

**Interim Report  
Task 2: Performance Testing—  
Task 2.4: Natural Mineral  
Analog Studies  
Performance and Chemical  
Characteristics of Brannerite  
in Natural Systems  
To Lawrence Livermore  
National Laboratory for  
Contract B345772**

*U.S. Department of Energy*

Lawrence  
Livermore  
National  
Laboratory

G. R. Lumpkin, M. Colella, and S. H. F. Leung

**April 30, 2000**

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This work was performed under the auspices of the U. S. Department of Energy, Lawrence Livermore National Laboratory under Contract W-7405-Eng.-48.



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**Physical and Chemical Characteristics of Brannerite in Natural  
Systems**

**to Lawrence Livermore National Laboratory for  
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GR Lumpkin, M Colella, and SHF Leung

30 April 2000

R00m023

Australian Nuclear Science and Technology Organisation  
Private Mail Bag 1, Menai, NSW 2234

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Commercial-In-Confidence

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DATE ISSUED  
**30 April 2000**

ISSUED TO  
**Lawrence Livermore National Laboratory**

REPORT NUMBER  
**R00m023**

JOB NUMBER  
**709m**

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COMMERCIAL-IN-CONFIDENCE

# Physical and Chemical Characteristics of Brannerite in Natural Systems

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## Summary

To investigate the long-term alteration behavior of brannerite, we have undertaken a study of 13 natural samples from various geological environments, including granites, granitic pegmatites, quartz veins, and placer deposits. Literature data and U-Th-Pb chemical dating carried out in this work indicate that the samples range in age from approximately 20 Ma to 1580 Ma. Where independent age data or estimates are available for comparison, the U-Th-Pb chemical ages are in reasonable agreement for the younger samples, but the older samples tend to show evidence for Pb loss (up to about 80%), a common feature of metamict Nb, Ta, and Ti oxide minerals. Our results show that many of the samples exhibit only minor alteration, usually within small patches, microfractures, or around the rims of the brannerite crystals. Other samples consist of variable amounts of unaltered and altered brannerite. Heavily altered samples may contain anatase and thorite as fine-grained alteration products. Certain samples exhibited fracturing of the associated rock matrix or mineral phase in the immediate vicinity of the brannerite grains. These fractures contain U bearing material and indicate that some U migrated locally from the source brannerite.

The following composition ranges were determined for the unaltered brannerite: 36-43 wt% TiO<sub>2</sub>, 30-58 wt% UO<sub>2</sub>, 0-15 wt% ThO<sub>2</sub>, 0-7 wt% CaO, and 0-7 wt% PbO. Additional minor constituents include up to 1.8 wt% Nb<sub>2</sub>O<sub>5</sub>, 2.3 wt% SiO<sub>2</sub>, 1.2 wt% Al<sub>2</sub>O<sub>3</sub>, 4.2 wt%

Y<sub>2</sub>O<sub>3</sub>, 3.5 wt% Ln<sub>2</sub>O<sub>3</sub> (Ln = Ce, Nd, Sm, Gd), 0.6 wt% MnO, 2.6 wt% FeO, and 0.7 wt% NiO. SEM-EDX analyses of unaltered areas indicate that the chemical formulae may deviate from the ideal stoichiometry. The U content ranges from 0.45 to 0.88 atoms per formula unit (pfu). Maximum amounts of the other major cations on the U-site are 0.50 Ca, 0.22 Th, 0.14 Y, and 0.08 Ln (lanthanide = Ce, Nd, Gd, Sm) atoms pfu. The Ti content ranges from 1.86 to 2.10 atoms pfu. Maximum values of other cations on the Ti-site are 0.15 Fe, 0.14 Si, 0.09 Al, 0.06 Nb, 0.04 Mn, and 0.04 Ni atoms pfu. Total cations commonly exceed 3.00 based on 6.00 oxygens, indicating that much of the U is present in a higher valence state than the assumed 4+ value. However, for the natural samples incorporation of OH for oxygen provides another possible explanation for high cation totals. This alternative should be investigated further, especially considering that we found some evidence in support of the incorporation of water (of unknown speciation) in natural brannerite.

The following composition ranges of the altered brannerite were determined: 36-82 wt% TiO<sub>2</sub>, 1-57 wt% UO<sub>2</sub>, 0-20 wt% ThO<sub>2</sub>, 0-5 wt% CaO, and 0-17 wt% PbO. Additional constituents include up to 6.3 wt% P<sub>2</sub>O<sub>5</sub>, 7.0 wt% As<sub>2</sub>O<sub>5</sub>, 2.6 wt% Nb<sub>2</sub>O<sub>5</sub>, 18 wt% SiO<sub>2</sub>, 5.9 wt% Al<sub>2</sub>O<sub>3</sub>, 1.8 wt% Y<sub>2</sub>O<sub>3</sub>, 3.6 wt% Ln<sub>2</sub>O<sub>3</sub>, 0.4 wt% MnO, and 16 wt% FeO. Altered regions of brannerite contain significant amounts of Si and other elements (e.g., P, As, and Fe) incorporated from the fluid phase, and up to about 95% by weight of the original amount of U has been lost as a result of alteration.

Electron diffraction patterns of all samples typically consist of two broad, diffuse rings that have equivalent d-spacings of 0.31 nm and 0.19 nm, indicating complete amorphization of the brannerite. Many of the grains also exhibit weak diffraction spots due to fine-grained inclusions of a uranium oxide phase and galena. Using the available age data, these samples have average accumulated alpha-decay doses of 2-170 x 10<sup>16</sup> alphas/mg. An approximate critical dose of 1-2 x 10<sup>16</sup> alphas/mg is estimated from this work. This dose is similar to that of relatively young natural pyrochlore and zirconolite samples. Our results indicate that brannerite is subject to amorphization and may lose U under certain P-T-X conditions, but the overall durability of the titanate matrix remains high as indicated by the occurrence of the mineral in placer deposits.

