15347
UCRL

P.O. 7762409

MASTER

Mineral Waste Form Development
for U.S. Defense Wastes

Progress Report to Lawrence Livermore National
Laboratory, As specified in Contract No. ~~2248301~~ 7762409

A. E. Ringwood
Research School of Earth Sciences
Australian National University

DISCLAIMER

February 10, 1981

Lawrence
Livermore
Laboratory

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MINERAL WASTE FORM DEVELOPMENT FOR U.S. DEFENSE WASTES

Progress Report to Lawrence Livermore National Laboratory

February 10, 1981

As specified in Contract No. 2248301

CONTENTS

	<u>PAGES</u>
1. Sodium Fixation in SYNROC D Formulations	1-14
2. Partition Behavior of Strontium in SYNROC	15-19
3. Conceptual Process for Immobilizing Defense High Level Wastes in SYNROC D	20-32
4. Preferred Composition of SYNROC	33-45
5. Reconnaissance Experiments on the Possible Role of Monazite for Actinide Immobilization in SYNROC D	46-57
6. Experiments Bearing on the Optimum Preparation and Heat-treatment of SYNROC Formulations, with Implications for the fixations of Cesium and Molybdenum.	58-85
7. Effects of Nuclear Radiation on the Crystal Structures of Zirconolite and Perovskite	86-132
8. Lead Isotopic Studies of Zirconolite and Perovskite and Their Implications for Long-Range SYNROC Stability	133-163

Deddick Pty. Ltd.
3 Vancouver St.
Red Hill
Canberra A.C.T. 2603
AUSTRALIA

Manager and author of progress report: A. E. Ringwood

SODIUM FIXATION IN SYNROC-D FORMULATIONS

A.E. Ringwood

Research School of Earth Sciences
Australian National University
Canberra, A.C.T. 2600, Australia

1. Introduction

SYNROC-D is a ceramic waste-form developed for the specific purpose of immobilizing US defense sludges (Ringwood et al., 1980). According to the recommended process, about 35% of inert additives would be intimately mixed with the calcined sludge, and after heat-treatment under controlled redox conditions, a dense ceramic waste-form is produced. The phases present in this material include zirconolite, perovskite, spinel solid-solutions and nepheline, with essentially all the sodium from the sludges being incorporated in nepheline. The Na_2O contents of both zirconolite and perovskite are typically about 0.4%, with no sodium contained in spinel ss. Nepheline, on the other hand, readily accepts about 20% Na_2O and so a SYNROC-D waste-form consisting of 25% nepheline has the capacity to immobilize the 5% Na_2O of an average sludge.

Although this waste form has excellent properties and is far superior to borosilicate glass, it nevertheless seems desirable to develop a further alternative waste-form in which sodium would be immobilized in titanate phases which are likely to be even more resistant to hydrothermal alteration than nepheline. However, in order to achieve this objective at reasonable cost, the sodium content of the sludges needs to be reduced, ideally to 2% Na_2O or less. This could presumably be achieved by more efficient washing procedures, which will form the subject of a

In this paper we describe how sodium is incorporated in the natural mineral analogues of SYNROC phases, and use this understanding to develop various experimental strategies for the immobilization of sodium in the refractory titanate phases of SYNROC-D.

2. Sodium Fixation in Natural Zirconolite (and Pyrochlore)

Natural zirconolites contain very little Na_2O ($<0.5\%$), however, the structurally-related pyrochlore group of minerals may contain several percent of Na_2O . A typical pyrochlore would correspond approximately to $\text{NaCaNb}_2\text{O}_6\text{F}$, with some substitution of Ti and Ta for Nb, and REE, U, Y, Mn^{2+} and Fe^{2+} proxying for Na and Ca. It might be possible to replace SYNROC zirconolite with a pyrochlore-type phase, but we have chosen not to do so, because (unlike zirconolite) some such pyrochlores can exhibit substantial ion exchange capacity under hydrothermal conditions (Chelischchev and Mar'ina, 1971). This would be an undesirable characteristic in a waste-form phase.

3. Sodium Fixation in Natural Perovskites

The perovskite family of minerals occur widely as accessory phases in alkaline igneous rocks (Deer et al., 1966). Perovskite proper is essentially CaTiO_3 . Varieties rich in rare earths, specifically cerium, have been called knopite. Lueshite is essentially pure NaNbO_3 . Dysanalite is an intermediate member of the series with some Nb replacing Ti, and charge balance maintained by substitution of Na for Ca. Loparite resembles knopite and dysanalite but is particularly rich both in rare earths and niobium. Analyses of typical members of the perovskite family

are given in Table 1. The entry of sodium into natural perovskites can be described in a somewhat oversimplified way, as solid solution between CaTiO_3 and two other components: $(\text{Na}_{0.5}\text{REE}_{0.5})\text{TiO}_3$ and NaNbO_3 .

4a. Sodium Fixation in SYNROC-D Perovskites: $\text{Na}_{0.5}\text{REE}_{0.5}\text{TiO}_3$

We have investigated experimentally the immobilization of sodium in the perovskite phase of SYNROC-D, as a solid solution involving each of the above two components. In the case of the $\text{Na}_{0.5}\text{REE}_{0.5}\text{TiO}_3$ component, two specific examples were considered: $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ and $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3$. In the former instance, Ce typifies behaviour of light lanthanides, while in the latter, Y behaves as the crystal-chemical analogue of the heavy lanthanides.

When $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ was added to a hollandite-zirconolite-perovskite assemblage at 5 kb, 1300°C , a solid solution with CaTiO_3 perovskite resulted. Some Na and Ce also partitioned into zirconolite when very high loadings (20%) of $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ were involved. Microprobe analyses of coexisting phases are given in Table 2.

When the $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3$ component was added to the assemblage "A" ($\text{CaTiO}_3 + \text{BaAl}_2\text{Ti}_6\text{O}_{16}$) at 5 kb and 1300°C , it formed a solid solution with perovskite. Similar results were obtained when this component was added to the assemblage "B" ($\text{CaTiO}_3 + \text{CaZrTi}_2\text{O}_7$). Microprobe analyses of product phases are listed in Table 3. Note that the perovskite ss. comprised about 50 wt.% of the $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3$ end-member, equivalent to about 5% Na_2O . Tables 2 and 3 show that in the presence of substantial REE, zirconolite also has the capacity to immobilize as much as 2% Na_2O .

Table 1. Microprobe analyses of naturally-occurring Perovskite-group minerals.

	Perovskite ¹	Lueshite ²	Dysanalite ³	Loparite ⁴
Nb ₂ O ₅	0.9	78.2	7.1	6.7
Ta ₂ O ₅	<.1	0.3	0.5	0.1
TiO ₂	54.6	2.6	45.8	48.1
ThO ₂	-	-	-	0.1
UO ₂	0.1	tr.	-	-
FeO	1.1	<.1	4.9	-
CaO	41.0	0.8	39.6	5.9
SrO	-	-	-	3.8
Na ₂ O	<.1	16.4	<.1	9.1
REE ⁵	2.2	1.6	1.8 ⁶	26.3 ⁷
Sum	99.9	99.9	98.9	100.0

1. Perovskite, from skarn, Lake Baikal, USSR. ANU/RSES SYNROC collection.
2. Lueshite, from type locality, Luesh, USSR. ANU/RSES SYNROC collection.
3. Dysanalite, more correctly named "niobian perovskite", since it contains so little sodium. Sample #16471, ANU Geology Dept. collection.
4. Loparite from type locality, Lovozero Massif, USSR. ANU/RSES SYNROC collection.
5. Rare earth elements.
6. CeO₂ only.
7. Includes 23.3% CeO₂.

Table 2. Incorporation of $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ in SYNROC phases.

	$\text{C5}^1 + 5\% \text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$			$\text{C5}^1 + 20\% \text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$		
	H	P	Z	H	P	Z
TiO_2	70.	56.8	48.3	69.	52.4	41.6
ZrO_2	.3	-	30.9	0.4	0.2	32.5
UO_2	-	0.5	1.8	0.1	0.3	1.8
Al_2O_3	10.8	0.5	2.5	12.4	2.1	3.1
Sm_2O_3	-	0.8	0.5	-	tr.	0.6
Ce_2O_3	-	7.5	-	-	20.	6.0
CaO	0.4	32.9	15.1	0.6	20.5	12.8
BaO	16.	-	-	16.	-	-
NiO	2.2	-	0.2	0.8	-	0.2
Na_2O	0.2	0.8	0.3	0.4	2.8	1.2
Sum	99.7	99.8	99.6	99.5	98.3	99.8

"C5" is a SYNROC composition comprising 40% hollandite, 35% zirconolite and 25% perovskite, doped with Sm and U.

H = hollandite
P = perovskite
Z = zirconolite

Experimental conditions: 5 kb, 1300°C , 1 hr, Pt capsule.

Table 3. Incorporation of $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3$ in SYNROC phases.

	A		B	
	H	P	Z	P
TiO_2	74.	55.3	48.4	55.8
ZrO_2	-	-	33.	1.
Y_2O_3	0.4	18.5	4.	13.
Al_2O_3	13.7	1.9	-	-
BaO	10.	-	-	-
CaO	0.8	18.9	11.6	25.3
Na_2O	0.8	5.1	2.4	4.8
Sum	99.7	99.7	99.4	99.9

A = $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3 + \text{BaAl}_2\text{Ti}_6\text{O}_{16} + \text{CaTiO}_3$ (2:1:1 by wt.)

B = $\text{Na}_{0.5}\text{Y}_{0.5}\text{TiO}_3 + \text{CaZrTi}_2\text{O}_7 + \text{CaTiO}_3$ (2:1:1 by wt.)

Experimental conditions: 5 kb, 1300°C , 1 hr, Pt capsule.

H = hollandite P = perovskite Z = zirconolite

We have produced a SYNROC-D waste-form in which sodium is immobilized as $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ component in perovskite. The model Savannah River composite sludge prepared by S.W. Anal. Chem. was used in the experiments. As prepared, it contains no uranium or sodium*. In order to correspond to a more realistic sludge composition, we added 3.3% UO_2 and 2.0% Na_2O to the starting material. As mentioned earlier, reducing the Na_2O content of the actual sludges to those levels should not prove too difficult if more efficient washing procedures are adopted. Table 4 lists the proportions of additives required to produce this SYNROC-D formulation with a nominal waste-loading of 63%. The product phase assemblage is also given in Table 4. Note that approximately 5 wt.% Ce_2O_3 is required to immobilize each 1% Na_2O . In an industrial scale process, cheap, crudely-refined, light rare earth mixed oxides $(\text{La,Ce,Nd})_2\text{O}_3$ derived from treatment of carbonatitic bastnäsite could be used. This would not result in unacceptable processing costs.

