Geochemical alteration of pyrochlore group minerals: Microlite subgroup

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ABSTRACT

A qualitative picture of microlite stability is derived from known mineral assemblages and reactions in the simplified system Na-Ca-Mn-Ta-O-H. Results suggest that microlite is stable under conditions of moderate to high \( a_{\text{Na}}^* \) and low to moderate \( a_{\text{Ca}}^* \). Microlite is often replaced during the latter stages of granitic pegmatite evolution by manganese-tantalite and fersmite or rynersonite, indicating increasing \( a_{\text{Ca}}^* \) and \( a_{\text{Mn}}^* \) relative to \( a_{\text{Na}}^* \). Primary (hydrothermal) alteration involves replacement of Na, F, and vacancies by Ca and O, represented by the coupled substitutions \( \text{Na}^+\text{F} \rightarrow \text{Ca}^2\text{O} \) and \( \text{Na}^+\text{O} \rightarrow \text{Ca}^2\text{O} \). Exchange reactions between microlite and fluid suggest conditions of relatively high pH, high \( a_{\text{Ca}}^* \), low to moderate \( a_{\text{Mn}}^* \), and low \( a_{\text{Na}}^* \) during alteration by evolved pegmatite fluids at 350–550 °C and 2–4 kbar. Secondary (weathering) alteration involves leaching of Na, Ca, F, and O, represented by the coupled substitutions \( \text{Na}^+\text{F} \rightarrow \text{Ca}^2\text{O} \) and \( \text{Na}+\text{O} \rightarrow \text{Ca}^2\text{O} \). Up to 80% of the A sites may be vacant, usually accompanied by a comparable number of anion \((X + Y)\) vacancies and \( H_2O \) molecules. Secondary alteration results from interaction with relatively acidic meteoric \( H_2O \) at temperatures below 100 °C. In both types of alteration, the U content remains remarkably constant. Loss of radioactive Pb due to long-term diffusion overprints changes in Pb content associated with primary alteration in most samples.

INTRODUCTION

Microlite, the Ta-rich member of the pyrochlore group (Hogarth, 1977), is largely restricted to evolved granitic pegmatites of the beryl-columbite, complex spodumene, and complex lepidolite types (Černý, 1989). The crystal structure is cubic \((Fd\overline{3}m, Z = 8)\), a derivative of the fluorite structure type, and has the general formula \( A_{2-x}B_xX_{6-x}Y_{1-x}pH_2O \) (Lumpkin, 1989). End-member microlite has the ideal composition \( \text{NaCaTa}_4\text{O}_6\text{F} \). A number of simple and coupled substitutions are possible, primarily involving Na, Ca, U, and vacancies at the A site; Ta, Nb, and Ti at the B site; and O, OH, F, and vacancies at the Y site (Lumpkin et al., 1986). The X site is normally fully occupied by O; however, small amounts of F and OH and vacancies may occur on the X site in natural samples (Lumpkin, 1989), consistent with previous work on synthetic pyrochlores (Groult et al., 1982; Rotella et al., 1982; Subramanian et al., 1983). Vacancies are tolerated mainly as defect components that can be written as \( A_1B_2X_6\square, \square AB_2X_6\square, \) and \( C_3B_2X_6M \) (Chakoumakos, 1984). In the latter case, the Y site is occupied by large monovalent cations like K, Rb, and Cs. The ability to accept a variety of elements, vacancies, and \( H_2O \) molecules suggests that microlite may be a useful indicator of relative changes in fluid composition in granitic pegmatites.

Alteration processes have been divided into primary and secondary types by Van Wambeke (1970) and Ewing (1975). Primary alteration is hydrothermal in nature and is usually associated with emplacement of the host rocks. This type of alteration is most likely to occur prior to significant radiation damage due to \( \alpha \) decay of \( ^{238}\text{U}, ^{235}\text{U}, \) and \( ^{232}\text{Th}, \) resulting in either a change in composition or replacement by one or more phases. Secondary alteration is a near-surface phenomenon associated with weathering and often occurs after the crystal structure has been rendered fully aperiodic (metamict) by radiation damage. Secondary alteration leads to major increases in vacancies due to leaching of A-site cations and Y-site anions and to increased hydration (Van Wambeke, 1970; Ewing, 1975; von Knorring and Fadipe, 1981; Lumpkin and Ewing, 1985; Lumpkin et al., 1986).