## 1. Introduction

Brannerite, ideally  $\text{UTi}_2\text{O}_6$ , is a common accessory phase in Synroc formulations designed for the encapsulation of actinide-rich, Pu-bearing nuclear wastes (e.g., Ebbinghaus et al., 1998). Even though brannerite is a minor phase in these ceramics, the pure end-member composition contains 62.8 wt%  $\text{UO}_2$ , therefore it may account for a significant fraction of the total amount of actinides in the waste form. To ensure that the presence of brannerite does not compromise the integrity of the waste form, a combination of laboratory experiments and natural analogue studies have been undertaken to assess both the aqueous durability and the radiation damage effects of this phase (e.g., Vance et al., 1999; Zhang et al., 1999).

In this report, we provide a summary of the compositional and structural results for a suite of 13 natural brannerite samples from several different localities, covering a range of geological ages and host rock environments. Samples have been characterized using optical microscopy, X-ray diffraction (XRD), scanning electron microscopy and microanalysis (SEM-EDX), and transmission electron microscopy (TEM). The results of these analyses are used to make a qualitative assessment of the chemical composition, aqueous durability, and radiation damage susceptibility of brannerite. The report concludes with a comparison of the behavior of brannerite, pyrochlore, and zirconolite in natural systems.

## 2. Experimental Procedures

### 2.1 Scanning Electron Microscopy and Microanalysis

SEM-EDX work was carried out on polished sections using a JEOL JSM-6400 SEM equipped with a Noran Voyager Si(Li) microanalysis system and operated at 25 kV for microanalysis and 15 kV for secondary and backscattered electron (BSE) imaging. EDX spectra were acquired for 500 seconds and processed using Noran Voyager software using digital top hat filtering of the background, multiple least squares peak fitting of library spectra, and full matrix corrections. The relative concentrations of all elements are reasonably accurate due to the optimization of correction parameters using a large collection of standards, including synthetic brannerite. EDX spectra were obtained from unaltered brannerite, altered brannerite, and associated mineral inclusions or alteration products.

## 2.2 Transmission Electron Microscopy

TEM work was performed on crushed fragments dispersed on holey carbon grids using a JEOL 2000FXII TEM equipped with a Link ISIS Si(Li) microanalysis system and operated at 200 kV. The instrument was calibrated for selected area diffraction (SAD) work over a range of objective lens currents with a gold standard. The chemistry of the brannerite fragments and mineral inclusions were checked by EDX. Spectra were acquired for 600 seconds live time (25-35% deadtime, 700-900 counts per second) and processed with the Link software package TEMQuant using previously established procedures (Lumpkin et al., 1994b).

## 3. Brannerite in Natural Systems

### 3.1 Geological Occurrence

The samples used in this study occur in a variety of host rocks (see Table 1). The most common host rocks are granites, granitic pegmatites, and quartz veins. Samples from the Swiss Alps primarily occur in relatively late granitic pegmatites in the Ticino region. These igneous rocks are generally intruded as dikes and consist of quartz, feldspars, and micas as the main minerals (Bianconi and Simonetti, 1967). Many rare element minerals occur in these highly fractionated rocks. Brannerite typically occurs in these rocks as small single crystals or groups of crystals enclosed in quartz or K-feldspar together with minor amounts of rutile and scheelite. In the French Alps, brannerite has been reported from Au bearing quartz veins at La Gardette, near Bourg d' Oisans (Geffroy, 1963). Here again, the brannerite occurs as individual bladed crystals or as groups of crystals enclosed within quartz.

Granitic pegmatites are also the source of brannerite in the Sierra Albarrana region of Spain (Perez et al., 1991). The pegmatites occur within Late Precambrian metamorphic rocks, mainly gneisses, banded migmatites, and schists and consist mainly of feldspars, micas, quartz, tourmaline, fluorapatite, and some garnet. Accessory minerals in these pegmatites include beryl, chrysoberyl, uraninite, monazite, xenotime, allanite, zircon, and columbite group minerals. Brannerite is generally associated with quartz in the internal zones of the pegmatite dikes and may be altered to anatase and sphene (Perez et al., 1991).

Brannerite samples from Crocker's Well, South Australia, are associated with late tectonic, plagioclase feldspar rich, granitoid intrusions of Precambrian age (Ludwig and Cooper, 1984). Major minerals of the granitic rocks include plagioclase, quartz, and K-feldspar. Here, the brannerite occurs as an accessory mineral in the granitic rocks, particularly in shear zones and fractures, and is usually associated with rutile. The thermal history of these rocks is not simple, as they were subjected to amphibolite grade regional metamorphism during the Early Ordovician (Ludwig and Cooper, 1984). Apart from the low temperature brannerite ore deposits, reports on other brannerite localities are generally sparse. Additional information on brannerite from Mono County, California was given by Pabst (1954), and in this paper the author also gives some background information and new data on the brannerite samples from Idaho and Morocco.

### 3.2 Age Data

Available data from the literature indicate that the brannerite samples range in age from approximately 10-25 Ma to 1580 Ma (see Table 2). This age range is comparable to the suites of natural pyrochlores and zirconolites studied previously, providing a good starting point for a comparison of the geochemical alteration and radiation damage effects. The youngest samples are from Alpine rocks of Switzerland and France. Samples from Switzerland occur in granitic pegmatites of the Ticino region and have reasonably well established ages (Graeser and Guggenheim, 1990). At this stage, we do not have definitive data on the age of the French sample; however, reports in the literature suggest an upper limit of 5-60 Ma based on chemical U-Pb dating (Geffroy, 1963) and a lower limit of about 10 Ma from Ar-Ar data (Marshall et al., 1998). In fact, what is apparently the youngest known crystal of brannerite was described by Graeser and Guggenheim (1990) from a locality near Binntal, Switzerland (see Tables 1 and 2). Although not available for research, the available data for this crystal indicate that it is partially crystalline, providing an extremely important reference point for the radiation damage studies.

