

TITANATE CERAMIC PHASES FOR SURPLUS PLUTONIUM IMMOBILISATION

A Jostsons¹, E R Vance¹ G R Lumpkin¹, K P Hart¹ and B B Ebbinghaus²

¹Materials Division Australian Nuclear Science and Technology Organisation, PMB1, Menai, NSW, 2234, Australia

²Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

ABSTRACT

A multi-phase pyrochlore-rich titanate ceramic has been chosen by the US Department of Energy for the immobilisation of surplus military plutonium. The pyrochlore-rich wastefrom was designed to have a high capacity for plutonium, uranium and neutron absorbers such as hafnium and gadolinium as well as tolerance for high impurity loadings from the plutonium feed stocks. More than 99 wt% of the plutonium is distributed among the pyrochlore, zirconolite and brannerite titanate phases that make up the multi-phase wastefrom.

This paper presents the results of our current studies on the preparation and characterisation of single phase Pu or U containing specimens of the three major titanates prevalent in the pyrochlore-rich ceramic wastefrom. The results cover aqueous durability, radiation damage sensitivity and natural mineral analogues of the above titanates.

INTRODUCTION

A synroc-based pyrochlore-rich titanate ceramic has been chosen by the United States Department of Energy (USDOE) for the immobilisation of excess weapons plutonium using the can-in-canister technology. The pyrochlore-rich titanate was designed to have a high capacity for plutonium, uranium and neutron absorbers such as hafnium and gadolinium with tolerance for impurities associated with the plutonium feedstocks. Under the chosen processing conditions of pressureless sintering for four hours at about 1350°C in air or argon the wastefrom mineralogy is dominated by the titanate phases pyrochlore, zirconolite, brannerite and rutile with the relative proportions of the phases dependent on impurities in the feedstocks. Elemental partitioning in this multi-phase wastefrom has been investigated extensively, demonstrating that the Pu, U, Hf and Gd are all present in pyrochlore, zirconolite and brannerite. The chemical durability of the multi-phase pyrochlore rich titanate ceramic in short-term laboratory tests is excellent and not very sensitive to realistic impurity loadings (1). Similarly, the leach rates of Hf and Gd are low and are much like those of Pu and U, thus ensuring that the immobilised Pu is not separated from the neutron absorbers over time in the repository.

Nevertheless, single phase studies of the key titanate hosts for Pu, U, Hf and Gd are essential to provide the necessary scientific inputs on the long-term durability of the multi-phase wastefrom to support the regulatory acceptance process for geological disposal. Samples of predominantly single-phase specimens are required for studies on:

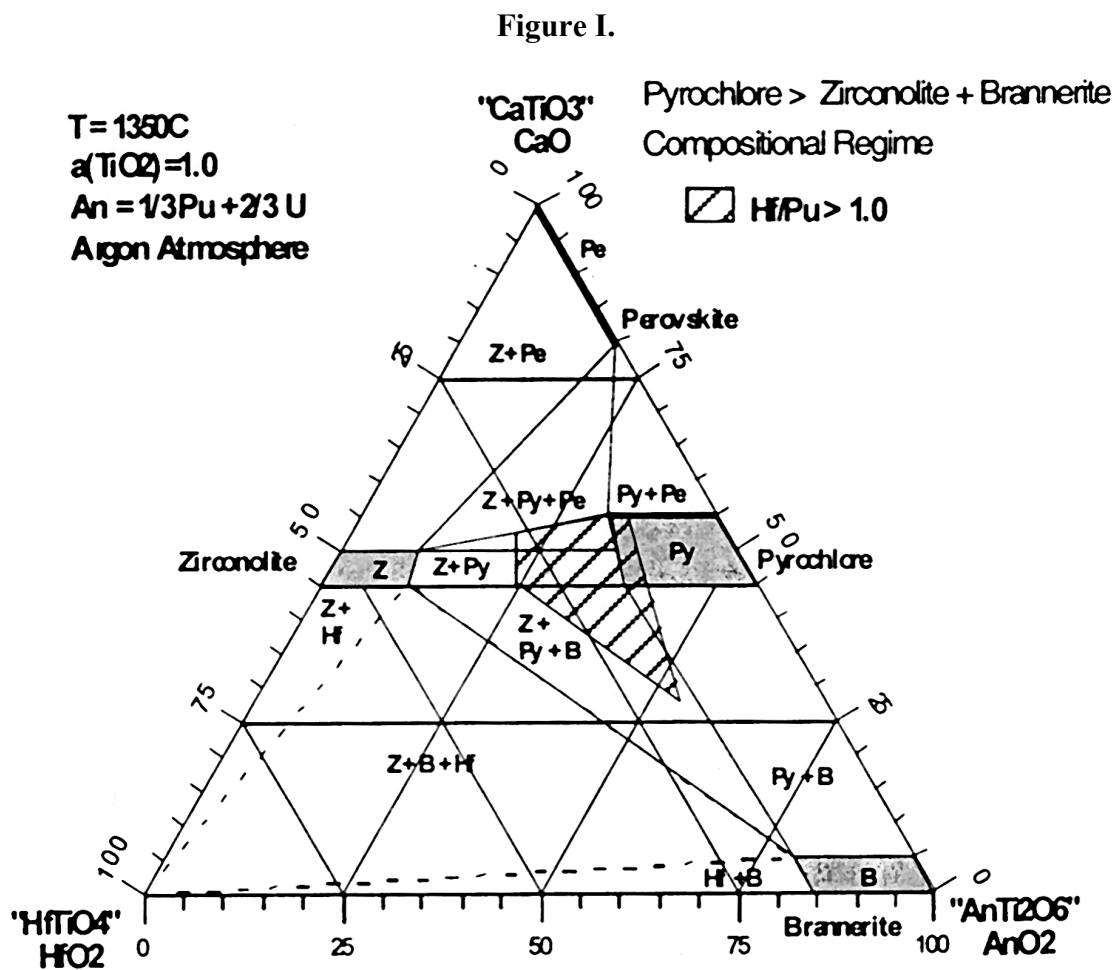
- Dissolution rates in aqueous media;
- Calorimetric measurements to measure relevant thermodynamic data;

- Radiation damage effects from α -decay;
- Quantitative x-ray diffraction data for use in non-destructive process control systems.

In this paper, we present the results of our on-going studies on the fabrication of single phase specimens of titanates relevant to plutonium immobilisation and their behaviour in standard laboratory leaching tests compared with multi-phase specimens. These tests do not simulate the effects of long-term alpha-decay damage. The effects of alpha-decay damage can be deduced from the results of studies of natural mineral analogs of pyrochlore, zirconolite and brannerite that have immobilised uranium and thorium over geological time-scales in known environments that are more severe than expected in the repository. Similarly, the relative effects of radiation damage can be inferred from studies of the amorphisation of the titanates during ion-beam bombardment. The results of recent studies, particularly on brannerite, are presented and discussed in the context of published work on pyrochlore and zirconolite.

MULTIPHASE TITANATES

The phase relationships in the pyrochlore-rich ceramic for Pu immobilisation can be depicted in a highly simplified ternary phase diagram as shown in Fig.1.



The baseline ceramic has six oxide components that need to be reduced to three variables on the basis of the following simplifying assumptions:

- TiO_2 is always in excess, so the TiO_2 activity is fixed at unity.
- UO_2 and PuO_2 behave sufficiently similarly in pyrochlore-rich titanates that they can be treated as one oxide, AnO_2 .
- Gd_2O_3 is distributed relatively evenly among the actinide-bearing phases, enabling it to be proportioned out of the phase diagram.

Typical contents of U, Pu and Gd, Hf in the main actinide containing phases of the pyrochlore-rich ceramic containing about 11.5 wt% PuO_2 and 23 wt% UO_2 , are shown in Table 1.