This paper has four purposes: (1) to describe potential replacement reactions and chemical changes that accompany primary alteration, (2) to determine the maximum number of A-site vacancies resulting from secondary alteration along with any attending cation exchange effects, (3) to estimate the maximum number of anion vacancies and determine whether they correlate with cation vacancies; and (4) to outline the \( P-T-X \) conditions of alteration for the microlite subgroup in granitic pegmatites. Results of this study are also relevant to the disposal of nuclear waste in ceramic materials that contain pyrochlore as a
TABLE 1. Localities, mineral associations, and descriptions of microlite specimens

<table>
<thead>
<tr>
<th>Sample nos.</th>
<th>Locality and lithologic unit</th>
<th>Alteration pattern and mineral association</th>
<th>$I/I_0^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>080, 130</td>
<td>Rutherford pegmatite, Amelia, VA, second intermediate zone</td>
<td>Crystals 1–2 cm with secondary alteration along microfractures; Ab + Qtz + Cbt + Fgn + Mzt + Ryn</td>
<td>0.05–0.12</td>
</tr>
<tr>
<td>185</td>
<td>Tin Mountain pegmatite, Custer, SD, quartz-spodumene-mica zone</td>
<td>Crystals 0.4–1.0 mm, heavily microfractured, complete secondary alteration; Lp + Qtz + Ms</td>
<td>0.00</td>
</tr>
<tr>
<td>188</td>
<td>Volta Grande, Minas Gerais, Brazil</td>
<td>Crystals 0.6–1.0 mm with secondary alteration along fractures; Lp + Ms + Qtz</td>
<td>0.00</td>
</tr>
<tr>
<td>202</td>
<td>Brown Derby pegmatite, Gunison County, CO, lepidolite-quartz zone</td>
<td>Crystals 3–5 mm with secondary alteration along fractures; Qtz + Ms</td>
<td>0.03</td>
</tr>
<tr>
<td>231</td>
<td>Opportunity pegmatite, Gunison County, CO, quartz zone</td>
<td>Crystals 1–2 mm with primary alteration as uniform rims; Qtz + Lp + Zrc + Cbt</td>
<td>0.20–0.70</td>
</tr>
<tr>
<td>324</td>
<td>Pidlo pegmatite, Mora County, NM, lepidolite-quartz zone</td>
<td>A crystal 1 x 1 x 2 cm, with patchy, primary alteration; mineral association unknown</td>
<td>0.90–1.00</td>
</tr>
<tr>
<td>327</td>
<td>Fungwe district, Zimbabwe</td>
<td>Crystals 1–6 mm with primary alteration as irregular rims, minor secondary alteration along fractures; Ab + Qtz + Ms + Mc + Lp + goethite</td>
<td>0.00–0.15</td>
</tr>
<tr>
<td>153, 260, P5.1</td>
<td>Harding pegmatite, Taos County, NM, cleavelandite subunit</td>
<td>Crystals 0.5–6.0 mm with primary alteration as irregular rims and patches, minor secondary alteration along microfractures; Mc + Qtz + Spd + Ms + Lp + Ab + Zrc + goethite</td>
<td>0.00</td>
</tr>
<tr>
<td>154, 264, 269, P15.1</td>
<td>Harding pegmatite, Taos County, NM, mclcline-spodumene zone</td>
<td>Crystals 0.5–2.0 mm with primary alteration as irregular rims, minor secondary alteration along microfractures; Lp + Ab + Ms + Qtz + Ryn + goethite</td>
<td>0.00</td>
</tr>
<tr>
<td>P2.1, P2.2, P7.1</td>
<td>Harding pegmatite, Taos County, NM, lepidolite-cleavelandite subunit</td>
<td>Crystals 0.4–1.0 mm, heavily microfractured, complete secondary alteration; Lp + Qtz + Cbt + Fgn + Mzt + Ryn</td>
<td>0.05–0.12</td>
</tr>
</tbody>
</table>

* $I/I_0$ ranges from 0.00 for fully metamict samples to 1.00 for highly crystalline samples. All samples from the UNM collection except for 080 (USNM 96739), 185 (AMNH 34311), 188 (AMNH 24560) and 202 (HU 1016185). Ab—albite, Cbt—columbite, Fgn—fergusonite, Lp—lepidolite, Mc—microcline, Ms—muscovite, Mzt—monazite, Qtz—quartz, Ryn—ryersonite or ferreinite, Spm—spodumene, Wgn—wodginite, Zrc—zircon.