In the absence of specific data, we have referred to the geological information compiled by Condie (1976) for some of the age estimates, including the assumed Laramide age for the

sample from Idaho and the Pan African age for the sample from Zambia. We do not have a reliable age for the sample from Morocco at this time; however, a literature search may provide useful information as this brannerite comes from a fairly well known locality. The brannerite sample from California is probably associated with Mesozoic igneous rocks of southern California (cf., Pabst, 1954). The samples from Spain occur in Late Precambrian rocks (Perez et al., 1991), although precise age data are not available. The oldest samples in our collection are from Crocker's Well, South Australia. In this case, the host rocks have a well defined age of 1580 Ma based on U-Th-Pb isotopic age dating of zircon (Ludwig and Cooper, 1984).

Younger samples from Ticino, Switzerland give chemical U-Pb ages (determined by SEM-EDX) that are consistent with the known ages of the pegmatite host rocks of the region. The U-Pb age of the sample from France is consistent with the age of the Swiss samples, in terms of their formation as late stage Alpine events. Other samples from Idaho and California also give chemical U-Pb ages that are in reasonable agreement with the estimated host rock ages. In contrast, brannerites from the older localities generally have chemical U-Pb ages that are younger than the ages of the host rocks, consistent with Pb loss from the relatively unaltered areas of the samples. In the case of the samples from Crocker's Well, this conclusion is supported by the U-Th-Pb isotopic ages of 550-670 Ma determined on two brannerite samples by Ludwig and Cooper (1984). The chemical U-Pb ages determined by SEM-EDX analysis of the unaltered areas of our samples indicate radiogenic Pb loss on the order of 8-78%, possibly increasing with age (see Table 2).

### 3.2 Sample Description

Optical microscopy and SEM-EDX work revealed that many of the samples are either unaltered or exhibit only minor alteration. In these cases, the alteration is usually confined within irregular patches, narrow veinlets, or around the rim of the sample. Typical examples are shown in Figure 2, Figures 4-9, and Figure 13. In these examples, the alteration always has a lower gray level in the BSE image relative to the unaltered brannerite, indicating a lower mean atomic number in the altered areas. This effect could be the result of U loss, hydration,

introduction of light elements, or a combination of all three. Qualitative SEM-EDX confirmed the U loss and also showed that Si is often present in the altered areas. Certain samples from California and Switzerland appear to be free of alteration (see Figures 7 and 9). Another sample from Switzerland (Figure 12, bottom) showed alteration only at a high contrast setting of the BSE detector, suggesting that elemental changes between the unaltered and altered areas are minor (see Section 5). This was confirmed by qualitative SEM-EDX analysis. This type of alteration is probably due to hydration as documented previously in minerals of the pyrochlore group (Lumpkin and Ewing, 1996; Lumpkin et al., 1999).

The remaining samples consist of variable amounts of unaltered and altered brannerite. Alteration typically follows microfractures into the interior of the brannerite (e.g., Figures 3, 10, 11, and 13). Some samples exhibit variation in the BSE contrast of the altered material (Figures 3 and 11), indicating that elemental concentration gradients may exist within the altered zones. In an advanced stage of alteration, a large proportion of the brannerite is affected and other secondary phases may be present. Sample B1, from Crocker's Well, South Australia, provides the best example of this advanced level of geochemical alteration. As shown in Figure 1, a large proportion of this sample altered and fine-grained (10-50  $\mu\text{m}$ ) anatase and thorite are present; presumably both of these minerals formed as a result of alteration of the host brannerite. Two other samples from Crocker's Well were examined and are not as severely altered as sample B1. This result is consistent with observations made by Ludwig and Cooper (1984), who found that the color of brannerite changed from black at deeper levels to olive-brown nearer to the ground surface at Crocker's Well.

Another important result from the SEM work is the observation of microfracturing of the associated rock matrix or intergrown mineral phases. In the heavily altered sample from Crocker's Well (Figure 1, top), the associated primary rutile exhibits several microfractures that are filled with a U rich secondary phase (or phases). A similar observation was made for sample B8 from Morocco (Figure 8). In this case, the quartz matrix is heavily fractured in the vicinity of the enclosed brannerite crystals and the fractures are filled with a U bearing material. To date, only qualitative EDS has been performed on these fracture-hosted alteration products, so the exact mineralogy is not known at this time. However, the results

give a clear indication of local transport of U away from the source brannerite during alteration. A third example of microfracturing of the rock matrix was observed in sample B12 from Switzerland (Figure 12, top), but in this sample the microfractures are largely barren, consistent with the low level of chemical alteration noted above. Finally, we note that primary compositional zoning is not a major feature of natural brannerite and was only observed in two samples (see Figures 2 and 6).

#### 4. Chemical Composition

Average compositions of relatively unaltered areas of each brannerite sample are given in Table 3 (assuming all Fe is Fe<sup>2+</sup> and all U is U<sup>4+</sup>). Individual analyses are listed in Appendix 1 for each sample, including the average, range, and standard deviation on the mean of the analyses. The following composition ranges of the unaltered brannerite were determined based on 5-10 analyses of each sample: 36-43 wt% TiO<sub>2</sub>, 30-58 wt% UO<sub>2</sub>, 0-15 wt% ThO<sub>2</sub>, 0-7 wt% CaO, and 0-7 wt% PbO. Additional minor constituents include up to 1.8 wt% Nb<sub>2</sub>O<sub>5</sub>, 2.3 wt% SiO<sub>2</sub>, 1.2 wt% Al<sub>2</sub>O<sub>3</sub>, 4.2 wt% Y<sub>2</sub>O<sub>3</sub>, 3.5 wt% Ln<sub>2</sub>O<sub>3</sub> (Ln = Ce, Nd, Sm, Gd), 0.6 wt% MnO, 2.6 wt% FeO, and 0.7 wt% NiO. As expected from the crystal structure of brannerite, Na<sub>2</sub>O is consistently near or below the detection limit of approximately 0.1 wt%. This is primarily due to the ionic radius of Na<sup>+</sup> (1.02 Å) being significantly larger than that of U<sup>4+</sup> (0.89 Å).