Table I. Actinides and Neutron Absorbers in the Primary Phases

Primary Phases	$\text{GdO}_{1.5}$ (mol%)	HfO_2 (mol%)	UO_2 (mol%)	PuO_2 (mol%)
Pyrochlore	5.2	5.3	10.9	5.7
Brannerite	4.5	3.5	16.1	7.2
Zirconolite-2M	4.0	16.2	4.1	2.9
Zirconolite-4M	3.7	10.7	5.2	4.5
Rutile	0.0	8.2	0.9	0.0

The UO_2/PuO_2 ratio does show some variations amongst the phases. Pyrochlore and brannerite have UO_2/PuO_2 ratios close to 2:1 whereas it is closer to 1:1 in zirconolite. All primary Pu-containing phases have been found to accommodate more neutron absorbers (Gd and Hf) than plutonium on a molar basis ($\text{Gd} = \text{Hf} = \text{Pu}$ on a molar basis in the overall starting composition).

The phase abundances observed in the baseline ceramic (without impurities) and in products tested with extreme levels of various impurities are shown in Table 2.

Table II. Phase Abundance in Baseline and Product Extremes

Mineralogy	Baseline (vol%)	Observed Range (vol%)
Pyrochlore	80	62-90
Brannerite	0-12*	0-22
Zirconolite (2M + 4M)	0	0-25
Rutile	8	0-16
Actinide Oxide	0.5	0.04-0.6
Other Minor Phases	0	0-6

*In the baseline ceramic brannerite is not observed in materials made from alkoxide route powders with good chemical mixing

Pyrochlore and zirconolite in titanate ceramics are closely related structurally and are derived from ordered anion-deficient fluorite structures. The fundamental structural units in titanate

pyrochlore and zirconolite are the TiO_6 octahedra arranged in three-dimensional or two-dimensional arrays, respectively. In the cubic pyrochlore with the empirical formula unit of $\text{A}_2\text{Ti}_2\text{O}_7$ the A site is 8-coordinated and can be occupied by Ca^{2+} , Gd^{3+} , U^{4+} and Hf^{4+} , amongst others. Ti^{4+} is 6-coordinated. The monoclinic zirconolite ($\text{CaZrTi}_2\text{O}_7$) has five distinct cation sites, permitting a wider variety of cations of different charge and ionic radius to be accommodated than in the cubic pyrochlore. Moreover, a particular cation may enter more than one site in zirconolite. In zirconolite, Ca^{2+} is 8-coordinated, Zr^{4+} is 7-coordinated and Ti^{4+} is 6- and 5-coordinated. With increasing loading of rare earths and actinides, zirconolite exhibits twinning (2) and a number of polytypes can form (3) before pyrochlore is stabilised.

The most common zirconolite found in the plutonium ceramic is the 2M polytype but the 4M polytype can form readily with feeds containing high levels of impurities that stabilise zirconolite relative to pyrochlore. Studies of the $\text{CaZrTi}_2\text{O}_7 - \text{CaUTi}_2\text{O}_7$ section of the phase diagram have shown (4) that with increasing uranium content the sequence of phases is zirconolite-2M, zirconolite-2M + 4M, zirconolite 4M + pyrochlore and eventually single phase pyrochlore. This sequence also applies for the $\text{CaZrTi}_2\text{O}_7 - \text{CaPuTi}_2\text{O}_7$ diagram and the composite Pu/U containing ceramics but is not shown in the simplified phase diagram in Fig.1.

SINGLE PHASE TITANATES

Waste elements are incorporated into the titanate phases in the pyrochlore-rich ceramic by a substitutional solid-solution mechanism. Where this substitution is aliovalent, charge compensation needs to be made to maintain charge neutrality. This substitution may take the form of an additional ion of appropriate valence substituting on either the same or a separate site in the lattice, or by formation of lattice vacancies or interstitials. The incorporation of multivalent waste ions, such as the actinides or the rare earths (including Ce, that is frequently used to simulate actinides) presents an additional challenge. A valence change will not only alter the charge compensation required but also lead to a change in ionic size, which in turn may restrict the sites onto which that ion may substitute. These effects have been discussed recently in some detail for zirconolite and perovskite by Begg et al. (5) who also studied the effect of processing atmosphere on the charge compensation mechanism.