**Experimental procedures**

**Electron microprobe analysis**

Analyses were performed using a JEOL 733 Superprobe operated at 15 kV and 20 nA with a probe diameter of 10 μm. Data were corrected for drift and dead time and then reduced using an empirical α-factor approach (Bence and Albee, 1968; Albee and Ray, 1970). Each element was counted for 40 s or until a standard deviation of 0.5% was reached. The elements F, Na, Mg, Al, K, Ca, Ti, Mn, and Fe were analyzed using Kα spectral lines. Lα lines were employed for Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, and REEs. For the elements Ta, W, Pb, Bi, Th, and U, Mα lines were used. Empirical overlap corrections were determined and used for peak interference problems. Minimum detection limits are typically 0.02–0.04 wt% for the oxides of Mg, Ca, Mn, Fe, Sr, Ba, Pb, Cs, and K; 0.04–0.06 wt% for the oxides of Nb, Ta, and Na; 0.06–0.08 wt% for the oxides of Ti, Zr, Sn, Al, Y, REEs, and Sb; and 0.08–0.12 wt% for the oxides of W, Bi, Th, U, and elemental F. Standards included natural microlite, manganotantalite, cassiterite, stibiotantalite, olivine, benitoite, cervusite, pollucite, anorthite, gadolinite, and synthetic NaNbO₄, CaWO₄, SrMoO₄, UO₂, CaTiO₃, ThSiO₄, ZrSiO₄, KTaO₃, YPO₄, and REEPO₄.

**X-ray diffraction analysis**

Powder diffraction patterns were obtained using a Scintag diffractometer operated at 40 kV and 30 mA. Patterns were recorded from 10 to 70° 2θ at 1° per minute using graphite-monochromatized CuKα radiation. BaF₂ and Si were used as internal and external standards, respectively. Lattice parameters were refined by the method of least-squares (Appleman and Evans, 1973). The level of radiation damage ($I/I_0$) was estimated from the total integrated intensity of all diffraction lines in the pattern relative to highly crystalline standards. Metamict and altered specimens were heated in air or N₂ for 1 h at 1000 °C and reanalyzed.

**Transmission electron microscopy**

Powders of selected samples were dispersed in acetone and deposited on holey-carbon filmed Cu grids. Samples were examined using a JEOL 2000FX transmission electron microscope (TEM) operated at 200 kV. High-resolution images were taken at a magnification of 410 000 using axial illumination and objective lens defocus values of −60 to −150 nm. A Tracor-Northern TN-5500 energy dispersive X-ray analyzer (EDS) was used to obtain analyses of specific areas. Spectra were acquired for 300 s real time (20–30% dead time) using an effective probe diameter of 10 nm. Data reduction was accomplished using the Tracor software package SMTF with empirical k factors determined from standards.

**Criteria for recognition of alteration**

Three basic criteria were used to differentiate between primary and secondary alteration: field relationships, microscopic observations, and alteration mechanisms. The first two criteria involve the use of mineral assemblages as a guide for the identification of hydrothermal alteration and weathering. In granitic pegmatites, primary constituent phase (e.g., Harker, 1988; Ringwood et al., 1988).
(hydrothermal) alteration is commonly indicated by replacement of earlier mineral assemblages by albite and lithium mica (Jahns, 1982; Hawthorne and Černý, 1982; Černý and Burt, 1984). Secondary alteration is indicated by the breakdown of feldspars and micas to clay minerals, a process often associated with the formation of iron oxyhydroxides like goethite.

Alteration mechanisms include intracrystalline diffusion and fluid transport through preexisting cracks and voids. Diffusion is an effective mechanism at high temperatures and is expected to be the dominant process during primary alteration. Fluid transport through cracks and voids with limited intracrystalline diffusion is probably the dominant mechanism operative at the relatively low temperatures characteristic of secondary alteration. The timing of alteration may be estimated where clear crosscutting relationships with radiation-induced microfracturing exist (Lumpkin and Ewing, 1985).

The above criteria were used to classify alteration in 20 specimens (Table 1). Typical examples of primary alteration are specimens from the Harding, Pidlite, and Zimbabwe pegmatites. Alteration patterns in these microlite samples are characterized by irregular rim diffusion, uniform rim diffusion, or a patchy interior distribution, respectively. Primary alteration appears to predate most of the radiation-induced microfracturing. The best examples of secondary alteration occur in microlite samples from Amelia, Virginia, in which alteration is localized along radiation-induced microfractures with limited intracrystalline diffusion. Individual microlite crystals in sample 185 from the Tin Mountain pegmatite, South Dakota, are heavily microfractured and completely altered. Alteration was classified as secondary (see Table 1) on the basis of small crystal size, density of microfracturing, and proximity to a 1-cm layer of kaolinite in the quartzspodumene-mica core of the pegmatite (Spilde and Shearer, 1987).

Investigation of the samples listed in Table 1 by optical microscopy, X-ray diffraction, and TEM shows that most have received extensive radiation damage. In many samples the structure has been rendered completely aperiodic (metamict) as the result of cumulative α-decay events (Lumpkin and Ewing, 1988). This study has failed to reveal conclusive evidence for natural recrystallization of chemically altered, metamict microlite. Recrystallization effects appear to be more common in radiation-damaged silicate minerals and have been observed, for example, in altered thorite group minerals from the Harding pegmatite (Lumpkin and Chakoumakos, 1988).