SEM-EDX analyses show that the chemical formula of relatively unaltered, natural brannerite may deviate considerably from the ideal UTi<sub>2</sub>O<sub>6</sub> stoichiometry. The U content ranges from 0.45 to 0.88 atoms pfu. Maximum amounts of the other major cations on the U-site are 0.50 Ca, 0.22 Th, 0.14 Y, and 0.08 Ln atoms pfu. The Ti content ranges from 1.86 to 2.13 atoms per 6 oxygens. Maximum values of the other cations on the Ti-site are 0.15 Fe, 0.14 Si, 0.09 Al, 0.06 Nb, 0.04 Mn, and 0.04 Ni atoms pfu. Total cations commonly exceed the ideal value of 3.00 (range = 3.02-3.36) when normalized to 6.00 oxygens, indicating that all of the Fe is probably in the 3+ state and that a significant amount of the U must also be in a higher valence state than the assumed 4+ value. These results are generally consistent with previous chemical analyses of natural brannerite for which UO<sub>2</sub> and UO<sub>3</sub> were determined

(see Pabst, 1954; Bianconi and Simonetti, 1967). Recent synthesis work also shows that up to 0.3 atoms per formula unit of Ca or Gd can be substituted for U in brannerites fired in air or Ar at 1350-1450°C (Vance et al., 1999). Diffuse reflectance spectroscopy carried out by Vance et al. (1999) indicates that some U is present as  $U^{5+}$ , thereby providing a charge-balancing mechanism for incorporation of Ca and Gd. However, another possibility that remains to be investigated is the possible incorporation of OH groups for oxygen.

## 5. Geochemical Alteration

Average compositions of altered areas of brannerite determined by SEM-EDX are given in Table 4. Individual analyses are listed in Appendix 2. Please note that all analyses are automatically normalized to a total of 100 wt% by the Noran software, so we cannot comment on the possible level of hydration using analytical totals as a guide. The following composition ranges of the altered brannerite were determined based on 5-15 analyses of each sample: 36-82 wt%  $TiO_2$ , 1-57 wt%  $UO_2$ , 0-20 wt%  $ThO_2$ , 0-5 wt%  $CaO$ , and 0-17 wt%  $PbO$ . Additional constituents include up to 6.3 wt%  $P_2O_5$ , 7.0 wt%  $As_2O_5$ , 2.6 wt%  $Nb_2O_5$ , 18 wt%  $SiO_2$ , 5.9 wt%  $Al_2O_3$ , 1.8 wt%  $Y_2O_3$ , 3.6 wt%  $Ln_2O_3$ , 0.4 wt%  $MnO$ , and 16 wt%  $FeO$ . As in the unaltered brannerite,  $Na_2O$  is also consistently near or below the detection limit of approximately 0.1 wt% in the altered areas.

Considering the ranges of altered compositions documented thus far, in the most heavily altered samples, up to 95% (by weight) of the original amount of  $UO_2$  was lost as a result of alteration. The observed U loss is compensated in part by incorporation of large amounts of Si and other elements from the attending fluid phase, including Al, P, Fe, As, and possibly Pb. During alteration, Y is also typically removed from the altered brannerite, but the behavior of Ca and Ln are more erratic and these elements may be either lost or gained. The range of compositions observed is entirely consistent with the variation in gray levels seen in the BSE images of altered brannerite. Furthermore, the quantitative evidence for U loss is consistent with the observation of U rich material located within fractures extending into the host rock matrix in two of the natural brannerite samples.

Although we have ample evidence for the chemical alteration of brannerite, there is very little direct evidence for corrosion or dissolution of the brannerite matrix. The crystals available for this investigation generally do not show extensive replacement features or morphological indicators of corrosion (e.g., serrated crystal rims, overgrowths, etc.). This result is consistent with studies of the processing of U ores which show that brannerite is highly resistant to dissolution in acidic fluids (e.g., Ifill et al., 1996). Under alkaline conditions, on the other hand, brannerite may be less resistant to dissolution (Szymanski and Scott, 1982).

## **6. Radiation Damage Effects**

Electron diffraction patterns obtained from relatively unaltered areas of all of the brannerite samples typically consist of two broad, diffuse rings characteristic of amorphous materials (representative patterns are shown in Figures 14, 16, 18, 20, 24, and 25). The diffuse rings have equivalent d-spacings of 3.1Å and 1.9Å, similar to those of many other metamict oxides and certain silicate minerals (Headley et al., 1981; Ewing and Headley, 1983; Lumpkin and Ewing, 1988; Lumpkin, 1992; Lumpkin et al., 1986, 1994a, 1998). Bright field images of these grains are typically featureless (Figures 15, 17, 19, 21, 24, and 25), consistent with the absence of long-range periodicity. None of the samples examined by TEM showed the presence of significant crystalline domains of brannerite, even though some of the samples are geologically young. Furthermore, the amphibolite grade thermal event (temperatures of 500-650°C are typical) experienced by the samples from Crocker's Well was insufficient to restore crystallinity in these geologically old brannerite samples.