Rather precise chemical accountancy is required to produce single-phase specimens of the titanates of relevance to Pu immobilisation. Such care in the formulation is not required in multi-phase titanates because the proportions of the other titanate phases simply vary somewhat and moreover they are all durable.

The basic methods used at ANSTO for preparation of single phase specimens are based on sol-gel type precursors for intimate (atomic-scale) mixing, calcination at $\sim 750^\circ\text{C}$ to remove many non-oxide constituents, ball-milling to further foster homogeneity, and high-temperature subsolidus sintering in the range $1350\text{-}1500^\circ\text{C}$ in an appropriate atmosphere. Given the practical difficulty in fabrication of precisely single-phase specimens the formulations have been designed to have a few percent ($< 5\text{wt}\%$) TiO_2 excess. The TiO_2 phase is even more leach-resistant than the actinide-bearing phases and hence acts as a minor inert diluent. There is some solubility of HfO_2 and UO_2 in TiO_2 but the effect of this can be calculated for in the analysis of single phase leaching, thermodynamics, radiation damage and crystallographic parameters.

Hafnium can in part or fully replace the Zr in zirconolite (6). Systematic studies of Pu-rich zirconolite have shown that Pu³⁺ and Pu⁴⁺ are the only viable valence states and that both can substitute on Ca sites in zirconolite whereas Pu⁴⁺ can only substitute for Zr. The existence of five distinct cation sites in zirconolite permits a wide variety of cations of different charge and ionic radius to be accommodated. Consequently, the production of essentially single-phase samples of zirconolite containing significant loadings of Pu, U and neutron absorbers is relatively easy. Similarly, nearly single-phase specimens of the 4M polytype of zirconolite have been prepared.

Essentially single-phase specimens of the Pu end member of pyrochlore containing less than 1 wt% of TiO₂ and zirconolite-4M have also been manufactured. The U end member pyrochlore specimens have been more difficult to prepare and the usual pyrochlore yield has been about 90 wt%. The minority phases in the uranium specimens have been TiO₂ and UO₂.

Dense UTi₂O₆ specimens yielding about 99 wt% brannerite could be prepared under low oxygen atmospheres by hot-pressing in metallic cans. The yield of Pu brannerites was never > 75 wt%. Vance et al. (7) have also been able to produce high yields of the uranium brannerite by dry ceramic processing techniques in air by the substitution of ~ 0.2 and 0.3 formula units of Ca and Gd respectively for U. Spectroscopic studies by Vance et al. (8) indicate that U⁺⁵ is present in these Ca and Gd stabilised brannerites.

AQUEOUS DURABILITY

Pyrochlore-rich ceramics, including essentially single-phase pyrochlores, have now been subjected to MCC-1 leach tests at 90°C in deionised water (pH~5.6) for up to one year (9). The Pu normalised total leach rates range from about 2 x 10⁻⁶ to 2 x 10⁻⁵ g/m².d after 250 days. These total Pu leach rates are comparable with those after similar leaching times from Synroc-C in which the long term Pu leach rate at 90°C asymptotes to about 5 x 10⁻⁶ g/m².d after 2000 days. These total normalised leach rates contain the contribution of Pu releases in solution, as colloids and as material absorbed on the leach vessel walls. The measured “total” leach rate does not include dissolved Pu that may be re-incorporated in the thin hydrous titania films formed on the specimen during alteration.

The total Pu release rates from titanate pyrochlores (see above) is very low, and within the experimental scatter, it is not possible at this stage to ascribe the range of Pu release in different samples to impurity effects in the range 1 ~ 13 wt% or to microstructural variation.