4b. Sodium Fixation in SYNROC-D Perovskite : NaNbO_3

The immobilization of sodium as an NaNbO_3 component (blue-shite) in solid solution in SYNROC perovskite has also been studied experimentally. When Nb_2O_5 was added to a model US defense sludge calcine, it was observed to partition strongly into perovskite, although small amounts of Nb also entered zirconolite and spinel (Table 5). Likewise, when niobium (as NaNbO_3) was added to the hollandite-zirconolite-perovskite SYNROC assemblage, it, too, formed a solid solution with perovskite (Table 6). Note that Na and Nb also enter both zirconolite and hollandite,

---

* Microprobe analysis of sludge calcined at 1000°C shows $\text{Al}_2\text{O}_3 = 31.2$, " Fe_2O_3 " = 55.0, $\text{NiO} = 4.9$, $\text{MnO} = 7.6$, $\text{CaO} = 3.4$, trace SO_3 , Cl , MgO .

Table 4. Incorporation of $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ in SYNROC-D.

	Spinel	Zirconolite	Perovskite
TiO_2	6.5	29.3	41.9
ZrO_2	<.1	25.3	<.2
UO_2	-	16.3	0.6
Ce_2O_3	-	3.8	25.1
Al_2O_3	25.1	4.2	2.4
Fe_2O_3	54.9	10.4	5.1
MnO	8.9	1.8	0.3
NiO	4.8	-	tr.
CaO	0.2	10.1	20.1
Na_2O	-	0.3	3.7
Sum	100.4	101.5	99.2

Starting material: S.W. Anal. Chem. model sludge
 (inc. 3.3% UO_2) with nominal 2%
 Na_2O . SYNROC-D formulation is
 63% calcined sludge plus 37%
 inert additives (19.1% TiO_2 ,
 3.3% ZrO_2 , 9.5% Ce_2O_3 , 4.8% CaO).

Experimental conditions: 5 kbar, 1200°C , 1 hr,
 Ni capsule.

Table 5. Incorporation of NaNbO_3 in SYNROC-D.

Assemblage:	"A"			"B"			"C"		
	P	Z	S	P	Z	S	P	Z	S
Nb_2O_5	36.8	8.0	2.1	38.1	3.	<.1	25.7	15.7	-
TiO_2	27.3	27.9	5.1	25.6	24.4	3.4	35.5	29.1	6.3
ZrO_2	-	34.	-	-	36.	-	-	22.0	-
UO_2	0.3	3.5	-	0.5	7.7	-	0.3	3.0	-
Al_2O_3	0.3	2.5	39.9	0.3	1.5	42.9	1.4	3.5	29.7
Sm_2O_3	2.4	1.3	-	2.7	3.1	-	-	-	-
Fe_2O_3	...all Fe as FeO ...			-	-	12.1	...all as FeO ...21.7		
FeO	1.9	7.2	35.7	1.9	7.7	17.4	3.7	10.5	26.5
MnO	0.4	2.4	10.5	0.7	3.2	8.1	1.8	5.0	8.0
NiO	0.3	0.3	6.3	0.2	1.1	16.6	-	-	7.7
CaO	19.3	11.7	-	19.6	10.8	-	28.1	10.8	-
Na_2O	10.5	1.5	-	9.1	0.9	-	4.0	0.3	-
Sum	99.5	100.3	99.6	98.7	99.4	100.5	100.6	99.9	99.9
Na/Nb atomic 1 : 1.1			1 : 1.1			1 : 1.4			

Experimental conditions: 5 kb, Ni capsule, 1 hr, 1150°C for assemblage "A", 1250°C for assemblage "B", 1200°C for assemblage "C".

Starting compositions "A" & "B": Model Savannah R. composite sludge (5% Na_2O) doped with Sm_2O_3 (~1%). Waste-loading 66%, (Inert additives: 15.0% TiO_2 , 4.0% ZrO_2 , 4.8% CaO , 16.2% Nb_2O_5).

"C": S.W. Anal. Chem. model sludge plus 3.3% UO_2 and nominal 2% Na_2O . Waste-loading 63% (Inert additives: TiO_2 = 17.8, ZrO_2 = 4.7, CaO = 6.5, Nb_2O_5 = 7.3).

P = perovskite   Z = zirconolite   S = spinel

Table 6. Incorporation of NaNbO_3 in SYNROC phases.

	SYNROC-C + 10% NaNbO_3			SYNROC-C + 20% NaNbO_3		
	H	Z	P	H	Z	P
Nb_2O_5	1.2	2.	13.4	1.7	5.	20.6
TiO_2	69.	49.6	49.1	69.	47.1	43.7
ZrO_2	-	28.	-	-	27.	-
UO_2	-	0.5	1.2	-	0.7	0.5
Al_2O_3	11.4	3.4	0.2	11.2	4.1	0.2
Sm_2O_3	-	0.2	0.5	-	0.2	0.3
NiO	2.6	0.4	0.1	1.9	0.2	0.2
CaO	0.2	14.5	33.4	0.4	13.8	27.9
BaO	15.	-	-	16.	-	-
Na_2O	0.3	0.6	3.8	0.5	1.2	6.4
Sum	99.7	99.2	99.7	100.7	99.3	99.5

Experimental conditions: 5 kb, 1300°C , 1 hr, Pt capsule.

SYNROC-C consists of 40% $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ hollandite, 35% zirconolite, 25% perovskite, doped with Sm, U.

H = hollandite   Z = zirconolite   P = perovskite

to a lesser degree.

These experiments establish that sodium can be very efficiently immobilized in solid solution in perovskite (as the NaNbO_3 component). However, in waste-form manufacture, a slight excess of niobium should be added (slightly greater than 1:1 atomic Na:Nb) in order to allow for entry of Nb into zirconolite, spinel etc., whilst preventing formation of soluble sodium niobates e.g. Na_3NbO_4 . If too great an excess of Nb_2O_5 is used (e.g. atomic Na:Nb = 1:1.7) then a new niobian pyrochlore-type phase may also occur (Table 7). Uranium (and hence quadrivalent actinides) are strongly partitioned into this phase. Because its long-term integrity has not yet been confirmed by a parallel study of natural mineral analogs, we would prefer to eliminate the phase from the SYNROC-D formulation by more careful control of Na:Nb ratios as illustrated by assemblage "C", Table 5. Here, atomic Na:Nb = 1:1.4, and the product assemblage consists of spinel, perovskite with NaNbO_3 in solid solution, and a niobian zirconolite which is very similar to the naturally-occurring mineral.

Conclusion

This experimental study shows that sodium in SYNROC-D can be effectively immobilized in solid solution in perovskite, instead of nepheline, if appropriate quantities of rare earths or niobium are introduced prior to heat-treatment, and silica is omitted. Preferentially, the sludge should contain <2% Na_2O although higher concentrations of sodium could be immobilized in this manner provided the costs of the additives were acceptable. The rare earth or niobium oxide additives are strongly partitioned

Table 7. Fixation of Na as NaNbO_3 component of perovskite : excess Nb_2O_5 forms new pyrochlore-type phase.

	Spinel	Perovskite	Zirconolite	"Pyrochlore"
Nb_2O_5	0.3	25.0	8.4	43.1
TiO_2	6.3	33.3	38.5	18.0
ZrO_2	<.1	<.3	29.1	3.5
UO_2	-	0.5	2.1	13.4
Al_2O_3	29.1	3.8	3.8	2.2
"FeO"	47.6	2.3	5.3	3.3
MnO	8.2	1.0	0.7	0.8
NiO	5.7	0.2	<.1	<.1
CaO	0.2	28.3	12.3	15.1
Na_2O	-	5.0	0.2	0.8
Sum	97.4	100.2	100.4	100.2

Na/Nb atomic 1 : 1.7

Starting composition: S.W. Anal. Chem. model sludge, with 3.3% UO_2 and nominal 2% Na_2O . Waste-loading of SYNROC-D formulation is 63%. Inert additives are 9.3% Nb_2O_5 , 13.3% TiO_2 , 5.8% ZrO_2 and 4.3% CaO .

Experimental conditions: 5 kbar, 1200°C , 1 hr, Ni capsule.

into perovskite, however, small quantities are also partitioned into other phases, particularly zirconolite. In order to allow for this, the additives would be incorporated with the sludges such that (atomic) Nb or REE would be just slightly in excess of sodium. In the case of niobium, this "excess" Nb also prevents the formation of soluble sodium-rich niobate phases in the SYNROC assemblage. However, too great an "excess" of Nb is undesirable, as new niobian pyrochlore-type phases would be produced.

Naturally-occurring sodium-bearing perovskites, e.g. lueshite and loparite, hundreds of millions of years old, occur in a variety of geological settings. These minerals have survived physical and chemical conditions far more extreme than would be encountered in any proposed radwaste repository, whilst continuing to successfully immobilize sodium and other radwaste elements. These facts give us confidence in the long-term integrity of SYNROC-D formulations wherein sodium is immobilized in solid solution in perovskite.

References

- Deer W.A., Howie R.A. and Zussman J. (1966) An introduction to the rock-forming minerals. Longmans, London, 518 p.
- Chelishchev N.F. and Marina N. (1971) Ion exchange properties of pyrochlore under supercritical conditions. Doklady Akad. Nauk. SSSR 197, 682-685.
- Ringwood A.E., Kesson S.E. and Ware N.G. (1980) Immobilization of US Defense Wastes using the SYNROC process. In: Scientific Basis for Nuclear Waste Management, Vol. 2, Ed. G.J. McCarthy. Plenum Press, New York. In press.

Appendix

(a) Immobilization of sodium in the accessory phase NaScTiO₄

It was shown experimentally that at 5 kb, 1300°C, NaScTiO₄ was not compatible with either hollandite, perovskite or zirconolite and so would not be a suitable accessory phase in any SYNROC formulation.

(b) Volatilization of sodium

The possibility that the sodium contents of sludges could be reduced by volatilization of sodium was investigated experimentally and shown not to be viable. No significant amounts of sodium were lost from the sludges after firing for an hour in air or in vacuum at 1200°C and 1300°C.

Partition Behavior of Strontium in SYNROC

A.E. Ringwood

Research School of Earth Sciences,
Australian National University,
Canberra, A.C.T. 2600, Australia.