Some of the grains in sample B4 from the Western Province of Zambia were found to contain 10-200 nm sized spherical voids (Figure 21), similar to previous observations on metamict zirconolite and columbite (Ewing and Headley, 1983; Lumpkin, 1992). These voids have been attributed to the accumulation of radiogenic He in the sample over time. Many of the samples examined thus far also exhibit weak diffraction spots in SAD patterns taken from certain grains (Figures 22 and 24). In most cases, the diffraction spots appear to be due to the presence of fine grained (generally 5-100 nm sized) inclusions of a uranium oxide phase and

galena (Figures 23 and 24). Preliminary TEM results are now available for altered areas of brannerite sample B12. Diffraction patterns and bright field images (Figure 26) of the altered material demonstrate that it consists of a mixture of both crystalline and amorphous material as shown by the presence of diffraction spots and diffuse rings, respectively. Measurement of d-spacings from the crystalline component does not provide a straightforward phase identification; however, the best match appears to be brookite with some anatase and possible galena. The bright field image of Figure 26 indicates that the crystallite dimensions are on the order of 50 nm or less.

Based on the Th and U contents and either the known age or the chemical U-Pb age determined by SEM-EDX (Table 2), the brannerites examined in this work have average calculated alpha-decay doses of  $2\text{--}170 \times 10^{16} \alpha/\text{mg}$ . Unfortunately, the critical amorphization dose ( $D_c$ ) cannot be determined from these samples because none of the grains retained crystallinity, even the geologically young samples. However, using literature data given in Tables 1 and 2 for a partially crystalline brannerite from Binntal, Switzerland (Graeser and Guggenheim, 1990), the critical dose appears to be close to  $1\text{--}2 \times 10^{16} \alpha/\text{mg}$ . The current data set for brannerite is shown in Figure 27. For comparison (see Figures 27), natural pyrochlores and zirconolites with ages of 100 Ma or less become amorphous at doses of approximately  $1 \times 10^{16} \alpha/\text{mg}$  (Lumpkin and Ewing, 1988; Lumpkin et al., 1994a, 1998).

## **7. Comparison with Perovskite, Pyrochlore, and Zirconolite**

The new data for natural brannerite allow us to establish a relative ranking of the durability of several actinide host phases in natural systems. In terms of total matrix dissolution, studies of natural samples indicate that the durability of the minerals increases in the order perovskite  $\ll$  brannerite  $\leq$  pyrochlore  $\leq$  zirconolite. The alteration of perovskite to anatase and other phases in natural systems is well known (e.g., Mariano, 1989; Banfield and Veblen, 1992; Lumpkin et al., 1998; Mitchell and Chakmouradian, 1998; Chakmouradian et al., 1999). In the carbonatite intrusive complexes of Brazil, for example, perovskite completely breaks down to anatase during severe weathering of the host rock. In certain cases, the lanthanide elements released upon dissolution of the host perovskite may be

retained locally within fine-grained secondary minerals such as phosphate minerals of the crandallite group, cerianite, and monazite (Mariano, 1989). Perovskite is also known to breakdown at higher temperatures and a number of alteration products have been identified (e.g., Mitchell and Chakmouradian, 1998). Furthermore, loparitic perovskites (loparite = end-member  $\text{Na}_{0.5}\text{Ln}_{0.5}\text{TiO}_3$ ) often exhibit chemical alteration to "metaloparite" by a process of cation leaching, hydration, and ion exchange between loparite and a hydrothermal fluid, probably at temperatures of approximately 400°C or lower (Lumpkin et al., 1998; Chakmouradian et al., 1999).

Brannerite, pyrochlore, and zirconolite, on the other hand, are known to survive the complete destruction of their host rocks during weathering. For example, the brannerite samples from Idaho occur in a placer deposit and have survived the weathering and breakdown of their host rocks with minimal dissolution of the original crystals. Pyrochlores, although subject to chemical alteration (see below), are also known to survive weathering and breakdown of their host rocks and in some cases the crystals are concentrated to ore grade in laterite deposits (Deans, 1966; Mariano, 1989). Some of these deposits are found overlying carbonatite intrusions in Brazil and formed under similar conditions to those where perovskite dissolved. Perhaps the best specimens of zirconolite known to man were obtained from the famous placer deposits of Sri Lanka. This occurrence demonstrates that zirconolite also survives the weathering process with minimal dissolution. Oversby and Ringwood (1981) have demonstrated that these crystals remained closed in terms of the U-Th-Pb isotopic systematics. Furthermore, electron microscopy investigations have failed to show evidence for chemical alteration in these zirconolites, in spite of the fact that they have alpha-decay doses up to approximately  $10^{17}$   $\alpha/\text{mg}$  and are completely metamict (Ewing et al., 1982; Lumpkin et al., 1986, 1994b).

Brannerite, pyrochlore, and zirconolite are susceptible to chemical alteration in certain geological environments. As described in this study, brannerite is susceptible to chemical alteration by ion exchange with the fluid phase and typically loses U and gains Si and other elements in the process. Several studies over the previous 15 years have now shown that pyrochlore group minerals are subject to chemical alteration by ion exchange and hydration in

a range of geological environments (Lumpkin and Ewing, 1985, 1995, 1996; Lumpkin et al., 1994a; Lumpkin and Mariano, 1996). The alteration process generally involves exchange of A-site cations (Na, Ca), Y-site anions (F, O), and sometimes X-site anions (O) with the attending fluid phase. These elemental losses may be offset to some extent by the incorporation of K, Sr, Ba, Pb, and H ions from the fluid. The end result is a hydrated, defect pyrochlore, but there is only limited evidence for loss of Th and U (e.g., Lumpkin and Ewing, 1996). In contrast, chemical alteration of natural zirconolite is relatively uncommon and the Th and U contents remain more or less constant (Lumpkin et al., 1994a). Limited corrosion of zirconolite has been documented in a natural hydrothermal vein system at temperatures of 500-600°C by a relatively acidic aqueous fluid with significant concentrations of H<sub>2</sub>S, HF, and HCl (Gieré and Williams, 1992). Complete replacement of zirconolite by zircon + sphene + rutile has been observed in metamorphic systems only at very high temperatures of 620-680°C (Pan, 1997). Several other examples of zirconolite alteration have been summarized by Hart et al. 1998, but none of these appear to involve significant losses of actinide elements.