The uranium leaching behaviour in 90°C MCC- 1 tests pyrochlore ceramics exhibits a more complex pattern. In most pyrochlores studied the total normalised U leach rate is similar within the experimental accuracy to that for Pu. However, in some pyrochlore-rich specimens, including a brannerite-rich formulation, the U release is in the range of 1 x 10⁻² to 1 x 10⁻⁴ g/m².d. Whereas there are no comparable differences between the two sets of specimens in the Pu leach rates, the low U leach rates are observed from some pyrochlore-rich ceramics that contain brannerite. The reasons for the higher U leach rates from some specimens are not understood at this time and further work is progressing to determine if the presence of U⁺⁵ species in the uranium containing titanate phases is responsible.

Gd releases from pyrochlores in this study range from $10^{-3} - 10^{-4}$ g/m².d but there is an order of magnitude of scatter in the data from triplicate samples and further work is required to refine analytical procedures. The leach rate of the other neutron absorber, Hf, is generally $< 5 \times 10^{-6}$ g/m².d, that is at the limit of detection currently available in our laboratory.

Systematic studies of brannerite dissolution over a pH range of 2-12, have been performed by Zhang et al. (10), on single-phase specimens produced by hot-pressing under reducing atmosphere. These show that at 70°C the U release is 1×10^{-4} g/m².d at pH = 7.9 though it can be as high as 1×10^{-2} g/m².d in acidic solutions at pH 2.1. Zhang et al., also showed that the U dissolution rate in air was an order of magnitude higher than that in leaching tests conducted in a nitrogen atmosphere glove box with only 20 ppm O₂.

Pyrochlore, zirconolite and brannerite all exhibit a minimum in the leach rate at a pH of 8. The relative durability of the titanates is zirconolite \geq pyrochlore $>$ brannerite. Zirconolite is less sensitive to leaching in acid media than pyrochlore although at pH = 7 to 8 the Pu leach rates appear to be identical at 90°C.

The current perspective on brannerite as the least resistant titanate for Pu immobilisation is based largely on the uranium leaching behaviour. A better perspective will be provided in the future when appropriate single-phase (U, Pu, Gd) Ti₂O₆ brannerites are manufactured and leach tested. The present results indicate that the presence of brannerite in near single-phase pyrochlore specimens does not affect the overall rate of Pu leaching. In the longer term under repository conditions brannerite may not be significant in the pyrochlore-rich wasteform. As long as brannerite is present as a minority phase that is not interconnected throughout the wasteform, the repository behaviour will be dominated by the more resistant phases.

MINERAL ANALOGUES

Geochemical Alteration Effects

The behaviour of pyrochlore in natural systems is now well established from mineralogical investigations of numerous samples from granitic pegmatites, carbonatites, and hydrothermal veins. These studies have established that the mineral is highly durable in terms of total dissolution, e.g., economic concentrations of pyrochlore are known to occur in laterites as a result of the near complete break down of the host rock in tropical climates. Pyrochlore group minerals are subject to alteration, typically by ion exchange with the attending aqueous fluid phase, and may lose Na, Ca and F in the process. However, Th and U usually remain constant during alteration (11, 12). In terms of chemical composition, recently discovered pyrochlores from Adamello, Italy, are the best available analogues for pyrochlore-rich titanate wasteforms (13). These pyrochlores contain 50 mol% of the CaUTi₂O₇ component in solid solution, together with smaller amounts of the Ree₂Ti₂O₇, Ca₂Nb₂O₇, and Ca₂TiWO₇ end-members. Although the pyrochlores are 42 million years old and have been rendered amorphous by alpha-decay damage, they have sustained only slight hydration and no elemental losses during their history.