**Tantalum oxide mineral reactions**

Based on our observations of oxide mineral associations in the granitic pegmatites of northern New Mexico and Amelia, Virginia, together with those of previous investigators (e.g., von Knorring and Fadipe, 1981; Foord, 1982; Černý and Ercit, 1985, 1989; Ercit, 1986), we present here a summary of some possible reactions between microlite and other tantalum oxide minerals. Results are confined to idealized phase relations in the system Na-Ca-Mn-Ta-O-H. This system is represented by the common association of microlite, manganotantalite, fersmite, and rynersonite-vigezzite. Exotic associations reviewed by Černý and Ercit (1985, 1989) include tantite (Ta₂O₅), calciotantite (CaTaO₉), and natrotantite (Na₂TaO₅).

In Figure 1 we have constructed schematic phase relations as a function of the activities of Na⁺, Ca²⁺, and Mn²⁺ based on idealized compositions, including NaTaO₅ and CaTaO₅. For simplicity, solid solution among microlite (NaCaTa₂O₈), rynersonite (CaTaO₅), and CaTa₂O₇ has been omitted. Our aim is to illustrate qualitatively how changes in fluid composition affect tantalum oxide mineral assemblages. Simple mineral reactions were used (Table 2), guided by known mineral associations or replacement features, to arrive at the topologies shown in Figure 1. For example, Figure 1a shows how the assemblages microlite + calciotantite + tantite, microlite + natrotantite, microlite + calciotantite, and microlite + rynersonite constrain the topology of the diagram.

The relations shown in Figures 1a–1c were combined
to provide a three-dimensional view of mineral compatibility in the Na-Ca-Mn-Ta-O-H system. Figure 2 indicates that microlite and manganotantalite may coexist over a range of fluid compositions characterized by moderate to high Ca, Na, and O. The actual stability field of microlite may be extended by incorporation of CaTa$_2$O$_6$ and CaTa$_4$O$_8$ components in solid solution (cf. Lumpkin et al., 1986).

A hypothetical example of the breakdown of microlite is shown in Figure 2. Microlite initially in equilibrium with a fluid at point A is exposed to a fluid whose composition is characterized by increasing Ca$^{2+}$ and decreasing Na$^+$ activities. Abbreviations: Ct = calciotantite, Mic = microlite, Mnt = manganotantalite, Nt = natrotantite, Ryn = rynersonite, Tn = tantite, 1 = NaTaO$_5$, 2 = Ca$_2$Ta$_2$O$_7$.

**Table 2.** Mineral reactions in the system Na-Ca-Mn-Ta-O-H

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.5H$_2$O + Ca$^{2+}$ + 2NaTaO$_5$ = NaCaTa$_2$O$_7$ + Na$^+$ + H$^+$</td>
<td></td>
</tr>
<tr>
<td>2. 2H$^+$ + 4NaTaO$_5$ = Na$_2$Ta$_2$O$_6$ + 2Na$^+$ + H$_2$O</td>
<td></td>
</tr>
<tr>
<td>3. 2H$_2$O + 2Ca$^{2+}$ + Na$_2$Ta$_2$O$_6$ = 2NaCaTa$_2$O$_7$ + 4H$^+$</td>
<td></td>
</tr>
<tr>
<td>4. 2H$^+$ + Na$_2$Ta$_2$O$_6$ = 2Ta$_2$O$_7$ + 2Na$^+$ + H$_2$O</td>
<td></td>
</tr>
<tr>
<td>5. 1.5H$_2$O + Na$^+$ + Ca$^{2+}$ + Ta$_2$O$_7$ = NaCaTa$_2$O$_7$ + 3H$^+$</td>
<td></td>
</tr>
<tr>
<td>6. H$_2$O + Ca$^{2+}$ + 2Ta$_2$O$_7$ = CaTa$_2$O$_7$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>7. 2H$_2$O + 2Na$^+$ + Ca$^{2+}$ + Ta$_2$O$_7$ = 2NaCaTa$_2$O$_7$ + 4H$^+$</td>
<td></td>
</tr>
<tr>
<td>8. H$_2$O + Ca$^{2+}$ + CaTa$_2$O$_7$ = 2CaTa$_2$O$_7$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>9. 0.5H$_2$O + Na$^+$ + Ca$_2$Ta$_2$O$_7$ = NaCaTa$_2$O$_7$ + H$^+$</td>
<td></td>
</tr>
<tr>
<td>10. H$_2$O + Ca$^{2+}$ + CaTa$_2$O$_7$ = CaTa$_2$O$_7$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>11. H$^+$ + Na$^+$ + Ca$_2$Ta$_2$O$_7$ = NaCaTa$_2$O$_7$ + Na$^+$ + 0.5H$_2$O</td>
<td></td>
</tr>
<tr>
<td>12. Mn$^{2+}$ + 2NaTaO$_5$ = Mn$_2$Ta$_2$O$_7$ + 2Na$^+$</td>
<td></td>
</tr>
<tr>
<td>13. H$_2$O + Mn$^{2+}$ + Na$_2$Ta$_2$O$_6$ = 2MnTa$_2$O$_7$ + 2Na$^+$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>14. H$_2$O + Mn$^{2+}$ + Ta$_2$O$_7$ = 2MnTa$_2$O$_7$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>15. 2H$^+$ + Mn$^{2+}$ + Ta$_2$O$_7$ = Mn$_2$Ta$_2$O$_7$ + 2Ca$^{2+}$ + H$_2$O</td>
<td></td>
</tr>
<tr>
<td>16. Mn$^{2+}$ + CaTa$_2$O$_7$ = MnTa$_2$O$_7$ + Ca$^{2+}$</td>
<td></td>
</tr>
<tr>
<td>17. H$_2$O + 2Mn$^{2+}$ + Ca$_2$Ta$_2$O$_7$ = 2MnTa$_2$O$_7$ + Ca$^{2+}$ + 2H$^+$</td>
<td></td>
</tr>
<tr>
<td>18. 0.5H$_2$O + Na$^+$ + Ca$^{2+}$ + MnTa$_2$O$_7$ = NaCaTa$_2$O$_7$ + Mn$^{2+}$ + H$^+$</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** NaCaTa$_2$O$_7$ = microlite, Mn$_2$Ta$_2$O$_7$ = manganotantalite, CaTa$_2$O$_7$ = calciotantite, Ca$_2$Ta$_2$O$_7$ = rynersonite or fersmite, Na$_2$Ta$_2$O$_6$ = natrotantite, Ta$_2$O$_7$ = tantite.