1. Introduction

SYNROC formulations aimed at immobilizing civilian high-level wastes comprise 3 major phases; hollandite, perovskite and zirconolite (SYNROC-C). It has been shown experimentally that Sr is strongly partitioned into perovskite, with lesser amounts entering zirconolite, and very little (typically $<0.2\%$) entering hollandite. Table 1 summarizes SrO contents (wt.%) for coexisting perovskite and zirconolite in SYNROC-C. Note that the values of the Sr partition coefficient ($K_{Sr}^{P/Z}$) are quite scattered. This reflects considerable variation in the SrO content of perovskite, whilst the SrO content of zirconolite is confined to a narrow range (1.0-1.3 wt.%). These results imply that the saturation limit for SrO in zirconolite is reached at about 1.3% whilst the variable surplus is taken up by perovskite.

A second series of experiments confirmed this interpretation (Table 2). A modified 2-phase SYNROC assemblage consisting only of hollandite and zirconolite was prepared and doped with $\sim 1\%$ SrO. Perovskite, being absent, is unable to provide a Sr "sink", and strontium is then obliged to partition between hollandite and zirconolite. The appearance of a new Sr-rich phase in the run products demonstrates that both hollandite and zirconolite have reached their saturation limits at SrO contents of 0.2 and 1.4% respectively. (The limited solid-solution of Sr in hollandite is somewhat surprising, since early experiments had synthesized pure Sr-hollandite ($SrAl_2Ti_6O_{16}$), and substantial solid-solution with the isostructural(?) Ba end-member was anticipated).

2. Modified SYNROC Formulations

Zirconolite + Hollandite:

This 2-phase SYNROC formulation is of interest because even without perovskite, it has the capacity to successfully immobilize

Table 1: Partition of Sr between coexisting zirconolite and perovskite in SYNROC-C.

	Zirconolite	Perovskite	$K_{Sr}^{P/Z}$
SrO content (wt.%)	1.3	2.5	1.9
	1.0	2.6	2.6
	1.2	7.8	6.5
	1.1	8.3	7.5
	1.0	8.5	8.5

Starting compositions: SYNROC-C (hollandite, perovskite + zirconolite) doped with ~1% SrO.

Experimental conditions: 5 kbar, 1300-1350°C, 1 hr, Ni caps.

Table 2: Partition of Sr between hollandite and zirconolite (perovskite absent)

	'A'			'B'		
	Hollandite	Zirconolite	Sr-phase	Hollandite	Zirconolite	Sr-phase
TiO ₂	69.	48.5	56.	68.	49.0	52.
ZrO ₂	0.3	32.4	12.2	0.2	31.8	24.1
Al ₂ O ₃	14.1	2.4	3.5	14.8	2.1	2.3
CaO	0.2	15.0	11.3	0.3	15.1	13.8
SrO	0.2	1.3	9.4	0.2	1.4	3.8
BaO	16.	-	8.	16.	-	4.
Sum	99.8	99.6	100.4	99.5	99.4	100.0

Rutile (analysis not shown) is present in both sets of products.

Starting compositions: BaAl₂Ti₆O₁₆ + CaZrTi₂O₇ (1:1 by wt.) doped with ~1% SrO.

Experimental conditions: Assemblage 'A': 5 kb, 1400°C, 3/4 hr, Pt caps.

Assemblage 'B': 5 kb, 1350°C, 3/4 hr, Pt caps.

civilian wastes. Elements such as rare earths and strontium which are largely partitioned into perovskite in SYNROC-C formulations would instead be accommodated by zirconolite. The above experiments imply that this could be achieved without any difficulty. Calcined civilian wastes typically contain 2-3% SrO, thus for a 2-phase SYNROC comprising 40 wt.% zirconolite and 60% hollandite, with a waste-loading of 10 wt.%, the SrO content of zirconolite would be about 0.7 wt.%. This is well below the saturation limit of zirconolite.

Zirconolite + Perovskite + Rutile:

These modified SYNROC assemblages were prepared and doped with low concentrations ($\sim 0.3\%$) of SrO in order to obtain a better estimate of the equilibrium partition coefficient for Sr between zirconolite and perovskite. Earlier experiments (Table 1) gave widely scattered values because the saturation limit of zirconolite was reached. Table 3 gives microprobe analyses of product phases, from which values of 2.3 and 4.0 for $K_{Sr}^{Z/P}$ are obtained.

"Strontian SYNROC"

We investigated the possibility of developing a modified SYNROC assemblage in which CaTiO_3 perovskite was replaced by SrTiO_3 . The specific experiment tested the compatibility between SrTiO_3 and $\text{CaZrTi}_2\text{O}_7$ at 5 kb, 1300°C . These phases were found to be incompatible, breaking down to produce TiZrO_4 and perovskite ss. $(\text{Ca,Sr})\text{TiO}_3$. These results show that "Strontian SYNROC" is not a viable concept.

Table 3: Partition of Sr between zirconolite and perovskite (hollandite absent).

	'A'		'B'		
	Zirconolite	Perovskite	Zirconolite	Perovskite	Rutile
TiO ₂	47.9	57.3	51.8	58.1	93.6
ZrO ₂	34.8	<.1	30.6	0.4	6.2
CaO	17.1	41.7	17.0	39.6	<.1
SrO	0.4	0.9	0.3	1.2	<.1
Sum	100.2	99.9	99.7	99.3	99.8
$\chi_{Sr}^{Z/P}$	2.3		4.0		

Starting compositions:

Assemblage 'A' : CaZrTi₂O₇ + CaTiO₃ (1:1 by wt.) doped with ~0.5% SrO.

" 'B' : CaZrTi₂O₇ + (CaTiO₃+2TiO₂) (1:1 by wt.) doped with ~0.5% SrO.

Experimental conditions:

5 kb, 1400°C 1 hr, Pt caps.

CONCEPTUAL PROCESS FOR IMMOBILIZING DEFENSE HIGH
LEVEL WASTES IN SYNROC-D

INTRODUCTION

United States defense nuclear wastes are presently in tank storage, largely as sludges comprising Fe, Mn, Ni, U and Na oxides and hydroxides, together with 0.5 to 5 percent of fission products and actinides (exclusive of uranium). The relative proportions of Al, Fe, Mn, Ni, U and Na in the sludges from different tanks vary considerably, however, (Fe+Al+Mn) are by far the major components and Fe is more abundant than Mn. It has been shown elsewhere (1,2) that the SYNROC process can readily be applied to the problem of defense waste immobilization, yielding a dense, inert ceramic waste-form, SYNROC-D.

This objective can be achieved as follows: about 30-50 wt.% of additional inert components ($\text{TiO}_2 + \text{ZrO}_2 + \text{CaO} \pm \text{Al}_2\text{O}_3 \pm \text{SiO}_2 \pm \text{Nb}_2\text{O}_5$) would be intimately mixed with the sludges, followed by heating under controlled oxygen fugacity conditions to form a ceramic synthetic rock composed of a specific mineral assemblage, comprised mainly of spinel, zirconolite, perovskite and nepheline. In keeping with the SYNROC strategy, the immobilization of fission products and actinides would be achieved by incorporating them as dilute solid solutions forming integral parts of the crystal lattices of zirconolite and perovskite. The additional thermodynamically-compatible phases (mainly spinel + nepheline) serve to immobilize the "inert" sludge components, mainly Fe, Al, Mn, Ni and Na oxides.

Despite the very wide range of chemical compositions of the sludges presently in tank storage, experimental investigations (1,2) show that the amounts and proportions of additives and also the treatment conditions needed to form satisfactory mineral

assemblages are quite similar. This facilitates the development of a relatively simple and economically efficient industrial-scale process for treating the wastes. To a large extent, this behaviour is a consequence of the fact that the principal inert components of the waste are oxides of Al, Fe, Mn and Ni. When heated under appropriate conditions, these components become immobilized in a suitably inert spinel-type mineral phase. Apart from the modest amount of SiO_2 or Nb_2O_5 needed to immobilize sodium, the remaining additives (TiO_2 , ZrO_2 , $\text{CaO} \pm \text{Al}_2\text{O}_3$) are dedicated primarily to the objective of immobilizing the very small proportion (0.5 to 5%) of fission products and actinides (exclusive of U) present in the waste.

Distributions of fission products and actinide elements among SYNROC-D minerals have been determined (1,2). Rare earths (and trivalent actinides) preferentially enter perovskite whilst uranium and tetravalent actinides enter zirconolite. Strontium is strongly partitioned into perovskite, whilst phosphorus forms $\text{Ca}_3(\text{PO}_4)_2$. Sulphur, bismuth, ruthenium, rhodium, and palladium alloy with nickel to form minor accessory minerals.

The sodium contents of sludges influence the selection of an optimum immobilization assemblage. Currently, washed Savannah River sludges contain 3 to 5 percent of sodium. At these relatively high levels, it is economical to immobilize sodium in the waste-form as nepheline, NaAlSiO_4 . To this end, free silica is included among the additives mixed with the sludge prior to calcination. The composition of a typical Savannah River sludge, together with the additives needed to convert the sludge into SYNROC-D is given in Table 1. When this mixture is calcined at about 1100°C under mildly reducing conditions (Ni-NiO oxygen fugacity buffer) it recrystallizes to form the SYNROC-D mineral

assemblage. Compositions and proportions of individual mineral phases of SYNROC-D are also given in Table 1.

It is also possible that the sodium content of the sludge could be reduced to below 2 percent by more intensive washing procedures. With these lower concentrations, the sodium is preferentially immobilized by adding Nb_2O_5 to the sludge instead of SiO_2 . In the resultant phase assemblage, sodium is immobilized as the component NaNbO_3 (which occurs as the natural mineral "lueshite", possessing the perovskite structure). In practice, the sodium is immobilized in a complex perovskite solid solution ($\text{CaTiO}_3\text{-NaNbO}_3$) (Table 2). Immobilization of Na_2O in this manner requires the addition of 4 to 5 times its weight as Nb_2O_5 prior to calcination. Otherwise the processing conditions are similar to those employed in immobilizing high-sodium sludges.

In the Savannah River and Hanford tanks, most of the fission product cesium occurs in the supernatant liquor. This is treated separately from the sludges. Currently, the preferred procedure is to segregate the cesium in a zeolite ion-exchanger and to calcine the product. This procedure could readily be used in the SYNROC-D process. After calcination, the granular cesium-bearing silicates would be mixed with the SYNROC components prior to hot-pressing. Alternatively, and preferably, the cesium would be separated on a titanate ion-exchanger and converted to a hollandite solid solution ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}\text{-Cs}_2\text{Al}_2\text{Ti}_6\text{O}_{16}$). This material would then be mixed with the SYNROC-D calcine prior to hot-pressing. These steps are further described below.