Oversby and Ringwood (14) have previously demonstrated that zirconolite has remained a closed system to U, Th, and Pb for up to 550 million years. The mineral is extremely resistant to

dissolution and can also survive the complete break down of the host rock during weathering. More recent mineralogical investigations have established an extensive data base from which the earlier observations are generally confirmed (15). The corrosion of zirconolite in natural systems is extremely rare and is restricted to very specific environments at elevated temperature and pressure (above 500°C and 1-2 kbar). Low temperature alteration of zirconolite is virtually non-existent in natural samples, an observation that has now been tested and confirmed by experiments carried out on Nd, Ce, Gd and Hf doped zirconolites at temperatures of 150-700°C in a variety of fluid compositions (16).

The geochemical alteration of brannerite has been poorly documented in previous work. Recent work carried out at the Australian Nuclear Science and Technology Organisation demonstrates that brannerite is also highly resistant to total matrix dissolution, but may be chemically altered along grain boundaries and microfractures in natural systems (17). Analytical data show that the universal alteration mechanism is preferential loss of U, compensated in part by uptake of Si and other minor elements from the fluid phase. Additionally, we have observed secondary alteration products such as TiO₂ phases and thorite at an advanced stage of alteration in some of the natural brannerite samples. The available data indicate that brannerite, pyrochlore, and zirconolite exhibit similar behaviour in terms of total dissolution. However, in terms of chemical alteration (ion exchange, U loss, etc.) the durability of these phases increases in the order brannerite <pyrochlore<zirconolite.

Radiation Damage Effects

Numerous investigations of alpha-decay damage in natural pyrochlore and zirconolite have been carried out over the last twenty years. The available data demonstrate that both minerals pass through a crystalline-amorphous transformation. The critical amorphisation dose (D_c) is approximately 1×10^{16} α /mg for samples with ages of less than 10^7 to 10^8 years (15). In comparison, the results of accelerated radiation damage experiments using ²³⁸Pu and ²⁴⁴Cm indicate that pyrochlore and zirconolite have D_c values close to 0.4×10^{16} α /mg (18, 19). Recent work on the thermal histories of the natural samples indicates that they have experienced temperatures of about 100-200°C averaged over time, providing a plausible explanation for the increased values relative to the accelerated damage experiments (20).

All of the natural brannerites studied at ANSTO are fully amorphous due to alpha decay of ²³⁸U and to a lesser extent ²³²Th (17). This result is due to a combination of the high U content and the minimum age of 20-25 Ma. The occurrence of partially crystalline brannerite from 11 Ma metacarbonate rocks at Binntal, Switzerland, allows for an estimate of the critical amorphisation dose which is approximately 2×10^{16} α /mg. This value is within a factor of two of the D_c values of pyrochlore and zirconolite samples of similar age. The available data for pyrochlore, zirconolite, and brannerite indicate that all three phases will have similar D_c values at the temperatures expected for geological repositories. Similar conclusions can be drawn from heavy ion irradiation experiments carried out by several independent groups, including our group, at the HVEM Tandem User Facility at Argonne National Laboratory. These results are summarised in Table III and show that the D_c values of pyrochlore, zirconolite and brannerite are about the same in natural samples and reasonably close to each other in the ion irradiation experiments carried out below about 200°C (21, 22).

Table III. Critical amorphisation dose (D_c) data for pyrochlore, zirconolite, and brannerite.

Phase	Radiation Source	Amorphisation Dose	References
Synthetic pyrochlore	^{238}Pu	$0.4 \times 10^{16} \alpha/\text{mg}$	13
Synthetic zirconolite	^{238}Pu	$0.3 \times 10^{16} \alpha/\text{mg}$	14
Natural zirconolite	$^{238}\text{U}, ^{232}\text{Th}$	$1 \times 10^{16} \alpha/\text{mg}$	10
Natural zirconolite	$^{238}\text{U} ^{232}\text{Th}$	$1 \times 10^{16} \alpha/\text{mg}$	10, 15
Natural brannerite	$^{238}\text{Pu} ^{232}\text{Th}$	$1-2 \times 10^{14} \text{ ions}/\text{cm}^2$	12
Synthetic pyrochlores	1.0-1.5 MeV Kr^+	$2-5 \times 10^{14} \text{ ions}/\text{cm}^2$	16, 17
Synthetic zirconolites	1.0-1.5 MeV Kr^+	$2-7 \times 10^{14} \text{ ions}/\text{cm}^2$	16, 17
Synthetic brannerites	1.5 MeV Kr^+	$1-2 \times 10^{14} \text{ ions}/\text{cm}^2$	This work

