energy reaches a maximum near the saturation dose level defined by swelling (0.4×10^{16} alphas/mg; $= 0.2 \times 10^{26}$ alphas/m³). Beyond this value the fully-metamict state is reached at 10^{16} alphas/mg as determined by TEM, accompanied by a reduction in E_t approaching 50 percent of the saturation value at a dose of 3×10^{16} alphas/mg ($= 1.5 \times 10^{26}$ alphas/m³). The stored energy at this point is 50 J/g, close to that of the natural zirconolites. The decrease in stored energy was attributed to "redamaging processes" leading to reduced disorder within the aperiodic structure or to reduced internal strain.

Krivokoneva and Sidorenko [18] examined the x-ray diffraction line broadening of natural pyrochlores and found a significant strain component which increased with increasing alpha-recoil damage. Similarly, lattice expansion in synthetic, ^{244}Cm -doped zirconolite ($\text{CaZrTi}_2\text{O}_7$) produces strain components which increase as a function of alpha-recoil dose [23]. Unlike the synthetic zirconolites [22], the natural pyrochlores do not show much variation in stored energy near the saturation dose and beyond. For instance, microlite #168 has experienced a dose of 0.2×10^{16} alphas/mg and microlite #153 a dose of 4×10^{16} alphas/mg, similar to values given above for synthetic zirconolites. However, the E_t value of #153 is greater than that of #168 (Tables 2, 3). Either the pyrochlore group minerals do not experience strain relaxation or the amount of strain involved is much less than in the synthetic zirconolites.

Detailed measurements in Table 3 suggest that the activation energies, E_a , correlate with peak temperatures of exotherms. Values of E_t appear to correlate inversely with E_a for the three pyrochlores. This may be the result of composition differences (Table 1), particularly for samples #153 and #204 which have nearly the same dose of $\sim 4 \times 10^{16}$ alphas/mg. For the pyrochlore group minerals, E_a ranges from 0.29 to 0.97 eV. These values exceed that of ^{244}Cm -doped glass (0.25 eV) but fall below the value found for synthetic $\text{CaPuTi}_2\text{O}_7$ (1.22 eV). In addition, the metamict pyrochlores release higher levels of energy during recrystallization relative to most other alpha-damaged natural or synthetic oxides and glasses.

6. CONCLUSIONS

The recrystallization energy values, E_t , for metamict members of the pyrochlore group range from 125-210 J/g. Samples with lower values, in the range of 40 to 125 J/g, are almost certainly due to the fact that they have been altered. Other metamict, complex oxides with stoichiometries of ABO_4 (e.g. fergusonite) or AB_2O_6 (e.g. samarskite) have lower values of recrystallization energy, 40-85 J/g, and thus are easily distinguished from pyrochlore group minerals. The temperature of the exotherm of recrystallization varies between 400° and 700°C, the exact temperature determined by the sample composition (i.e. 400°-600°C for pyrochlores and microlites; 650°-700°C for betafites. The betafites characteristically have a greater number of A-site cation deficiencies and a higher content of H_2O , both of which may be related to the higher temperature of the recrystallization exotherm. The E_t values for the pyrochlore group minerals are consistently higher than those measured in synthetic, Pu-doped zirconolite (50 J/g at doses of 3×10^{16} alphas/mg = 1.5×10^{26} alphas/m³) and natural zirconolite (40-50 J/g at doses of 2×10^{16} alphas/mg = 1.0×10^{26} alphas/m³). The data do not suggest a decrease in energy for pyrochlore group minerals at doses beyond the saturation value as a result of either (i) reordering at the atomic level of already damaged areas or (ii) a reduction of internal strain by the same redamaging process [22].

Activation energies of recrystallization, E_a , range between values of 0.29 to 0.97 eV. Higher activation energies are measured for the

exotherms at higher temperatures. The activation energies are intermediate between those measured for a ^{244}Cm -doped glass (0.25 eV) and that for synthetic $\text{CaPuTi}_2\text{O}_7$ (1.22 eV). This range of activation energies suggests real differences in the annealing history of alpha-recoil damage in complex-oxides of different stoichiometries (e.g. AB_2O_6 vs. $\text{A}_2\text{B}_2\text{O}_7$) and structures (e.g. pyrochlore vs. zirconolite) during the thermal history of a nuclear waste repository.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under grant *DE-FG04-84ER45099 (R. C. Ewing). The paper has benefitted from a critical review by B. C. Chakoumakos.