**CHART 3.** Triangular plot of divalent A-site cations (mainly Ca), monovalent A-site cations (mainly Na), and A-site vacancies in unaltered and altered microlite samples.

**Primary alteration**

Electron microprobe analyses of microlite samples from the Harding pegmatite (Tables 3 and 4') demonstrate that the major chemical effects of primary alteration are decreased Na and increased Ca, Fe, Mn, and O. The amounts of U, F, and inferred H$_2$O (estimated by difference) tend to remain relatively constant, although lower F and higher inferred H$_2$O contents were noted in a few samples. Similar results were found in sample 324 from the Pidlite pegmatite, Mora County, New Mexico, and in sample 327 from the Fungwe district, Zimbabwe. Structural formulas of sample 324 indicate that Ca, Mn, Fe, and O increased and that Na, Fe, and and decreased as a result of alteration. For sample 327, structural formulas clearly indicate strong Ca enrichment and Na depletion during primary alteration. Following a typical pattern, the amount of O increased in the altered areas, whereas Fe and Mn decreased. The Mn content and inferred H$_2$O remained constant, but Fe decreased during alteration.

To receive a copy of Table 4, order Document AM-92-488 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
A triangular plot of A-site cations and vacancies (Fig. 3) demonstrates the consistent increase in divalent cations during primary alteration. Monovalent cations (essentially Na) usually decrease but in a few cases remain relatively constant. A-site vacancies tend to decrease or remain relatively constant. Two samples showed minor increases in the number of A-site vacancies. A similar plot of anions and vacancies (Fig. 4) indicates that O increases, F tends to decrease or remain relatively constant, and anion vacancies usually decrease. The U contents of altered areas remain unchanged in comparison to unaltered areas (Fig. 5). Apart from Pb, which shows minor decreases in some samples, the divalent cations Ca, Mn, and Fe generally increase during alteration. Average increases in these cations are approximately 0.25 Ca, 0.05 Mn, and 0.03 Fe atoms per formula unit (Fig. 6). Major substitutions inferred from these results are \( \text{H}^+ \rightarrow \text{Ca}^2+ \), \( \text{Na}^+ \rightarrow \text{Ca}^2+ \), and \( \text{Na}^+ \text{OH} \rightarrow \text{Ca}^2+ \text{O} \). The latter substitution is postulated for the cases where F remains relatively constant and O increases. The simple substitution \( \text{F} \rightarrow \text{OH} \) is also possible but is largely masked by coupled substitutions.