CONCLUSIONS

The current studies on essentially single phase synthetic and natural titanates of interest to Pu immobilisation contribute to the larger data base required for eventual repository acceptance documentation. Further work is ongoing to support the development of mechanisms for leaching of these highly durable materials and the role of radiation effects. The results report in this paper

ACKNOWLEDGMENTS

This work was supported in part by the US Department of Energy through a sub-contract from Lawrence Livermore National Laboratory. The authors also gratefully acknowledge discussions with and access to results of work in progress by Dr Y Zhang.

REFERENCES

- 1 A. JOSTSONS, E.R. VANCE, and B. B. EBBINGHAUS, "Immobilisation of Surplus Plutonium in Titanate Ceramics" Proc. of Global '99, Jackson Hole, Wy, 29 Aug-3 Sept 1999 (CD-ROM) (1999)
- 2 P. E. FIELDING and T. J. WHITE, "Crystal Chemical Incorporation of High Level Waste Species in Aluminotitanate-based Ceramics: Valence, Location Radiation Damage and Hydrothermal Durability", J Mater. Res. 2(3), pp 387-413 (1987).
- 3 H. J. ROSSELL, "Solid Solution of Metal Oxides in the Zirconolite Phase $\text{CaZrTi}_2\text{O}_7$. I Heterotype Solid Solutions", J. Solid State Chem. 99, p 38 (1992)
- 4 E. R. VANCE, G. R. LUMPKIN, M. L. CARTER, C. J. BALL, and B. D. BEGG, "The incorporation of U in Zirconolite ($\text{CaZrTi}_2\text{O}_7$)", in preparation
- 5 B. D. BEGG, E. R. VANCE, and G. R. LUMPKIN, "Charge Compensation and The Incorporation of Cerium in Zirconolite and Perovskite", in Mat. Res. Soc. Proc. Vol 506, pp 79-86 (1998).