## 8. Conclusions

This study has provided some of the first in depth results on the chemical composition, geochemical alteration, and alpha-decay damage effects of natural brannerites. The main conclusions of this work are summarized here in outline form:

- The U content of natural brannerite is quite variable and U can be replaced by significant amounts of Ca, Th, Y, and lanthanides.
- The Ti content is less variable, with minor replacement of Ti by Fe, Si, Al, Nb, Mn, and Ni.
- Calculated formulae based on 6 oxygen atoms suggest that some of the U may be present in a higher valence state.
- There is little evidence for corrosion or dissolution of the brannerite matrix. Comparison with other minerals indicates that the matrix durability increases in the order perovskite << brannerite ≤ pyrochlore ≤ zirconolite.

- Brannerite is subject to chemical alteration with preferential loss of U, compensated in part by uptake of Al, Si, P, Fe, As, and other minor elements from the fluid phase.
- In terms of chemical alteration and U loss, comparison with other minerals indicates that chemical durability increases in the order brannerite < pyrochlore < zirconolite.
- Secondary alteration products may include anatase and thorite at an advanced stage of alteration.
- Brannerite is subject to amorphization by alpha-decay damage processes. The critical amorphization dose is approximately  $1\text{--}2 \times 10^{16} \alpha/\text{mg}$ , slightly higher than the  $D_c$  values of natural pyrochlore and zirconolite.

### **Acknowledgements**

We are grateful to Mark Blackford and Arthur Day for assistance with the electron microscopy and maintenance of the transmission and scanning electron microscopes. Samples used in this study were kindly provided by Carl Francis (Harvard University), Ross Pogson (The Australian Museum), Terry Williams (The British Museum), Nicolas Meisser (Museum of Geology, Lausanne), and Volkmar Trommsdorff (ETH Zürich).

### **References Cited**

- Banfield, J.F. and Veblen, D.R., *Amer. Mineral.* **77**, 545 (1992).
- Bianconi, F. and Simonetti, A., *Schweiz. Mineral. Petrogr. Mitt.* **47**, 887 (1967).
- Chakhmouradian, A.R., Mitchell, R.H., Pankov, A.V., and Chukanov, N.V., *Mineral. Mag.* **63**, 519 (1999).
- Condie, K.C., *Plate Tectonics and Crustal Evolution*, Pergamon Press, New York, 1976.
- Deans, T., in: *Carbonatites*, edited by O.F. Tuttle and J. Gittins (John Wiley, New York, 1966), pp. 385-416.

- Ebbinghaus, B.B., Van Konynenburg, R., Ryerson, F.J., Vance, E.R., Stewart, M.W.A., Jostsons, A., Allender, J.S., Rankin, T., and Congdon, J., Waste Management '98, Tucson, AZ, 1998, Proceedings on CD-ROM.
- Ewing, R.C. and Headley, T.J., *J. Nucl. Mater.* **119**, 102 (1983).
- Ewing, R.C., Haaker, R.F., Headley, T.J., and Hlava, P.F., in: *Scientific Basis for Nuclear Waste Management V*, edited by S.V. Topp (Elsevier, New York, 1982) pp.249-256.
- Geffroy, J., *Bull. Soc. Fr. Minéral. Cristallogr.* **86**, 129 (1963).
- Gieré, R. and Williams, C.T., *Contrib. Mineral. Petrol.* **112**, 83 (1992).
- Graeser, S. and Guggenheim, R. *Schweiz. Mineral. Petrogr. Mitt.* **70**, 325 (1990).
- Hart, K., Mitamura, H., Vance, E., Banba, T., and Lumpkin, G., Final Report, Japan-Australia Co-operative Program on Research and Development of Technology for the Management of High Level Radioactive Wastes, 1985 to 1998 (ANSTO/E736, 1998).
- Headley, T.J., Ewing, R.C., and Haaker, R.F., *Nature* **293**, 449 (1981).
- Ifill, R.O., Cooper, W.C., and Clark, A.H., *CIM Bulletin* **89**, 93 (1996).
- Ludwig, K.R. and Cooper, J.A., *Contrib. Mineral. Petrol.* **86**, 298 (1984).
- Lumpkin, G.R., *J. Nucl. Mater.* **190**, 302 (1992).
- Lumpkin, G.R. and Ewing, R.C., in: *Scientific Basis for Nuclear Waste Management VIII*, edited by Jantzen C.M., Stone J.A. and Ewing R.C (Mater. Res. Soc. Proc. 44, Pittsburgh, 1985) pp. 647-654.
- Lumpkin, G.R. and Ewing, R.C., *Phys. Chem. Minerals* **16**, 2 (1988).
- Lumpkin, G.R. and Ewing, R.C., *Amer. Mineral.* **80**, 732 (1995).
- Lumpkin, G.R. and Ewing, R.C., *Amer. Mineral.* **81**, 1237 (1996).
- Lumpkin, G.R., and Mariano, A.N., in: *Scientific Basis for Nuclear Waste Management XIX*, edited by W.M. Murphy and D.A. Knecht (Mater. Res. Soc. Proc. 412, Pittsburgh, 1996) pp. 831-838.
- Lumpkin, G.R., Colella, M., Smith, K.L., Mitchell, R.H., and Larsen, A.O., in: *Scientific Basis for Nuclear Waste Management XXI*, edited by I.G. McKinley and C. McCombie (Mater. Res. Soc. Proc. 506, Pittsburgh, 1998) pp. 207-214.