The substitutions noted above can be related to pervasive, subsolidus alteration by exchange reactions of the form:

\[
\begin{align*}
\text{H}_2\text{O} + \text{Ca}^{2+} + [\text{CaTa}_2\text{O}_7\text{O}_{1-n}]_{\text{ins}} &= [\text{Ca}_2\text{Ta}_2\text{O}_7\text{O}_{1-n}]_{\text{ins}} + 2\text{H}^+ \\
\text{H}_2\text{O} + \text{Ca}^{2+} + [\text{NaCaTa}_2\text{O}_7\text{F}]_{\text{ins}} &= [\text{Ca}_2\text{Ta}_2\text{O}_7\text{O}_{1-n}]_{\text{ins}} + \text{Na}^+ + \text{H}^+ + \text{HF}
\end{align*}
\]
reaction is favored by relatively high $a_{\text{Ca}^{2+}}$ and pH and by low $a_{\text{Fe}^{3+}}$ in the fluid phase. Equations 19, 20a, and 20c indicate that temperature and the activities of $a_{\text{H}_2\text{O}}$ and HF also play a role in controlling the composition of microlite. In situations where F remains relatively constant, Reactions 20b and 20c best account for chemical changes attending primary alteration.

**Secondary alteration**

Examination of Figure 3 shows that alteration causes compositions to move toward the $\Box^* - A^2^+$ join as Na is removed at a faster rate than divalent cations. Among the divalent cations, Figure 6 shows that Ca is lost, whereas Mn and Fe usually show slight to moderate gains (up to 0.15 atoms per formula unit). Minor increases in Pb also occur in some specimens. With the exception of sample 188, Ba shows slight increases in only a few of the microlite samples. Once Na is completely leached from the $A^*$ site, compositions then move toward the $\Box^*$ vertex of Figure 3 as Ca continues to be removed. In sample 080, the compositions plot along a curved trend, indicating a gradual increase in the relative rate of Ca loss with progressive alteration.

Alteration trends represented by the anions (Fig. 4) closely follow those of the cations (Fig. 3). Figure 4 shows that, initially, $F$ is removed from the $Y$ site, causing compositions to move toward the $\Box^* + Y^*$ join. As alteration proceeds, $O$ is removed from the $X$ and $Y$ sites, causing compositions to approach the $\Box^* + Y^*$ vertex of
Figure 4. Notice in Figure 4 that data for sample 080 follow a curved path complementary to the cation trend shown in Figure 3.

Combined results for cations and anions indicate that Schottky defects are produced by substitutions of the form $\text{ANaYF} \rightarrow \text{A}[\text{Y}]$, $\text{ACaYO} \rightarrow \text{AlY}$, and $\text{ACaxO} \rightarrow \text{ADxf}$. Simple substitutions such as $\text{Y} \rightarrow \text{YOH}$ and $\text{ACa}^2+ \rightarrow 2\text{H}^+$ are possible but tend to be masked by coupled substitutions. Also, structural considerations indicate that only minor amounts of OH$^-$ will be tolerated at the Y site in conjunction with large numbers of cation vacancies (Subramanian et al., 1983). The major substitutions result in highly defective, hydrated microlite samples characterized by increases of 4 to 13 wt% H$_2$O. Furthermore, Figure 5 shows that the U content of microlite remains remarkably constant as a result of secondary alteration.

In most samples, vacancies reach maximum values of $\Delta \text{O} = 1.5, \Delta \text{O} = 1.0$, and $\Delta \text{O} = 0.5$ per formula unit (Tables 3 and 4). Sample 188 from Minas Gerais, Brazil, consists of crystals of unaltered microlite with thin alteration rinds of bariummicrolite in which vacancies reach maximum values of $\Delta \text{O} = 1.8$, $\Delta \text{O} = 1.0$, and $\Delta \text{O} = 0.8$ per formula unit. Structural formulas indicate virtually complete leaching of Ca, Na, and F, compensated in part by entry of minor amounts of Ba, Pb, Fe, REEs, Cs, and 10–12 wt% H$_2$O.

Secondary alteration, or weathering, of microlite can be approximated by reactions of the form:

$$3\text{H}^+ + \text{H}_2\text{O} + [\text{NaCaTa}_2\text{O}_5\text{F}]_{\text{mss}}$$
$$= [\text{Ta}_3\text{O}_5\cdot2\text{H}_2\text{O}]_{\text{mss}} + \text{Na}^+ + \text{Ca}^{2+} + \text{HF}$$

(21)

$$2\text{H}^+ + 1.5\text{H}_2\text{O} + 0.5\text{Ba}^{2+} + [\text{NaCaTa}_2\text{O}_5\text{F}]_{\text{mss}}$$
$$= [\text{Ba}_2\text{Ta}_2\text{O}_5\cdot2\text{H}_2\text{O}]_{\text{mss}} + \text{Na}^+ + \text{Ca}^{2+} + \text{HF}.$$  

(22)

The right side of each reaction is favored by relatively low $T$, low pH, and low $a_{\text{H}_2\text{O}}$, $a_{\text{Ca}^{2+}}$, and $a_{\text{HF}}$ in the fluid phase. Additionally, Reaction 22 is favored by relatively high $a_{\text{Ba}^{2+}}$ in solution.