DESCRIPTION OF CONCEPTUAL FLOWSHEET

A simplified conceptual flowsheet showing the essential

23
TABLE 1

IMMOBILIZATION OF AVERAGE SAVANNAH RIVER SLUDGE COMPOSITION

	Average Sludge Calcine	Inert Additives
SiO ₂	0.6	7.5
TiO ₂	-	15.0
ZrO ₂	-	4.0
UO ₂	2.3	-
Al ₂ O ₃	21.2	-
Fe ₂ O ₃	27.1	-
MnO	6.1	-
NiO	3.4	-
CaO	2.0	4.9
NaO	3.8	-
FP,A ¹	2.1	-
Sum wt. %	69.	31.

Typical Examples of Coexisting Phases

	Zirconolite	Perovskite	Spinel	Nepheline
Estimated Proportions, wt. %	16	11	55	18
SiO ₂	-	-	-	41.0
TiO ₂	32.5	53.6	14.3	0.5
ZrO ₂	32.7	<.1	0.2	-
UO ₂	11.2	3.0	<.1	-
Al ₂ O ₃	1.1	0.1	17.2	35.2
Fe ₂ O ₃	7.1 ³	2.7 ³	20.5	1.1 ³
Sm ₂ O ₃	2.5	6.8	-	-
FeO	-	-	31.0	-
MnO	0.9	<.3	10.8	-
NiO	2.1	0.2	5.7	-
CaO	9.8	34.1	0.2	0.8
Na ₂ O	0.7	<.5	<.1	21.4
Sum wt. %	100.6	100.5	99.9	100.1

¹Fission products plus actinides excluding U.

²Experimental conditions: Ni capsule, 5 kb, 1150°C, 1 hr.
Starting material doped with 1-2% Sm₂O₃.

³Total iron assumed as Fe₂O₃.

TABLE 2

Immobilization of average Savannah River sludge (Table 1) but with sodium reduced to 2 percent by more intense washing. Silica addition is replaced by niobium oxide according to ratio $\frac{\text{Nb}_2\text{O}_5}{\text{Na}_2\text{O}} \sim 4.2$. This result is the incorporation of sodium into perovskite rather than nepheline.

	<u>Spinel ss.</u>	<u>Zirconolite</u>	<u>Perovskite ss.</u>
Nb ₂ O ₅	<.1	3.7	38.1
TiO ₂	3.49	24.4	25.6
ZrO ₂	<.1	36.0	-
UO ₂	-	7.7	0.5
Al ₂ O ₃	43.6	1.5	0.3
Sm ₂ O ₃	-	3.1	2.7
Fe ₂ O ₃	11.2	-	-
FeO	18.2	7.7	1.9
MnO	8.1	3.2	0.7
NiO	15.7	1.1	0.2
CaO	-	10.8	19.6
Na ₂ O	-	0.9	9.1
sum	100.3	100.1	98.7

Experimental conditions: 5kb, 1250° Ni caps, 1 hr.

steps required for immobilization of Savannah River sludges in SYNROC-D is given in Figure 1.

Stage 1: Thirty to forty percent of inert SYNROC-D additives are intimately mixed with the washed sludge according to the formulation of Table 1 (assuming a high-sodium sludge). The slurry is continuously and strongly agitated to achieve homogeneity of mixing. A small amount of a suitable reducing agent (e.g. powdered metallic iron) is added in order to reduce Mn^{4+} to Mn^{2+} and about half of the Fe^{3+} to Fe^{2+} . Alternatively, a small amount of powdered metallic aluminium could be mixed at this stage and the actual reduction performed at high temperatures developed in the spray calciner (Stage 2).

Stage 2: The strongly agitated slurry is introduced into a spray calciner operating at about $600^{\circ}C$. The function of the spray calciner is to devolatilize the slurry and produce a very homogeneous, free-flowing and chemically reactive mix of sludge components with added SYNROC oxides. Mildly reducing conditions are required within the spray calciner so that all manganese and about half of the total iron remain divalent. The off-gases are passed through filters and the collected dust returned to the sludge-tank.

Stage 3: About 3 to 5 percent of metallic nickel powder is mixed with the SYNROC powder exiting from the spray calciner. The degree of mixing is not required to be exceedingly thorough. The function of the nickel is to maintain the SYNROC redox state close to the nickel-nickel oxide oxygen fugacity buffer during subsequent processing steps. With careful control of redox state in the spray calciner, it might prove possible to omit stage 3.

Stage 4: The powder emerging from the spray calciner has a very low density. Before the powder can be conveniently hot-pressed (Stage 5) it is desirable to pre-compact it to a higher density (e.g. about 50 percent of theoretical). According to one approach, the powder could be cooled in a controlled atmosphere to ambient temperatures and then either compressed into granules or formed into pellets, using simple and readily available technology. Alternatively, and preferably, the powder from Stage 3 would be formed into pellets at the exit temperature from Stage 3, i.e. about 600°C. This procedure may require additional research and development, but would be advantageous in terms of thermal efficiency and processing time. Moreover, the resultant pellets are likely to be mechanically stronger than pellets or granules formed at ambient temperatures.

Stage 5: The next step consists of uniaxially hot-pressing the pellets in several discrete stages in the final canister in which they are to be disposed of. The process is analogous to processes of in-can glass-melting (3). However, the heat-transfer problems encountered by the latter process are avoided because of prior devolatilization of the feed powder and pre-compaction into pellets or granules which possess acceptable thermal conductivities. The process of in-can uniaxial hot-pressing is currently under development by the Australian Atomic Energy Commission. Special procedures are being developed to provide radial support to the can walls during the pressure stroke and to preventing oxidation.

Pellets or granules from Stage 4 would be dropped into stainless steel cans about 3 meters long by 0.5 m diameter. The cans would possess thick walls and would be maintained at a

temperature of about 1050°C by an external induction heater. When pellets had accumulated to a height of about 1 meter and had been uniformly heated to 1050°C , they would be uniaxially compressed to near-theoretical density by means of a vertical retractable piston, driving a floating ceramic (alumina) disc (Fig. 1). The piston would then be retracted and the cycle continued until the can was nearly full. Remaining space would be filled with an inert ceramic material (e.g. MgO) and the canister removed and cooled.

A parallel production line would also be producing silicate or titanate pellets containing immobilized cesium which had been removed from the supernatant liquor in the tanks and concentrated via zeolite or titanate ion-exchangers. If necessary, these pellets could be produced in batches using the same system as was being used to produce SYNROC-D pellets from the sludges. Pellets containing immobilized cesium would be dropped into the canister simultaneously with the sludge pellets so that both materials were well-mixed prior to hot-pressing. The final SYNROC-D would thus contain its full complement of fission-product cesium.

Stage 6: After cooling, the canisters are sealed by welding and decontaminated.

Hot isostatic pressing as an alternative to Stage 5

According to the process outlined above, formation and compaction of SYNROC-D is accomplished by in-can uniaxial hot-pressing. This would be performed within the main processing canyon, necessitating remote control and maintenance. Alternatively, this step could be accomplished by hot isostatic pressing. This

technology has been extensively developed by the ASEA company in Sweden. ASEA engineers are confident that the process can be operated entirely by remote control. However, the equipment is too complex for remote maintenance. It is therefore envisaged that the hot isostatic pressing operation would occur not in the canyon but in a shielded, decontaminated enclosure which would permit direct maintenance of the equipment, combined with remote control of the processing operation. After filling a canister with pellets or granules, it would be evacuated and sealed. After decontamination it would be transferred to a "clean room" where it would be encapsulated in a second container, evacuated and sealed. The doubly-encapsulated canister would then be isostatically hot-pressed.

QUALITY CONTROL

Monitoring of chemical composition, homogeneity of mixing and other relevant properties would be accomplished by periodically withdrawing pellets and granules at Stage 4 and studying them by remote means. Monitoring of the hot-pressing step would be accomplished in two separate operations. Pellets from Stage 4 would be hot-pressed in a small, laboratory-sized unit which accurately reproduced the temperature-pressure-time conditions which are employed on the large production unit. The small samples produced by this parallel laboratory-scale operation should possess identical properties to the massive SYNROC-D in the large canisters. These samples would then be used for quality control testing. As a double-check on this procedure, actual samples of SYNROC-D would be recovered periodically by drilling and coring from the large canisters after hot-pressing. After the cores had been removed, the canisters would be re-sealed.

APPLICATION OF SYNROC PROCESS TO CIVILIAN HIGH LEVEL WASTES

High level wastes produced by reprocessing of fuel rods used for nuclear power generation differ from the defense wastes in several respects. The civilian wastes do not contain the large amounts of Fe, Al, Ni, Mn and Na present in defense waste as processing additives. Moreover, the civilian high level wastes consist initially of a solution of fission products and actinides in nitric acid. Thirdly, in the solidification of civilian wastes, cesium remains associated with the other fission products, whereas in defense wastes, it is treated separately.

Despite these differences, the conceptual flow-sheet for immobilizing civilian HLW in SYNROC-C is similar to that depicted in Figure 1. The inert additives ($\text{TiO}_2 + \text{ZrO}_2 + \text{BaCO}_3 + \text{CaCO}_3 + \text{Al}(\text{OH})_3$) of SYNROC-C (4) would be intimately mixed by ball-milling outside the processing canyon and then added to the nitric acid solution of high level wastes within the canyon. The agitated slurry would then be spray calcined at about 600°C , resulting in decomposition of nitrates and the production of a fine homogeneous powder, which would be converted into pellets or granules. Subsequent heat treatment must be carried out under conditions which minimize the volatility of cesium and ruthenium and maintain molybdenum in the quadrivalent state. To achieve these objectives, it may be necessary to insert an additional processing stage by preheating the pellets (granules) in a controlled atmosphere at $800\text{--}1000^\circ\text{C}$ in a suitable kiln prior to hot-pressing. Apart from this step, which may not prove to be necessary, the processing of civilian wastes to produce SYNROC-C would be similar to that depicted in Figure 1.

CONCLUSION

It has been suggested that the immobilization of high level wastes in SYNROC would require a much more complicated process than immobilization in borosilicate glasses. This contention is not supported by the flowsheet shown in Figure 1. Most of the individual processing steps are similar for both processes. The only major difference is the substitution of a hot-pressing step for the glass melter. It is expected that the proposed uniaxial hot-pressing system will be simpler to operate than a glass melter. The alternative isostatic hot-pressing system may be somewhat more complex, but this is offset by the fact that it will be situated in a direct-maintenance area.

It is believed that the immobilization of defense wastes in SYNROC-D possesses important advantages over an alternative process which involves immobilizing the sludges in borosilicate glass.

(1) It is possible to immobilize about 3 times the weight of sludge in a given volume of SYNROC-D as compared to borosilicate glass. The costs of fabrications, transport and ultimate geologic storage are correspondingly reduced.