REFERENCES

- [1] P. E. D. Morgan, A. B. Harker, J. F. Flintoff, T. M. Shaw and D. R. Clarke, *Advances in Ceramics* 8, eds. G. G. Wicks and W. A. Ross (American Ceramic Society, Columbus, 1984) p. 234.
- [2] A. B. Harker and J. F. Flintoff, *The Scientific Basis for Nuclear Waste Management VII*, ed. G. McVay (Elsevier, New York, 1984) p. 513.
- [3] P. E. D. Morgan, T. M. Shaw and E. A. Pugar, *Advances in Ceramics* 8,

- eds. G. G. Wicks and W. A. Ross (American Ceramic Society, Columbus, 1984) p. 209.
- [4] A. E. Ringwood, *Mineral. Mag.* 49 (1985) 159.
- [5] J. L. Hutchison, J. C. Barry, R. L. Segall and T. J. White *Proc. EMAG 1983 Conference, Guildford Institute of Physics Conference Series, No. 68 (1984) 403.*
- [6] J. A. Cooper, D. R. Cousens, R. A. Lewis, S. Myhra, R. L. Segall, R. St. C. Smart, P. S. Turner and T. J. White, *J. Am. Ceram. Soc.* 68 (1985) 64.
- [7] T. J. White, R. L. Segall, J. L. Hutchison and J. C. Barry, *Proc. R. Soc. Lond. A392 (1984) 343.*
- [8] F. W. Clinard, Jr., D. L. Rohr and R. B. Roof, *Nucl. Instr. Meth. Phys. Res. B1 (1984) 581.*
- [9] F. W. Clinard, Jr., D. E. Peterson and D. L. Rohr, *J. Nucl. Mat.* 126 (1984) 245.
- [10] J. W. Wald and P. Offerman, *The Scientific Basis for Nuclear Waste Management V, vol. 11, ed. W. Lutze (Elsevier, New York, 1982) p. 369.*
- [11] J. W. Wald and W. J. Weber, *Advances in Ceramics 8, eds. G. G. Wicks and W. A. Ross (American Ceramic Society, Columbus, 1984) p. 71.*

- [12] D. D. Hogarth, *Amer. Mineral.* 62 (1977) 403.

- [13] G. R. Lumpkin and R. C. Ewing, *Scientific Basis for Nuclear Waste Management VIII*, vol. 44, eds. C. M. Jantzen, J. A. Stone and R. C. Ewing (Materials Research Society, Pittsburgh, 1985) p. 647.

- [14] J. W. Colby, *Advances in X-ray Analysis* 11 (1968) 287.

- [15] D. E. Appleman and H. T. Evans, Jr., *Natl. Tech. Inf. Serv. Document PB-216* (1973) 188 pages.

- [16] G. R. Lumpkin, B. C. Chakoumakos and R. C. Ewing, *Amer. Mineral.* 71 (1986) in press.

- [17] D. D. Hogarth, *Can. Mineral.* 6 (1961) 610.

- [18] G. K. Krivokoneva and G. A. Sidorenko, *Geochem. Int.* (1971) 113.

- [19] G. R. Lumpkin and others, *Radiation Effects in Natural Zirconolites*, *J. of Mat. Res.*, in preparation.

- [20] R. C. Ewing, R. F. Haaker, T. J. Headley and P. F. Hlava, *The Scientific Basis for Nuclear Waste Management*, vol. 6, ed. S. V. Topp (Elsevier, New York, 1982) p. 249.

- [21] R. C. Ewing and T. J. Headley, *J. Nucl. Mat.* 119 (1983) 102.

[22] E. M. Foltyn, F. W. Clinard, Jr., J. Rankin and D. E. Peterson, J. Nucl. Mat.,
in press.

[23] B. C. Chakoumakos and R. C. Ewing, Geol. Soc. of Am. Abst. (1985).

[24] E. R. Vance and J. B. Metson, Phys. Chem. Minerals, ~~in press~~, 12 (1985) 255.

FIGURE CAPTIONS

FIGURE 1. DTA traces of pyrochlore group minerals showing commonly observed exothermic and endothermic effects (refer to Table 2).

FIGURE 2. Temperature dependence of the rate constant k_t determined for two microlites and one betafite (refer to Table 3).

Table 1. Electron microprobe analyses and structural formulas of three natural pyrochlore group minerals.

	204	153	168		204	153	168
WO ₃	---	0.06	0.47	W	---	0.00	0.01
Ta ₂ O ₅	1.74	70.2	63.9	Ta	0.03	1.77	1.53
Nb ₂ O ₅	34.1	4.77	8.11	Nb	1.07	0.20	0.32
TiO ₂	17.2	0.40	0.53	Ti	0.90	0.03	0.04
ZrO ₂	0.03	---	---	Sn	---	0.00	0.10
SnO ₂	---	0.00	2.77				
ThO ₂	0.32	0.00	0.03	ΣB	2.00	2.00	2.00
UO ₂	24.5	8.56	2.62				
Y ₂ O ₃	0.27	0.00	0.13	U	0.38	0.18	0.05
RE ₂ O ₃	0.86	0.13	0.24	REE	0.03	0.00	0.01
Sb ₂ O ₃	---	0.05	0.13	Mn	0.02	0.01	0.00
Bi ₂ O ₃	---	0.17	0.11	Fe	0.18	0.01	0.01
MnO	0.42	0.09	0.04	Ca	0.56	0.86	1.25
FeO	3.04	0.06	0.07	Pb	0.01	0.05	0.00
CaO	7.49	8.62	13.2	Na	0.01	0.60	0.42
SrO	0.01	---	---	□A	0.81	0.29	0.26
BaO	0.08	0.00	0.02				
PbO	0.51	1.85	0.03	O	6.11	6.39	6.25
Na ₂ O	0.05	3.32	2.46	F	0.05	0.37	0.58
Cs ₂ O	---	0.02	0.00	□Y	0.84	0.24	0.17
H ₂ O	8.5	1.2	3.8				
F	<u>0.24</u>	<u>1.25</u>	<u>2.09</u>	H ₂ O	1.97	0.37	1.12
SUM	99.55	100.75	100.75				
O = F	<u>-0.10</u>	<u>-0.53</u>	<u>-0.88</u>	dose*	3.7	4.0	0.2
TOTAL	99.45	100.22	99.87	dpa**	41	45	2.6