- Lumpkin, G.R., Day, R.A., McGlinn, P.J., Payne, T.E., Gieré, R., and Williams, C.T., in: Scientific Basis for Nuclear Waste Management XXII, edited by D.J. Wronkiewicz and J.H. Lee (Mater. Res. Soc. Proc. 556, Pittsburgh, 1999) pp. 793-800.
- Lumpkin, G.R., Ewing, R.C., Chakoumakos, B.C., Gregor, R.B., Lytle, F.W., Foltyn, E.M., Clinard, F.W. Jr., Boatner, L.A., and Abraham, M.M., J. Mater. Res. **1**, 564 (1986).
- Lumpkin, G.R., Hart, K.P., McGlinn, P.J., Payne, T.E., Gieré, R., and Williams, C.T., Radiochim. Acta **66/67**, 469 (1994a).
- Lumpkin, G.R., Smith, K.L., Blackford, M.G., R. Gieré, R., and Williams, C.T., Micron **25**, 581 (1994b).
- Lumpkin, G.R., Smith, K.L., Blackford, M.G., Gieré, R., and Williams, C.T., in: Scientific Basis for Nuclear Waste Management XXI, edited by I.G. McKinley and C. McCombie (Mater. Res. Soc. Proc. 506, Pittsburgh, 1998) pp. 215-222.
- Mariano, A.N., in: Geochemistry and Mineralogy of Rare Earth Elements, edited by B.R. Lipin and G.A. McKay (Mineralogical Society of America, Washington, D.C., 1989) pp. 309-348.
- Marshall, D.D., Meisser, N., and Taylor, R.P., Mineral. Petrol. **62**, 147 (1998).
- Mitchell, R.H. and Chakhmouradian, A.R., Can. Mineral. **36**, 939 (1998).
- Oversby, V.M. and Ringwood, A.E., Rad. Waste Manage. **1**, 289 (1981).
- Pabst, A., Amer. Mineral. **39**, 109 (1954).
- Pan, Y., Can. Mineral. **35**, 105 (1997).
- Perez, B.C., Gonzalez, J., and Gonzalez, J., Los Minerales y la Minería de la Sierra Albarrana y su Entorno, Fundacion Enresa, Madrid, 1991.
- Szymanski, J.T. and Scott, J.D., Can. Mineral. **20**, 271 (1982).
- Vance, E.R., Watson, J.N., Carter, M.L., Day, R.A., Lumpkin, G.R., Hart, K.P., Zhang, Y., McGlinn, P.J., Stewart, M.W.A., and Cassidy, D.J., Proceedings of the 102<sup>nd</sup> American Ceramic Society Annual Meeting, Indianapolis, IN, 1999, in press.
- Zhang, Y., Lumpkin, G., Hart, K., and Day, R., Seventh International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '99, Lake Tahoe, NV, 1999 (unpublished).



**Table 1.** Localities, host rocks, and mineral associations of natural brannerite.

| Locality                | Samples   | Host rock          | Mineral associations          |
|-------------------------|-----------|--------------------|-------------------------------|
| Crocker's Well, SA      | B1, 5, 6  | granite            | quartz, feldspars, rutile     |
| Cordoba, Spain          | B3, 10    | granitic pegmatite | quartz, feldspars, muscovite  |
| W. Province, Zambia     | B4        | U ore deposit?     | not determined                |
| San Bernardino Co., CA  | B7        | granite?           | quartz, albite, biotite, etc. |
| Bou-Azzer, Morocco      | B8        | quartz veins       | quartz, sulfides, clays       |
| Stanley, Idaho          | B11       | placer deposit     | unknown                       |
| Ticino, Switzerland     | B2, 9, 12 | granitic pegmatite | quartz, feldspars, muscovite  |
| Bourg d' Oisans, France | B13       | quartz veins       | quartz                        |
| Binntal, Switzerland*   | -----     | dolomite marble    | dolomite, sartorite           |

\*See Graeser and Guggenheim (1990), there is only one crystal from this locality, formed by hydrothermal alteration of the dolomite host rock.

**Table 2.** A summary of the available age data for natural brannerite.

| Locality                | Nominal age (Ma) | Chemical age (Ma) | Comments         |
|-------------------------|------------------|-------------------|------------------|
| Crocker's Well, SA      | 1580             | 340-690           | Pb loss (56-78%) |
| Cordoba, Spain          | 600-800          | 360-480           | Pb loss (20-55%) |
| W. Province, Zambia     | 500-700          | 460               | Pb loss (8-34%)  |
| San Bernardino Co., CA  | 65-225?          | 190               | concordant?      |
| Bou-Azzer, Morocco      | unknown          | 170               |                  |
| Stanley, Idaho          | 40-80            | 70                | concordant       |
| Ticino, Switzerland     | 20-25            | 20-30             | concordant       |
| Bourg d' Oisans, France | 10-50            | 25                | concordant       |
| Binntal, Switzerland*   | 11               | n.a.              | n.a.             |

\*See Graeser and Guggenheim (1990) and references therein. The mineralization is much younger than the age of the dolomite host rock (Triassic, 190-225 Ma).