**U-Pb systematics**

Microprobe analyses were used to evaluate the behavior of U and Pb in microlite subsequent to crystallization. The Harding suite was selected because a large number of samples are available, the geologic age is well established at 1300 m.y. (Aldrich et al., 1958; Brookins et al., 1979), significant metamorphic overprinting is absent, and the microlite samples have low Th and high U contents (Lumpkin et al., 1986). Figure 7 shows a U-Pb plot including both unaltered and altered microlite samples from the Harding pegmatite. Most of the data fall below the 1300-m.y. reference line. Except for specific examples, the magnitude of Pb loss is poorly correlated with alteration. The maximum degree of Pb loss approaches 80% in both unaltered and altered material, suggesting that long-term diffusion is a viable explanation of the results. The high-Pb data points in Figure 7 are from the core of a microlite grain in sample 269 and represent either Pb gain during alteration or common Pb incorporated during crystallization.

Data for microlite samples from other approximately 1300-m.y.-old pegmatites are generally consistent with the Harding suite. Microlite crystals from the Pidlite pegmatite exhibit Pb loss of 0–35% in unaltered cores and 60–75% in altered rims. These results are consistent with either episodic Pb loss during primary alteration or a subsequent long-term diffusion gradient preserved over a distance of 0.5–1.0 mm from core to rim. In comparison, heavily microfractured microlite crystals (samples 202 and 231) from the Quartz Creek district, Colorado, consistently show 60–80% Pb loss in both unaltered and altered areas. In this case the alteration is classified as secondary (Table 1). The U-Pb systematics reported above indicate that radiation-induced microfracturing plays an important role in controlling the long-term loss of radiogenic Pb in microlite.

**DISCUSSION**

**Chemical effects of alteration**

Chemical changes that accompany alteration are summarized in Figure 8 using idealized end-members to show major element trends. Most unaltered compositions fall near the NaCaTa$_2$O$_5$F-CaTa$_2$O$_6$ join or just within the NaCaTa$_2$O$_5$F-Ca$_2$Ta$_2$O$_6$ composition field. Four alteration vectors are indicated by the data in Figures 3 and 4: (1) filling of Schottky defects by CaO, (2) NaF → CaO exchange, (3) formation of Schottky defects by removal of NaF, and (4) creation of Schottky defects by removal of CaO. Although there are obvious differences between individual samples, primary alteration paths lie consistently between trends 1 and 2 (Fig. 8).
Secondary alteration follows a distinctly different path between trends 3 and 4, gradually approaching trend 4 as alteration proceeds to completion. In cases of extreme secondary alteration, this path ultimately requires that some O be removed from the X site. The occurrence of paired vacancies (Schottky defects) is consistent with the geometry of the pyrochlore structure type, in which $\text{YAO}_4$ tetrahedra and $\text{AX}_2Y_2$ distorted cubic sites exist within large cavities of a stable $\text{BrX}_6$ octahedral framework (Subramanian et al., 1983; Chakoumakos, 1984). These large cavities are interconnected in three dimensions by channels, through which A- and Y-site ions can be removed in combinations that maintain overall charge balance.

Microlite also commonly exhibits slight to moderate increases in Mn and Fe during primary or secondary alteration. In the Harding microlite samples, values of $\Sigma A > 2.00$ atoms per formula unit require that essentially all of the Fe and part of the Mn incorporated during primary alteration to be located at the B site as $\text{Fe}^{3+}$ and $\text{Mn}^{3+}$ (Lumpkin et al., 1986). During secondary alteration, microlite may exhibit slight to moderate increases in the Ba content. A slight increase in Cs was noted in the barium-microlite sample from Brazil.

The exceptional stability of U in the A site results in part from the coordination geometry, where true leaching is restricted to cations of low formal valence. Removal of a $\text{U}^{4+}$ or $\text{U}^{6+}$ ion would be difficult to charge balance in combination with Y-site anions alone. Long-term loss of radiogenic Pb in microlite is supported by the work of Aldrich et al. (1958), who found that microlite samples from the Harding pegmatite give discordant U-Pb ages. The authors investigated two samples, one with 0.7 wt% U and 0.1 wt% Pb and another with 7.7 wt% U and 1.1 wt% Pb. Both gave $^{238}\text{U}-^{206}\text{Pb}$ and $^{235}\text{U}-^{207}\text{Pb}$ isotopic ages of 900–1000 m.y., consistent with loss of 20–30% of the radiogenic Pb.