(2) The mineral assemblage of SYNROC-D is vastly more stable in the presence of groundwaters than are borosilicate glasses. The long-lived actinide elements in particular, are immobilized much more securely in SYNROC-D than in glass.

(3) SYNROC-D is composed of thermodynamically compatible phases which possess crystal structures identical to those of natural minerals which are known to have survived in geological environments at elevated pressures and temperatures for periods of 500 to 2000 million years and to have retained radioactive elements quantitatively for these periods despite strong radiation

damage (5). It is this evidence, provided by NATURE herself, which can demonstrate to the community that the shorter times required for radwaste immobilization under the much less extreme P,T conditions present in a suitable geological repository can be successfully achieved. Glass, as a waste-form is intrinsically incapable of providing this assurance.

REFERENCES

- (1) Ringwood, A.E. (1979) Immobilization of high level nuclear wastes generated by the US defense program (unpublished report).
- (2) Ringwood, A.E., S.E. Kesson and N.G. Ware (1979) Immobilization of US defense nuclear wastes using the SYNROC process. J. Am. Ceram. Soc. (in press).
- (3) Morris, J.C. and B. Chidley (1976) Preliminary experience with the new Harwell inactive vitrification pilot plant, in Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. 1, 241-257, IAEA Vienna.
- (4) Ringwood, A.E., S.E. Kesson, N.G. Ware, W.O. Hibberson and A. Major (1979) The SYNROC process: A geochemical approach to nuclear waste immobilization. Geochem. J. 13, 141-165.
- (5) Ringwood, A.E., V.M. Oversby and W. Sinclair (1979) Effects of radiation damage on SYNROC. J. Am. Ceram. Soc. (in press).

A.E. RINGWOOD

PREFERRED COMPOSITION OF SYNROC

A.E. Ringwood

INTRODUCTION

The objective of the SYNROC process (Ringwood et al., 1979a,b) is to incorporate high-level nuclear waste species as components of dilute solid solutions in the crystal lattices of the constituent minerals - hollandite, zirconolite and perovskite. Since there are upwards of thirty elements in radwaste, possessing different radii and charges, surprise is sometimes expressed that these elements can be incorporated and successfully immobilized in such a relatively simple waste-form. Concern has also been expressed that because of its crystalline nature, SYNROC may not be a sufficiently "stable" waste form, i.e. it might not be able to tolerate substantial deviations in the composition of the high level waste arising from the use of different fuel cycles. These topics are examined below in the context of selecting a recommended or "preferred" bulk composition for SYNROC.

MINERAL CHEMISTRY

The basic formulae of the principal minerals of SYNROC are hollandite $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$, zirconolite $\text{CaZrTi}_2\text{O}_8$, and perovskite CaTiO_3 . It is important to appreciate that the first two minerals display very wide variations in stoichiometry, whilst perovskite also displays significant variations. The hollandite formula may be written $\text{Ba}_x\text{Al}_{2x}\text{Ti}_{8-2x}\text{O}_{16}$ where x can vary from 0.3 to 1.8. In SYNROC, where $x \leq 1$, the hollandite phase can be regarded as a solid solution between ideal $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ ($x = 1$) and rutile ($x = 0$, $\text{Ba}_0\text{Al}_0\text{Ti}_8\text{O}_{16}$). A typical hollandite containing 70 wt.% TiO_2 has the formula

$\text{Ba}_{0.8}\text{Al}_{1.7}\text{Ti}_{1.3}\text{O}_{15}$ and can be regarded as a solid solution between $\text{BaAl}_2\text{Ti}_2\text{O}_{13}$ (46.5%) and TiO_2 (13.5%). Hollandite with 75% TiO_2 contains about 40% excess TiO_2 in solid solution. Thus we see that hollandite serves as a buffer for TiO_2 in SYNROC and can either donate it to the other minerals, or absorb it, as required.

Zirconolite, $\text{CaZrTi}_2\text{O}_7$, also exhibits a substantial degree of solid solution towards a hypothetical end member " CaTi_2O_7 " (or $\text{CaTiO}_3 + 2\text{TiO}_2$). Pure zirconolite dissolves about 10 mole % of CaTiO_3 at 1350°C and has the composition $\text{Ca}(\text{Zr}_{0.9}\text{Ti}_{0.1})_2\text{O}_7$. Since the third mineral component of SYNROC is perovskite, CaTiO_3 , we see that there is an important equilibrium linking all three minerals

We shall see that existence of the wide ranges of stoichiometry for hollandite and zirconolite, combined with the above equilibrium between all three minerals are important elements in making SYNROC a "forgiving" waste form.

The second major characteristic of SYNROC which makes it a forgiving waste form is the capacity of the individual minerals to incorporate a remarkably wide range of cations possessing different radii and charges into their structures. Nearly all the elements occurring in radwaste can be incorporated in SYNROC minerals. It is recommended that about 10 weight percent of radwaste calcine (Table I) be introduced into solid solution in SYNROC minerals. At this level of concentration, all three minerals are greatly undersaturated with respect to any individual component; hence wide variations in waste composition are possible

Table 1. Composition of a 10 gm batch of radwaste calcine PX-46 with U increased to represent 99.1% removal during Purex extraction (Mendel et al., 1977).

Oxide	wt % in Calcine
Sr_2SO_4	0.10
Ba_2SO_4	0.10
Ni_2SO_4	0.10
PbO	0.10
MgO	0.10
CaO	0.10
ZrO_2	0.10
SiO_2	0.10
Y_2O_3	0.10
La_2O_3	0.10
Th_2O_3	0.10
UO_2	0.10
PuO_2	0.10
MnO_2	0.10
Fe_2O_3	0.10
Co_2O_3	0.10
Ni_2O_3	0.10
Cu_2O	0.10
Ag_2O	0.10
TeO_2	0.10
U_2O_5	0.10
Other actinides as A_2O_3	0.10

without causing any new phase to appear.

As usual, we proceed to consider in detail how a 100 gm batch of UCN-1 containing 10 wt% of typical radwaste (Table 1) can be brought into equilibrium.

Barium

Barium elements are readily incorporated in perovskite and zirconolite, in the approximate ratios 1/11 (average). Only a rather small percentage as BaO components and is not significantly incorporated in zirconolite. However, to enter zirconolite in approximate 1/11, a component is necessary. Also, the rare earth zirconolite zirconolite contains 6 wt% of TiO_2 . Different behavior of these elements present in radwaste will behave differently. However, their abundances are very small.

Chromium

Chromium zirconolite. The reaction is

The TiO_2 component is provided by excess of this phase. Chromium present in UCN-1. One mole of CrO_3 can be added for every mole of CrO_3 . Immobilization of the 1.1 gm CrO_3 in Table 1 will thus require 0.1 gm TiO_2 .

Uranium and other tetravalent actinides

Most of uranium enters zirconolite as a CaTi_2 component, with U replacing Zr. The situation is similar to that with Cr, and requires a maximum of 0.44 gm TiO_2 . Some U can enter zirconolite replacing Ca, with electro-neutrality achieved by substitutions of 2Al^{3+} for 2Ti^{4+} and/or Fe^{2+} for Ti^{4+} . Some U also enters perovskite. However, the amounts are sufficiently small that specific allowances are not required.

Cassiterite, Pyrochlore, and Titanite

... are either $(\text{Al}, \text{Ti})_2\text{O}_3$, hollandite as $\text{Cs}_2\text{Al}_2\text{Ti}_2\text{O}_{10}$, and $\text{Rb}_2\text{Al}_2\text{Ti}_2\text{O}_{10}$ elements. The quantities shown in Table 1 are given in terms of Al, Ti, and Cs or Rb, in order to enter.

... ..

... ..

... ..

... ..

... ..

... ..

... ..

... ..

... ..

At the redox state under which SYNROC is produced, these elements are reduced to the elemental state and alloy with small amounts of metallic nickel which are introduced. SYNROC thus has a few percent dispersed metallic and sulphide phases.

Summary

The previous discussion showed that in order to immobilize nearly all the components of radwaste in SYNROC, only modest additions of TiO_2 and Al_2O_3 are necessary. Specifically, the immobilization of 16 wt radwaste (Table 1) would require the addition of 1.2 wt Al_2O_3 and 1.9 wt TiO_2 . Note that the 1.9 addition is buffered by the capacity of hollandite to form solid solution with excess TiO_2 . Thus the immobilization equilibria in SYNROC are insensitive to this component and wide variations in waste composition can be accommodated without difficulty. The only obligatory condition is that sufficient alumina be added to facilitate entry of Ba , Cs and excess Na into hollandite. This is best guaranteed by adding a significant excess amount of Al_2O_3 over that needed to form the stoichiometric hollandite component. Excess Al_2O_3 crystallizes as a $\text{BaAl}_2\text{Si}_2\text{O}_{10}$ -type phase. Provided excess Al_2O_3 is present, substantial variations in the non-valent cation component (mainly Cs^+) of the waste can be tolerated without adverse effects.

CURRENTLY PREFERRED SYNROC FORMULATION

An earlier formulation (Ringwood et al., 1979a) was calculated assuming a stoichiometric $\text{BaAl}_2\text{Ti}_2\text{O}_{10}$ hollandite in SYNROC, and contained 9.0% of BaO . With subsequent experience, it seemed possible that this composition might not be ideal since the hollandites found in SYNROC were usually richer in TiO_2 . A second formulation was then produced, using a typical low- BaO , high TiO_2 hollandite (Ringwood et al., 1979b). However, hollandite is sometimes reluctant to crystallize from this composition because of

Table 2. Properties of the polymer.