**Table 3.** Average compositions of relatively unaltered areas of 13 brannerite samples.

|                                | B1   | B2   | B3   | B4   | B5   | B6   | B7   | B8   | B9   | B10  | B11  | B12  | B13  |
|--------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Nb <sub>2</sub> O <sub>5</sub> | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.9  | 0.0  | 0.0  | 0.0  | 0.8  | 0.0  | 0.1  |
| SiO <sub>2</sub>               | 0.5  | 0.1  | 0.1  | 1.6  | 0.4  | 1.0  | 0.3  | 0.6  | 0.0  | 0.0  | 0.1  | 0.0  | 0.0  |
| TiO <sub>2</sub>               | 39.3 | 39.8 | 37.9 | 39.8 | 37.8 | 40.1 | 40.8 | 39.9 | 40.8 | 37.4 | 39.0 | 39.8 | 41.9 |
| ThO <sub>2</sub>               | 7.5  | 2.0  | 2.2  | 2.6  | 12.2 | 11.6 | 9.0  | 0.4  | 1.8  | 1.1  | 6.3  | 1.7  | 1.0  |
| UO <sub>2</sub>                | 40.2 | 55.3 | 50.0 | 45.1 | 34.5 | 36.7 | 38.4 | 50.6 | 55.9 | 52.0 | 46.5 | 56.5 | 52.4 |
| Al <sub>2</sub> O <sub>3</sub> | 0.2  | 0.2  | 0.9  | 0.8  | 0.3  | 0.2  | 0.3  | 0.2  | 0.1  | 0.3  | 0.2  | 0.0  | 0.2  |
| Y <sub>2</sub> O <sub>3</sub>  | 1.7  | 0.8  | 0.7  | 1.7  | 1.2  | 1.3  | 3.1  | 1.1  | 0.0  | 0.5  | 2.2  | 1.1  | 1.2  |
| Ln <sub>2</sub> O <sub>3</sub> | 2.2  | 0.4  | 0.3  | 1.2  | 1.6  | 1.5  | 1.5  | 1.1  | 0.2  | 0.4  | 1.1  | 0.0  | 2.2  |
| CaO                            | 1.5  | 0.5  | 3.5  | 3.2  | 6.5  | 2.3  | 3.4  | 2.8  | 0.5  | 4.1  | 1.4  | 0.0  | 0.3  |
| MnO                            | 0.1  | 0.0  | 0.3  | 0.1  | 0.1  | 0.1  | 0.1  | 0.5  | 0.0  | 0.1  | 0.0  | 0.0  | 0.0  |
| FeO                            | 1.5  | 0.6  | 1.5  | 0.9  | 2.1  | 1.5  | 0.7  | 1.3  | 0.4  | 1.0  | 1.8  | 0.7  | 0.4  |
| NiO                            | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.6  | 0.0  | 0.5  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| PbO                            | 5.3  | 0.2  | 2.5  | 3.0  | 3.2  | 3.2  | 1.5  | 1.1  | 0.2  | 3.2  | 0.6  | 0.2  | 0.0  |

\* Average of 5-10 analyses per sample. See Appendix 1 for details.

**Table 4.** Average compositions of altered areas of 8 brannerite samples.

|                                | B1   | B3a  | B3b  | B6   | B8a  | B8b  | B10a | B10b | B11a | B11b | B11c | B12  | B13  |
|--------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| P <sub>2</sub> O <sub>5</sub>  | 1.1  | 1.8  | 1.3  | 0.1  | 0.1  | 0.0  | 0.4  | 4.3  | 0.5  | 3.7  | 3.2  | 0.2  | 0.1  |
| As <sub>2</sub> O <sub>5</sub> | 0.0  | 0.0  | 0.0  | 0.2  | 5.9  | 1.8  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| Nb <sub>2</sub> O <sub>5</sub> | 0.0  | 0.0  | 0.0  | 0.1  | 0.2  | 0.3  | 0.0  | 0.0  | 0.6  | 1.8  | 1.4  | 0.0  | 0.3  |
| SiO <sub>2</sub>               | 16.5 | 6.3  | 2.2  | 11.6 | 9.6  | 2.0  | 3.1  | 0.4  | 1.8  | 4.2  | 3.1  | 0.0  | 2.6  |
| TiO <sub>2</sub>               | 45.8 | 44.3 | 71.1 | 47.4 | 39.2 | 68.9 | 39.5 | 73.9 | 45.6 | 58.7 | 69.0 | 40.2 | 57.7 |
| ThO <sub>2</sub>               | 13.5 | 3.4  | 2.4  | 13.8 | 1.8  | 1.1  | 1.1  | 3.0  | 6.2  | 12.6 | 5.1  | 1.5  | 1.0  |
| UO <sub>2</sub>                | 8.2  | 30.0 | 12.7 | 11.3 | 32.0 | 17.4 | 42.0 | 7.5  | 38.8 | 3.7  | 2.8  | 56.0 | 23.5 |
| Al <sub>2</sub> O <sub>3</sub> | 0.6  | 0.9  | 1.7  | 0.7  | 0.4  | 1.1  | 1.1  | 3.0  | 0.2  | 1.2  | 2.8  | 0.2  | 0.3  |
| Y <sub>2</sub> O <sub>3</sub>  | 0.0  | 0.0  | 0.0  | 0.4  | 0.0  | 0.0  | 1.0  | 0.0  | 1.4  | 0.0  | 0.0  | 0.7  | 0.5  |
| Ln <sub>2</sub> O <sub>3</sub> | 1.5  | 0.7  | 0.2  | 2.2  | 0.6  | 0.1  | 2.1  | 0.2  | 1.2  | 0.3  | 0.1  | 0.3  | 2.3  |
| CaO                            | 3.6  | 0.6  | 0.4  | 4.3  | 3.3  | 0.9  | 2.4  | 1.1  | 0.5  | 1.0  | 0.6  | 0.0  | 1.0  |
| MnO                            | 0.0  | 0.0  | 0.0  | 0.1  | 0.0  | 0.0  | 0.2  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.1  |
| FeO                            | 1.7  | 0.9  | 3.5  | 1.3  | 0.5  | 4.0  | 1.2  | 3.5  | 1.2  | 10.7 | 11.4 | 0.6  | 4.3  |
| NiO                            | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| PbO                            | 7.6  | 11.0 | 4.5  | 7.0  | 6.4  | 2.2  | 5.6  | 2.9  | 1.7  | 2.0  | 0.6  | 0.2  | 6.0  |

\* Average of 4-6 analyses for each type of alteration in each sample. See Appendix 2.