**Conditions of alteration**

Members of the microlite subgroup show well-defined primary and secondary alteration in terms of both textural and chemical features. We suggest that this is related to the depth of emplacement of the host rocks. Most granitic pegmatites of the rare-element class are emplaced at depths of 4–12 km (Jahns, 1982; London, 1984; Černý, 1989; Chakoumakos and Lumpkin, 1990). Because of the small size of granitic pegmatites, the cooling rate is rapid in comparison with much larger granitic plutons. On the basis of cooling models for a finite slab with dimensions of $2 \times 2 \times 0.02$ km, Chakoumakos and Lumpkin (1990) estimated that the magmatic phase of the Harding pegmatite lasted only 100–1000 yr. Emplacement at relatively deep crustal levels means that subsequent hydrothermal activity will usually have ended long before granitic pegmatites reach the surface following uplift and erosion.

Primary alteration of microlite occurred during the late magmatic to hydrothermal stages of pegmatite emplacement at $P = 2–5$ kbar and $T = 350–550$ °C (cf. Chakoumakos and Lumpkin, 1990). Alteration is influenced by the presence and evolution of a dense silicate liquid and supercritical $\text{H}_2\text{O}-\text{CO}_2$-$\text{NaCl}_{aq}$ fluid rich in volatiles and fluxing elements such as F, Li, Be, B, P, Rb, and Cs (Jahns, 1982; London, 1986, 1987; Černý, 1989). Exchange reactions between microlite and fluid suggest conditions of relatively high pH, high $a_{\text{H}_2\text{O}}$, and low $a_{\text{Na}_2\text{O}}$, often accompanied by elevated $a_{\text{Mn}^{3+}}$ and $a_{\text{Fe}^{3+}}$. The requirement of $\text{Fe}^{3+}$ and $\text{Mn}^{3+}$ to occupy the B site in some of the Harding microlite samples suggests that relatively high $f_{\text{O}_2}$ conditions prevailed during alteration. This is supported by high $U^{4+}/U^{6+}$ ratios in microlite (Jahns and Ewing, 1976) and the incorporation of $\text{V}^{5+}$ and $\text{Bi}^{3+}$ in thorite during primary alteration (Lumpkin and Chakoumakos, 1988). Modeling of mineral reactions in the system Na-Ca-Mn-Ta-O-H indicates that if the increases in $a_{\text{Ca}^{2+}}$ and $a_{\text{Mn}^{3+}}$ proceed far enough, microlite will be replaced by rhenierite (or fersmite) and manganotantalite.

Secondary alteration is characteristic of near-surface conditions with $T < 100$ °C and $P < 1$ kbar. Alteration occurs in the presence of relatively large volumes of meteoric $\text{H}_2\text{O}$ and is mainly controlled by radiation-induced microfractures. Exchange reactions between microlite and meteoric $\text{H}_2\text{O}$ suggest conditions of relatively low $a_{\text{Ca}^{2+}}$, $a_{\text{Na}_2\text{O}}$, $a_{\text{H}_2\text{O}}$, and pH, resulting in leaching of Na, Ca, F, and O accompanied by hydration. In special circumstances, cations like Cs, Ba, or Pb may be picked up by meteoric $\text{H}_2\text{O}$ through dissolution of unstable silicate minerals and subsequently exchanged with microlite during secondary alteration.
CONCLUSIONS

This investigation shows that the microlite subgroup is a useful indicator of geochemical processes occurring at hydrothermal temperatures during the latter stages of pegmatite emplacement. Relative changes in fluid composition can be assessed through the use of tantalum oxide mineral associations, replacement reactions, intra-crystalline zoning patterns, and subsequent primary alteration effects.

Results of this study are also relevant to nuclear waste disposal using ceramic waste forms and show that pyrochlore structure types are susceptible to leaching of cations and anions at low temperatures. This effect may be enhanced by prior radiation damage and microfracturing. The next two papers in this series will address alteration effects in the pyrochlore and betafite subgroups, encompassing a broader range of compositions and geologic environments, including carbonatites and nepheline syenite pegmatites.

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REFERENCES CITED


ERRATUM

Manganese, ferric iron, and the equilibrium between garnet and biotite, by M. L. Williams and J. A. Grambling (v. 75, p. 886–908). The final term in Equations 12 and 13 should be negative. Also, the first term is slightly low due to rounding errors. The correct form of Equation 13 is

\[ T(K) = [-17368 - 79.5(P) + 1579 - \frac{W_{MgFe}(X_{alm} - X_{sep})}{W_{Fe^{2+}}} - 12550(X_{an}) - 8230(X_{w})] \]

\[ - R[\ln K_D - 0.782 - \ln(Fe^{2+}/Fe^{3+})^*] \]  

(13)

where \( K_D \) includes only Fe\(^{2+}\) and starred terms refer to the composition of the minerals in the calibration experiments. Note that, for clarity, the final term has been maintained as in Equation 12. Also, in Table 10, \( W_{MnMn}^{COO} \) should be changed to 7285, 20775, and 10031 for Models 1, 2, and 3, respectively.