Sample	Intrinsic Viscosity		Intrinsic Viscosity	
	in CHCl_3		in CH_2Cl_2	
1	0.15	0.15	0.15	0.15
2	0.15	0.15	0.15	0.15
3	0.15	0.15	0.15	0.15
4	0.15	0.15	0.15	0.15
5	0.15	0.15	0.15	0.15
6	0.15	0.15	0.15	0.15
7	0.15	0.15	0.15	0.15
8	0.15	0.15	0.15	0.15
9	0.15	0.15	0.15	0.15
10	0.15	0.15	0.15	0.15
11	0.15	0.15	0.15	0.15
12	0.15	0.15	0.15	0.15
13	0.15	0.15	0.15	0.15
14	0.15	0.15	0.15	0.15
15	0.15	0.15	0.15	0.15
16	0.15	0.15	0.15	0.15
17	0.15	0.15	0.15	0.15
18	0.15	0.15	0.15	0.15
19	0.15	0.15	0.15	0.15
20	0.15	0.15	0.15	0.15
21	0.15	0.15	0.15	0.15
22	0.15	0.15	0.15	0.15
23	0.15	0.15	0.15	0.15
24	0.15	0.15	0.15	0.15
25	0.15	0.15	0.15	0.15
26	0.15	0.15	0.15	0.15
27	0.15	0.15	0.15	0.15
28	0.15	0.15	0.15	0.15
29	0.15	0.15	0.15	0.15
30	0.15	0.15	0.15	0.15
31	0.15	0.15	0.15	0.15
32	0.15	0.15	0.15	0.15
33	0.15	0.15	0.15	0.15
34	0.15	0.15	0.15	0.15
35	0.15	0.15	0.15	0.15
36	0.15	0.15	0.15	0.15
37	0.15	0.15	0.15	0.15
38	0.15	0.15	0.15	0.15
39	0.15	0.15	0.15	0.15
40	0.15	0.15	0.15	0.15
41	0.15	0.15	0.15	0.15
42	0.15	0.15	0.15	0.15
43	0.15	0.15	0.15	0.15
44	0.15	0.15	0.15	0.15
45	0.15	0.15	0.15	0.15
46	0.15	0.15	0.15	0.15
47	0.15	0.15	0.15	0.15
48	0.15	0.15	0.15	0.15
49	0.15	0.15	0.15	0.15
50	0.15	0.15	0.15	0.15
51	0.15	0.15	0.15	0.15
52	0.15	0.15	0.15	0.15
53	0.15	0.15	0.15	0.15
54	0.15	0.15	0.15	0.15
55	0.15	0.15	0.15	0.15
56	0.15	0.15	0.15	0.15
57	0.15	0.15	0.15	0.15
58	0.15	0.15	0.15	0.15
59	0.15	0.15	0.15	0.15
60	0.15	0.15	0.15	0.15
61	0.15	0.15	0.15	0.15
62	0.15	0.15	0.15	0.15
63	0.15	0.15	0.15	0.15
64	0.15	0.15	0.15	0.15
65	0.15	0.15	0.15	0.15
66	0.15	0.15	0.15	0.15
67	0.15	0.15	0.15	0.15
68	0.15	0.15	0.15	0.15
69	0.15	0.15	0.15	0.15
70	0.15	0.15	0.15	0.15
71	0.15	0.15	0.15	0.15
72	0.15	0.15	0.15	0.15
73	0.15	0.15	0.15	0.15
74	0.15	0.15	0.15	0.15
75	0.15	0.15	0.15	0.15
76	0.15	0.15	0.15	0.15
77	0.15	0.15	0.15	0.15
78	0.15	0.15	0.15	0.15
79	0.15	0.15	0.15	0.15
80	0.15	0.15	0.15	0.15
81	0.15	0.15	0.15	0.15
82	0.15	0.15	0.15	0.15
83	0.15	0.15	0.15	0.15
84	0.15	0.15	0.15	0.15
85	0.15	0.15	0.15	0.15
86	0.15	0.15	0.15	0.15
87	0.15	0.15	0.15	0.15
88	0.15	0.15	0.15	0.15
89	0.15	0.15	0.15	0.15
90	0.15	0.15	0.15	0.15
91	0.15	0.15	0.15	0.15
92	0.15	0.15	0.15	0.15
93	0.15	0.15	0.15	0.15
94	0.15	0.15	0.15	0.15
95	0.15	0.15	0.15	0.15
96	0.15	0.15	0.15	0.15
97	0.15	0.15	0.15	0.15
98	0.15	0.15	0.15	0.15
99	0.15	0.15	0.15	0.15
100	0.15	0.15	0.15	0.15

Table 3. Properties of the polymer.

Table 1. Currently preferred STP003 formulation.

References

- Ringwood, A.M., Kesson, S.E., Ware, N.G., Hibberson, W. and
Mayer, A. (1979a) Immobilization of high level nuclear
reactor wastes in SYNROC. Nature 278, 219-221.
- Ringwood, A.M., Kesson, S.E., Ware, N.G., Hibberson, W. and
Mayer, A. (1979b) The SYNROC process: A geochemical
approach to nuclear waste immobilization. Geochim. et Cosmochim. 43,
191-201.
- Ringwood, A.M., Overby, T.M. and Sinclair, W. (1980) The effects
of radiation damage on SYNROC. Scientific Basis for Nuclear
Waste Management 2 (in press). Plenum, New York.

Table 4. Simplified 2-phase SYNROC composition.

	Leilandite 40	Dirosenite 60	wt%
Al_2O_3	85.2	48.5	50.2
FeO	-	31.1	19.3
Al_2SiO_5	17.4	3.3	7.5
SiO_2	20.9	-	11.5
CaO	-	15.1	9.6
Total	100.0	100.0	100.0

Table 3. Simplified SYNROC formulation.

	<u>wt.-%</u>
2- RANK CEMENT (from Table 4)	85
3- Granite aggregate (from Table 1)	10
4- Water	1.0
5- Oil	4.0

Reconnaissance experiments on the possible role of monazite for actinide immobilization in SYNROC-D

A.I. Ringwood

Research School of Earth Sciences
Australian National University
Canberra, A.C.T. 2600, Australia

1. Introduction

Monazite, a light-lanthanide orthophosphate, is presently under evaluation as a candidate for the immobilization of actinides [1,2]. Natural monazites have survived a variety of geological and geochemical environments far more extreme than those to be encountered in a radwaste repository. They also appear to be highly resistant to metamictization despite high α -particle fluxes from U and Th in their crystal lattices [3]. Moreover, preliminary laboratory leaching experiments indicate that monazite has a leach rate approximately 3 orders of magnitude less than that of borosilicate glass [2]. All of these above characteristics are highly desirable in a mineral-ceramic waste-form.

Natural monazite $(Ce,La)PO_4$ typically contains 4-12% ThO_2 with rare specimens containing as much as 30% ThO_2 [4]. UO_2 contents as high as 16% have been reported in some samples [5]. Monazite is isostructural with the high temperature polymorph of $ThSiO_4$, and it has been proposed that in nature, Th (and possibly U) enters the monazite lattice by means of the coupled substitution $Th^{4+}Si^{4+} = Ln^{3+}P^{5+}$ [4]. In laboratory experiments [1] McCarthy and co-workers found that Th alone could be persuaded to enter monazite in this manner. In order for U to enter the lattice it was necessary to involve Ca in a coupled substitution i.e.

$$U^{4+}Ca^{2+} = 2Ln^{3+}.$$

A reconnaissance experimental investigation exploring the possibility of using monazite as an actinide host in SYNROC-D has been undertaken. The results and conclusions derived from this study are described below.

2(1) Experimental studies of binary systems. I. Monazite

The compatibility of monazite with individual SYNROC phases has been studied experimentally at 5 kb, 1300-1400°C. Two synthetic monazite compositions LaPO_4 and $\text{La}_{.5}\text{Sm}_{.5}\text{PO}_4$ were used. Numerous experimental difficulties were encountered. In a number of runs the binary systems were well below their solidi, and as a result the product phases were very fine-grained and poorly crystalline. This hindered microprobe and X-ray diffraction analyses. In order to obtain crystals large enough for microprobe analyses, it was necessary to carry out experiments within 20° of the solidus.

(a) Monazite + Perovskite

This pair is not compatible and breaks down to rutile plus several Ca,REE phosphates; examples of which are shown in Columns 1 and 2, Table 1. The solidus was located near 1390°C.

(b) Monazite + Zirconolite

This pair is likewise incompatible, with Ca from zirconolite reacting to produce a new Ca,REE orthophosphate, and an unidentified Ca,REE titanate. ZrTiO_4 and ZrO_2 are also produced in the breakdown. The solidus was located near 1420°C. Typical examples of these products are given in Columns 3-5, Table 1.

(c) Monazite + Hollandite ($2\text{BaAl}_2\text{Ti}_6\text{O}_{16}$)

These phases are believed to be compatible. When previously synthesized monazite and hollandite were run together, no new phases were formed. Moreover, an active oxide mix with the composition of monazite : hollandite 1:1 wt.% crystallized at 1350°C, 5 kb to the two-phase assemblage. (Traces of rutile in some runs are attributed to mixing difficulties). The solidus was located near 1385°C.

(d) Monazite + Nepheline

Nepheline is an optional phase in the SYNROC-D mineralogy. Its compatibility with monazite was confirmed at 1400°C, 5 kb by a strategy analogous to that described in (c) above. No

Table 1. Compositions of Phases Produced by Reaction of Monazite with Perovskite or Zirconolite.

	1	2	3	4	5
TiO_2	<.5	<.5	-	-	47.7
ZrO_2	-	-	-	-	1.
La_2O_3	36.	52.	21.	19.	5.
Sm_2O_3	-	-	10.	12.	30.
CaO	26.7	14.1	29.4	30.8	16.6
P_2O_5	36.4	32.8	39.6	38.7	-
Sum	99.	99.	100.	100.	100.

1 and 2: New Ca,REE phosphates produced by reaction of monazite (LaPO_4) with perovskite (2:1 by weight) at 5 kb, 1350°C for 1 hr.

3: Ca,REE orthophosphate produced by reaction of Monazite ($\text{La}_{.5}\text{Sm}_{.5}\text{PO}_4$) with zirconolite (1:1 by wt.) at 5 kb, 1350°C for 1 hr.

4: Ca,REE orthophosphate produced as above at 1400°C .

5: Ca,REE titanate produced as above at both 1400° and 1350°C .

new phases were observed when the previously-synthesized minerals were run together, moreover, an active oxide mix recrystallized to the two-phase assemblage. The euhedral form of tiny monazite crystals, and the slight fluctuations in Ca -intensity during microprobe analyses of nepheline, lead us to suspect that at 1400°C , 5 kb, this particular binary system is above its solidus.

(c) Monazite + Spinel

Experiments discussed in more detail in the next section suggested that monazite is compatible with typical spinels formed during SYNROC-D manufacture.

(1) Monazite + Pseudobrookite/Rutile

Al_2TiO_5 and TiO_2 were produced as by-products in early experiments involving hollandite. Monazite appears to be compatible with these two phases.

(11) Experimental studies of binary systems. II. Xenotime

The compatibility of the heavy-lanthanide orthophosphate xenotime, with SYNROC phases was also studied experimentally at 5 kb, 1300 – 1400°C . A synthetic xenotime $\text{Sm}_{.5}\text{Y}_{.5}\text{PO}_4$ was used, with Y acting as a crystallo-chemical analog for heavy rare earths. Xenotime proved to be incompatible with hollandite, perovskite and zirconolite, giving rise to complex Ca or Ba , REE phosphates and pyrochlore-type phases. Sm typically partitions into the complex phosphate, with Y forming a separate Y-rich phosphate phase. No further studies involving xenotime have been carried out.