* $n \times 10^{16}$ α/mg

** displacements per atom

Table 2. DTA/TGA data for pyrochlore group, ABO_4 , and AB_2O_6 type oxide minerals.

Sample No.	Museum No.	Exotherms (°C)		Endotherms (°C)		Wt. Loss (%)	E_T (J/g)
BETAHITE SUBGROUP							
155 Madagascar	SU 52559		650	180		10.1%	13
171 Madagascar	AMNH 21590	425	700	160	475	6.6	50
178 Mexico	AMNH 28426		675	185		9.8	184
186 Finland	AMNH 17758		700	175		11.3	63
204 Canada	HU 124374		660	165	480	8.5	126
PYROCHLORE SUBGROUP							
214 Canada	HU 1024503	410	620	140		3.8	143
230 USSR	W.W. Pinch	430	570		490(?)	1.0	34
251 New Mexico	UNM	425	700	165	490	7.2	42
MICROLITE SUBGROUP							
080 Virginia	USNM 96739	570	740	150		1.0	201
147 New Mexico	UNM		545, weak			0.1	4
153 New Mexico	UNM	465	600	160		1.2	214
168 Virginia	AMNH 067251	545	615 740	170		3.8	147
201 Maine	HU 90883		425, weak			1.2	13
ABO_4 OXIDES							
124 Fergusonite	UNM	485	580 670	160			130*
AB_2O_6 OXIDES							
227 Brannerite	UNM	510	655 800				71
250 Samarskite	J.W. Adams	465	645	155	390		41
R3 Aeschnite	C.O. Hutton	305	495 725	450	525		50
R5 Polycrase	C.O. Hutton	335	530 770	120	395		59
R18 Euxenite	C.O. Hutton	360	740 900		400		63

* could be as low as 70 J/g, see text.

Table 3. DTA data for pyrochlore group minerals compared to synthetic zirconolite and glasses.

Sample No.	Temp. Range	Peak	Interval	E_a (eV)	$A(s^{-1})$	$E_T(J/g)$
153 Microlite	200-780°C	465°C	80°C	0.29	0.14	259
	200-455		17.5	0.34		
168 Microlite	300-880	545	60	0.53	0.87	181
	300-535		15	0.15		
204 Betafite	440-800	660	40	0.97	570	133
CaPuTi ₂ O ₇	485-715			1.22	60,000	28
²⁴⁴ Cm-doped glasses [13]				0.25		117

Table 4. X-ray diffraction data (nm) on annealed samples.

Betafites:					
#155	a = 1.03308(8)	Rutile	a = .4641(2)	UNb ₂ O ₈	a = .6360(5)
			c = .300 (1)		c = .4009(4)
#171	a = 1.0291(2)	FeNbO ₄	a = .5609(2)	YNbO ₄	a = .5303(2)
			b = .4662(1)		b = 1.0998(3)
			c = .5013(1)		c = .5056(1)
					β = 9.432(3)
#178	a = 1.0306(1)	Rutile	a = .46220(9)		
			c = .29891(8)		
#186	a = 1.02524(5)	Rutile	a = .46613(5)		
			c = .30217(4)		
#204	a = 1.0279(1)	Rutile	a = .46373(6)		
			c = .29972(4)		
Pyrochlores:					
#214	a = 1.0279(1)				
#230	a = 1.0379(1)				
#251	a = 1.0340(1)	FeNbO ₄	a = .57811(3)	YNbO ₄	a = .5334(3)
			b = .46038(5)		b = 1.1046(2)
			c = .50575(2)		c = .5071(1)
					β = 9.431(3)
Microlites:					
#080	a = 1.0380(1)				
#147	a = 1.0394(1)				
#153	a = 1.0381(1)				
#168	a = 1.0396(1)	CaTa ₂ O ₆	a = .5367(2)		
			b = 1.1045(3)		
			c = .7494(3)		
#201	a = 1.0403(1)				