WM'00 Conference, February 27 – March 2, 2000, Tucson, AZ

- 6 E. R. VANCE, A. JOSTSONS, R. A. DAY, C. J. BALL, B. D. BEGG, and P. J. ANGEL, "Excess Pu disposition in Zirconolite-rich Synroc". In W M Murphy and D A Knecht (eds), Scientific Basis for Nuclear Waste Management XIX, Mat. Res. Soc., Pittsburgh, PA, pp 41-48 (1996).
- 7 E. R. VANCE, J. N. WATSON, M. L. CARTER, R. A. DAY, G. R. LUMPKIN, K. P. HART, Y. ZHANG, P. J. McGLINN, M. W. A. STEWART and D. J. CASSIDY, "Crystal chemistry, radiation effects and aqueous leaching of brannerite, UTi_2O_6 " Proc. Annual Meeting of American Ceramic Society, Indianapolis, 28 April, 1999 in press.
- 8 E. R. VANCE, J. N. WATSON, M. L. CARTER, R. A. DAY, and B. D. BEGG, "Chrystal Chemistry of brannerite, UTi_2O_6 ", J. Amer. Ceram. Soc., submitted for publication.
- 9 K. P. HART, Y. ZHANG, E. LOI, Z. ALY, M. W. A. STEWART, A. BROWNSCOMBE, B. B. EBBINGHAUS and W. BOURCIER, "Aqueous dissolution of titanate ceramics designed to immobilise excess Pu", In D Shoesmith, (ed), Scientific Basis for Nuclear Waste Management XXIII, Mat. Res. Soc., Pittsburgh, PA, in press.
- 10 Y. ZHANG, K. P. HART, R. A. DAY, G. R. LUMPKIN, M. COLELLA, P. J. McGLINN, G. LETURCQ and B. THOMAS, "Kinetic leaching studies of synthetic brannerite", Applied Geochemistry, submitted for publication.
- 11 G. R. LUMPKIN and R. C. EWING (1995) Geochemical alteration of pyrochlore group minerals: pyrochlore subgroup. American Mineralogist, 80, 732-743
- 12 G. R. LUMPKIN and R. C. EWING (1996) Geochemical alteration of pyrochlore group minerals: betafite subgroup. American Mineralogist, 81, 1237-1248.
- 13 G. R. LUMPKIN, R. A. DAY, P. J. McGLINN, T. E. PAYNE, R. GIERE and C. T. WILLIAMS (1999), "Investigation of the long-term performance of betafite and zirconolite in hydrothermal veins from Adamello, Italy". In D J Wronkiewicz and J H Lee (eds), Scientific Basis for Nuclear Waste Management XXII, Mat.Res.Soc.Proc.Vol.556, Pittsburgh, PA, in press.
- 14 V. M. OVERSBY and A. E. RINGWOOD (1981) "Lead isotopic studies of zirconolite and perovskite and their implications for long range SYNROC stability". Radioactive Waste Management, 1, 289-307.
- 15 G. R. LUMPKIN, K. P. HART, P. J. McGLINN, T. E. PAYNE, R. GIERE and C. T. WILLIAMS (1994) "Retention of actinides in natural pyrochlores and zirconolites". Radiochimica Acta, 66/67, 469-474.
- 16 J. MALSTROM, E. REUSSER, R. GIERE, G. R. LUMPKIN, M. DUGGELIN, D. MATHYS and R. GUGGENHEIM (1999) "Zirconolite corrosion in dilute acidic and basic fluids at 180-700°C and Mpa. In D J Wronkiewicz and J H Lee (eds.), Scientific Basis for Nuclear Waste Management XXII, Mat. Res. Soc. Proc. Vol.556, Mat. Res. Soc. , Pittsburgh, PA, in press.

WM'00 Conference, February 27 – March 2, 2000, Tucson, AZ

- 17 G. R. LUMPKIN, S. H. F. LEUNG and M. COLELLA (1999) “Composition, geochemical alteration, and alpha-decay damage effects of natural brannerite. Scientific Basis for Nuclear Waste Management XXIII, submitted.
- 18 F. W. CLINARD Jr., D. E. PETERSON, D. L. ROHR and L. W. HOBBS (1984) “Self-irradiation effects in ^{238}Pu -substituted zirconolite. I. Temperature dependence of damage”. *Journal of Nuclear Materials*, 126, 245-254.
- 19 F. W. CLINARD Jr, D. L. ROHR and R. B. ROOF (1984) “Structural damage in a self-irradiated zirconolite-based ceramic”. *Nuclear Instruments and Methods in Physics Research*, B1, 581-586.
- 20 G. R. LUMPKIN, K. L. SMITH, M. G. BLACKFORD, R. GIERS and C. T. WILLIAMS (1998) “The crystalline-amorphous transformation in natural zirconolite: evidence for long-term annealing”. In I G McKinley and C McCombie (eds.), *Scientific Basis for Nuclear Waste Management XXI*, *Mat.Res.Soc.Proc. Vol.506*, Pittsburgh, PA, pp. 215-222 (1998).
- 21 K. L. SMITH, N. J. ZALUZEC and G. R. LUMPKIN (1997) “In situ studies of ion irradiated zirconolite, pyrochlore and perovskite”. *Journal of Nuclear Materials*, 250, 36-52.
- 22 S. X. WANG, L. M. WANG, R. C. EWING, G. S. WAS and G. R. LUMPKIN (1998) “Ion irradiation-induced phase transformation of pyrochlore and zirconolite”. *Nuclear Instruments and Methods in Physics Research*, B148, 704-709 (1998).