3. Experimental investigation of the compatibility of monazite with US defence wastes.

Having shown that monazite is incompatible with zirconolite and perovskite, the possibility of using monazite instead of zirconolite + perovskite as the actinide host in a SYNROC-D formulation was then studied experimentally. Three model compositions based on the composite Savannah R. sludge [6] were prepared. The first, "SiO₂-free SC" represents the unwashed composite sludge

Table 2. Compositions of Calcined Model Defence Sludges used in Compatibility Tests with Monazite.

	SiO ₂ -free SC ¹	Nepheline-sat. SC ²	Washed Average Sludge ³
SiO ₂	-	11.6	-
UO ₂	3.4	3.0	3.4
Al ₂ O ₃	30.4	27.5	29.6
Fe ₂ O ₃	49.5	35.2	47.3
MnO	8.9	7.9	7.3
SiO	4.9	4.4	4.7
CaO	2.9	2.6	3.2
Na ₂ O	5.6	5.0	tr
FP/A ⁴	(3)	(3)	(3)
Sum	99.	100.	99.

1. Average unwashed Savannah R. sludge, SiO₂-free.
2. As above, with enough SiO₂ added to allow all Na the opportunity to crystallize as nepheline.
3. Model Savannah R. composite sludge prepared by Southwestern Anal. Chem. Labs. Representative quantities of UO₂ added later by ANL.
4. Fission products plus actinides.

(5.6% Na_2O). The second composition, "Nepheline-saturated SC" is a modification of the first where sufficient SiO_2 has been added to allow all 5.6% Na_2O the opportunity to crystallize as nepheline. A third composition, representing a thoroughly-washed composite sludge (prepared by Southwestern Analytical Chem. Labs.†) was also used. The compositions of these three starting materials are given in Table 2.

Mixtures of monazite + calcined sludge in 1:2 weight proportions were used for all experiments. These were carried out in Si capsules at 5 kb, 1100-1200°C. At the higher end of the temperature range there is unmistakable evidence of extensive melting.

All experiments with monazite plus "SiO₂-free SC" or "nepheline-saturated SC" are similar. Recognizable spinels (10-50 μm diameter) are set in a corroded, pitted and poorly polished matrix. Monazite and nepheline (too small for quantitative analysis) have been detected in this matrix, which is believed to include a P - Na - Si glass or other water-soluble phases. Clearly the existence of such matrix material would result in a waste-form with very poor leaching behaviour and mechanical properties. Microprobe analysis indicates that almost all the uranium initially present in the model sludges has been lost during polishing as a water-soluble species.

When monazite was added to the well-washed, low-Na composite sludge calcine (Table 3, Column 3), the ceramic product was again found to be pitted and corroded following polishing procedures for probe analysis. As well as spinel, both essentially pure LaPO_4 and a Ca,La phosphate could be recognized. However, U did not partition into either of these phosphate phases. Instead it formed small, discrete grains of UO_2 scattered throughout the sample.

4. Partition behaviour of Cs

Experimental systems used to confirm the compatibility of monazite with hollandite were also doped with ~1% Cs_2O , SrO and UO_2 in order to observe partition behaviour. An unexpected result was obtained using one batch of starting material. Whilst some

†The requisite amount of UO_2 was subsequently added at ANU.

Cs entered hollandite as expected, the bulk of the Cs was concentrated in a strange new Ba,REE phosphate. Microprobe analyses of typical coexisting hollandite and phosphate are given in Table 3. Optically, the phosphate "phase" was poorly resolved and could well have been multi-phase, however, no SiO_2 or Al_2O_3 contamination was detected. A newly-prepared batch of starting material run under the same conditions yielded monazite + hollandite (+ trace rutile) with Cs partitioned entirely into the hollandite. No new phosphate phase appeared.

These latter experiments confirm our belief that the initial Cs-partition experiments yielded anomalous results. However, a further series of experiments were carried out to evaluate plausible mechanisms for Cs substitution in monazite and in Ba,Lu phosphates.

Having confirmed that Cs does not enter pure LaPO_4 , the possible coupled substitution $\text{Cs}^+ + \text{La}^{3+} = 2\text{Ba}^{2+}$ was investigated using several Cs-doped compositions along the join LaPO_4 - $\text{Ba}_3(\text{PO}_4)_2$, namely 9:1, 8:2, 6:4 and 4:6 by wt. At 5 kb, 1400-1500°C a miscibility gap is observed between essentially pure LaPO_4 and an intermediate orthophosphate. The composition of monazite and this coexisting Ba,Lu orthophosphate are given in Table 4. Note that Cs does not enter either phase. (Cs signals can be detected by the probe from rare pits in the sample surface). It was concluded that the coupled substitution suggested above is not a viable mechanism.

5. Partition behaviour of Sr

In the above series of experiments, Sr was observed to partition into the Ba,Lu orthophosphate phase (Table 4). As described in Section 3, the addition of monazite to a low-Na model defence sludge calcine resulted in the formation of a new Ca,Lu phosphate. On the basis of the close similarity in the crystallochemical behaviour of Sr and Ca, we predict that any Sr in military wastes would partition into this phase and not into monazite.

6. Partition behaviour of U and quadrivalent actinides

The above compositions on the join LaPO_4 - $\text{Ba}_3(\text{PO}_4)_2$ were also

Table 3. Anomalous phase assemblage obtained by reaction of monazite ($\text{La}_{0.5}\text{Sm}_{0.5}\text{PO}_4$) with hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) at 5 kb, 1350°C, for 1 hr.

	Hollandite	New Phosphate "Phase"
TiO_2	68.	4.8
VO_2	<.1	1.3
Al_2O_3	13.9	<.1
La_2O_3	<.2	26.
Sr_2O_3	<.2	30.
SrO	<.1	0.7
BaO	17.	5.
Ca_2O	0.5	3.
$\text{P}_{2.5}\text{O}_5$	-	23.6
Sum	99.	99.6

Table 4. Coexisting monazite and Ba,REE orthophosphates produced in runs along the join $\text{LaPO}_4\text{-Ba}_3(\text{PO}_4)_2$ ¹.

	Monazite ²			Ba,REE orthophosphate ²		
	a	b	c	a	b	c
EuO_2	<.1	<.1	<.1	<.1	<.1	<.1
La_2O_3	69.	69.	70.	13.	12.	11.
BaO	<.3	<.3	<.3	59.	62.	63.
SrO	<.1	<.1	<.1	2.2	1.3	0.7
Ca_2O	<.1	<.1	<.1	<.1	<.1	<.1
P_2O_5	30.2	30.8	30.5	25.6	24.8	24.7
Sum	99.	100.	101.	100.	100.	99.

1. All experiments carried out in Pt capsules at 5 kb, 1460°C for 1 hr, and doped with approx. 1% each CO_2 , Ca_2O and SrO .
2. Starting compositions along the $\text{LaPO}_4\text{-Ba}_3(\text{PO}_4)_2$ (wt. fractions) are for phosphate pair (a), 1:9; for pair (b) 2:3; for pair (c) 4:6.

doped with 4% UO_2 so that its partition behaviour could be studied. Microprobe analysis confirmed that U did not enter either monazite or the new Ba,Lu phosphate. Instead it was concentrated in a third phase too small for quantitative analyses. The coupled substitution $\text{U}^{4+} \text{Ba}^{2+} = 2\text{Lu}^{3+}$ which might be anticipated on the basis of work by [1], did not operate, suggesting U only enters the monazite structure under very special circumstances.

This conclusion was further verified when monazite was added to calcium and uranium-bearing model defence sludges. Almost all uranium was lost from the product waste-forms derived from high-Ba unwashed sludge calcines, during polished-section preparation. At least some uranium was retained in the product waste-forms derived from low-Ba (well-washed) calcines, however, the uranium formed discrete grains of UO_2 and did not enter either monazite (LaPO_4) or a new Ba,Lu (ortho?) phosphate.

7. Conclusions

The experimental studies described in previous sections have shown that monazite is compatible with the SYNROC phase, hollandite, but not compatible with zirconolite or perovskite. However, monazite was found to be compatible with spinel and nepheline, two major phases in SYNROC-D (a titanate ceramic developed for defence waste immobilization). The suitability of monazite as an actinide host in a modified SYNROC-L formulation was likewise evaluated experimentally.

Monazite did not accept U into its crystal lattice in any of our experiments. In a sample binary system, neither pure LaPO_4 nor its coexisting Ba,Lu orthophosphate would accept U (although Sr was taken up by the latter phase). This indicates that the coupled substitution mechanism Ca^{2+} (or Ba^{2+}) $\text{U}^{4+} = 2\text{La}^{3+}$ described by [1] operates only with careful experimental control over stoichiometry. In the complex, multicomponent defence waste compositions, uranium occurred as discrete grains of UO_2 and did not enter either monazite (LaPO_4) or a coexisting Ca,Lu phosphate. This again demonstrates that very careful experimental control is necessary in order to achieve the coupled substitution. Such rigorously-controlled synthesis conditions would add excessive complications to the manufacture of a suitable waste-form. In

a hot cell, considerable tolerance with respect to waste-stream variation is highly desirable.

The ceramic products produced by the addition of monazite to model defence sludges showed substantial pitting, corrosion and partial loss of key elements such as uranium, during polished section preparation. This was especially evident with high-Na sludge calcines; the low-Na washed calcines yielded marginally better products. Materials with such obviously poor mechanical and leach-resistant characteristics would not prove acceptable as waste-forms.

In view of the compatibility between monazite and hollandite a new two-phase waste-form might be considered, since hollandite has the capacity to accept Cs, Rb, Mo and Ba [7] and monazite has the potential to accept REE, U, Th and possibly Sr into its crystal lattice, as evidenced by natural minerals and synthesis experiments e.g. [1]. However, our experiments suggest that in order for uranium (and hence tetravalent actinides) to be accommodated in the monazite lattice, extremely careful control and monitoring of waste-form processing conditions would be required. The resulting technical complexity in manufacturing a monazite-hollandite waste-form would seem to be rather unattractive.

References

- [1] McCarthy G.J., White W.D., and Pfoerisch D.E. (1979) Mater. Res. Bull., in press.
- [2] Boatner L.A. and Beall G.W. (1979) Abstract A4 in Mater. Res. Soc. Ann. Mtg. Abstracts.
- [3] Ewing R.C. (1977) in Ceramic and Glass Radioactive Waste Forms, ERDA Conf. 770102, 139.
- [4] Deer W.A., Howie R.A. and Zussman J. (1966) An Introduction to the Rock-forming Minerals, Longmans, London.
- [5] Gramaccioli G.M. and Segelstad T.V. (1978) Amer. Mineral. **63**, 757.
- [6] Garvin R. (1979) Unpublished analytical data.
- [7] Ringwood A.E., Hesson S.E., Ware N.G., Hibberson W.A., Major A. (1979) Nature **278**, 219.

EXPERIMENTS BEARING ON THE OPTIMUM PREPARATION
AND HEAT-TREATMENT OF SYNROC FORMULATIONS, WITH
IMPLICATIONS FOR THE FIXATION OF CESIUM AND
MOLYBDENUM

A.E. Ringwood, V.M. Oversby and S.E. Kesson

Research School of Earth Sciences
The Australian National University
Canberra, A.C.T. 2600, Australia

INTRODUCTION

PART I: PREPARATION OF STARTING MATERIALS

- (a) SYNROC-C mixes
- (b) Hollandite mixes

PART II: INITIAL CALCINATION EXPERIMENTS

- (a) Total volatile loss in air as a function of temperature
- (b) Heating experiments at Ni-NiO controlled redox conditions
- (c) Heating experiments at Fe-FeO controlled redox conditions

PART III: KINETICS OF FORMATION OF SYNROC MINERALS

- (a) Introduction
- (b) SYNROC-C
- (c) Hollandite
- (d) Discussion

PART IV: HOT-PRESSING OF HOLLANDITE AND SYNROC-C PREPARATIONS

- (a) Introduction
- (b) Experimental results: Hollandite
  - (i) Hollandite mixes pre-treated in air; hot pressed in Ni
  - (ii) Hollandite mixes pre-treated in air; hot pressed in Fe
  - (iii) Hollandite mixes pre-treated at Ni-NiO; hot pressed in Ni
  - (iv) Hollandite mixes pre-treated at Fe-FeO; hot pressed in Fe
- (c) Experimental results: SYNROC-C
  - (i) SYNROC-C pre-treated in air; hot-pressed in Ni
  - (ii) SYNROC-C pre-treated in air; hot-pressed in Fe
  - (iii) SYNROC-C pre-treated in air; hot-pressed in Co
  - (iv) SYNROC-C pre-treated at Ni-NiO; hot-pressed in Ni
  - (v) SYNROC-C pre-treated at Fe-FeO; hot-pressed in Fe

PART V: TECHNOLOGICAL SIGNIFICANCE

- (a) Preferred redox conditions for SYNROC processing
- (b) Preferred hot-pressing temperatures
- (c) Cesium volatility
- (d) Calcination

PART I: PREPARATION OF STARTING MATERIALS(a) SYNROC-C mixes

A batch of SYNROC-C sufficient to yield 100g of calcined oxides was prepared. The composition of the final oxide mix is $\text{TiO}_2 = 59.5\%$, $\text{ZrO}_2 = 11.4\%$, $\text{Al}_2\text{O}_3 = 6.0\%$, $\text{BaO} = 7.2\%$ and $\text{CaO} = 15.9\%$. The mixture was prepared by adding appropriate weights of TiO_2 , ZrO_2 , $\text{Al}(\text{OH})_3$, BaCO_3 , and CaCO_3 to a large ceramic vessel (2 litre capacity). Approximately 1 litre of methanol and 50 to 60 ceramic mixing balls (1 cm diameter) were added; the vessel was sealed and placed in a horizontal position on a device which slowly rotated the vessel for 24 hours. This procedure ensured adequate mixing of the powders to produce a homogeneous mixture. After mixing, the slurry of alcohol and powder was transferred to a beaker by pouring through coarse plastic mesh to remove the mixing balls. Any material adhering to the balls was rinsed into the beaker with methanol. The powder was allowed to settle for about 1 day and the methanol was decanted. The moist powder was left at room temperature until dry to touch, transferred to a smaller container and oven dried at 110°C for several hours. This powdered mixture was used for all subsequent SYNROC-C experiments.

A simulated high level waste was prepared by making two solutions. The first solution contained species which are likely to form precipitates with cations found in HLW, namely Mo, Te and P. This solution is called the "anion" solution. The second solution contains all of the other waste components and is called the "cation" solution. A mixture of 10ml cation solution plus 4ml anion solution produces 0.928g of calcined oxides. The mixture does not contain Pd or Tc. If these components were present the weight of oxides would be about 1g. Rhenium is used in place of Rh and Ru which were not available at the time solutions were prepared. The composition of the simulated waste is given in Table 1. It is a slightly simplified version of the Battelle PW-4b waste.

EXPERIMENTS BEARING ON THE OPTIMUM PREPARATION
AND HEAT-TREATMENT OF SYNROC FORMULATIONS, WITH
IMPLICATIONS FOR THE FIXATION OF CESIUM AND
MOLYBDENUM

INTRODUCTION

The production of SYNROC on a large scale will require careful control of processing conditions in order to achieve optimum results. One of the problems sometimes encountered is that substantial proportions of the total cesium and molybdenum occurred not in titanate phases such as hollandite, but in minor phases which could be readily leached. This is clearly undesirable and hence a large number of experiments have been carried out in an attempt to elucidate and solve this problem. This report consists of five parts. Part I describes the manner of preparation of SYNROC mixes. In addition to SYNROC, a further mix of hollandite composition containing cesium and molybdenum was also prepared. The concentrations of these elements correspond to the predicted levels in the hollandite phase of a SYNROC formulation with a 10% waste-loading. Part II deals with the first stage of calcination of powdered SYNROC and hollandite mixes, at temperatures of 600-1000°C under a wide range of redox conditions. In Part III, the implications of the above experiments for the kinetics of formation of SYNROC phases are briefly discussed. Part IV describes the products of hot-pressing the previously calcined mixtures under various redox conditions. Finally, in Part V, conclusions relevant to designing a preferred industrial process are briefly summarized.

Table 1. Composition of simulated high level waste in weight percent of oxides.

<u>Oxide</u>	<u>%</u>
Cr ₂ O ₃	0.94
FeO	3.71
NiO	0.65
UO ₂	5.93
Rb ₂ O	0.97
Cs ₂ O	7.86
SiO	2.89
BaO	4.27
CeO ₂	13.10
Nd ₂ O ₃	16.70
Sm ₂ O ₃	3.43
Y ₂ O ₃	1.63
ZrO ₂	13.46
Re ₂ O ₇	8.09
MoO ₂	12.56
TeO ₂	1.99
P ₂ O ₅	1.83
Total	100.00

SYNROC-C samples doped with simulated HLW were prepared in the following manner. Sufficient premixed SYNROC powder (prepared as described above) to yield 8.0g of SYNROC oxides plus 0.4g of TiO₂ was mixed with water to form a thick slurry. Dilute HNO₃ (approximately 3N) was added to the slurry to decompose the carbonate present. After carbonate reaction ceased a slight excess (approximately 5ml) of dilute HNO₃ was added. Al(NO₃)₃ sufficient to yield 0.3g Al₂O₃ was dissolved in a small amount of water. To this solution 10ml of cation waste was added and the solution was then combined with the SYNROC powder slurry.

Table 2. Composition in weight percent oxides of SYNROC-C doped with simulated HLW.

<u>Oxide</u>	<u>wt. %</u>
TiO ₂	53.59
CaO	13.19
Al ₂ O ₃	8.10
ZrO ₂	10.75
BaO	6.44
Cr ₂ O ₃	0.09
FeO	0.36
MnO	0.06
UO ₂	0.57
Rb ₂ O	0.09
Cs ₂ O	0.76
SrO	0.28
CeO ₂	1.26
Nd ₂ O ₃	1.61
Sm ₂ O ₃	0.33
Y ₂ O ₃	0.16
Re ₂ O ₇	0.78
MoO ₂	1.21
TeO ₂	0.19
P ₂ O ₅	0.18
Total	<u>100.00</u>

The slurry was transferred to a dropping vessel and mechanically stirred while the 4ml of anion solution were added. The final volume was about 100ml.

A steel tube (34cm long, 4cm O.D., 2.3cm I.D.) was placed in a furnace and preheated to 650°C. The SYNROC plus waste slurry was allowed to drip into the hot steel tube at the rate of 1½ to 2ml per minute. At this rate, each drop of solution was calcined before the next drop entered the tube. The slurry was mechanically stirred throughout the dropping operation. On completion of calcination, the tube and contents were held at 650°C for 1 hour, and then cooled to room temperature. The result is a pale grey somewhat sintered powder. Theoretical yield of calcined mixture is 9.63g. Composition of the mixture is given in Table 2.

(b) Hollandite mixes

A batch of hollandite powder with composition $\text{TiO}_2 = 68.63 \text{ wt.}\%$, $\text{Al}_2\text{O}_3 = 13.72\%$, $\text{BaO} = 17.65\%$ was prepared by mixing TiO_2 , $\text{Al}(\text{OH})_3$ and BaCO_3 powders under methanol in a 75ml vessel for 24 hours. The method was identical to that described for SYNROC-C preparation. A solution of CsNO_3 and ammonium molybdate in 2M HNO_3 was prepared to contain 0.198g Cs_2O and 0.351g MoO_3 . The hollandite powder was mixed with H_2O , dilute HNO_3 added to remove carbonate and the Cs, Mo solution mixed in. The slurry was processed in a steel tube as previously described for SYNROC-C. The composition of the final hollandite mix is given in Table 3.

Table 3. Cs,Mo-bearing hollandite composition.

<u>Oxide</u>	<u>wt. %</u>
TiO_2	68.11
Al_2O_3	13.04
BaO	16.75
Cs_2O	1.84
<u>MoO_3</u>	<u>3.20</u>
Total	<u>100.00</u>

PART II: INITIAL CALCINATION EXPERIMENTS

(a) Total volatile loss in air as a function of temperature

A study of weight loss as a function of temperature was carried out on both SYNROC-C and hollandite samples prepared by calcining at 650°C. Cumulative weight loss as a function of temperature is given in Table 4. Both powders appear to be hygroscopic, with SYNROC releasing 2.7% of volatiles when reheated to 600°C (50°C below the preparation temperature) and hollandite releasing 5.4% volatiles at 600°C. The SYNROC powder showed very little additional loss of volatiles above 600°C, while the hollandite continued to lose volatiles up to 800°C. To avoid complications arising from adsorbed gases, all powders were heated to either 600°C or 750°C and stored in a dessicator before being used for subsequent experiments.

Table 4. Cumulative weight loss on heating in air.

Temp.	SYNROC-C	Hollandite
500°C	2.0%	n.d.
550°C	n.d.	4.7%
600°C	2.7%	5.38%
650°C	n.d.	5.76%
700°C	2.8%	6.07%
800°C	3.0%	6.39%
900°C	3.4%	6.48%

(b) Heating experiments at Ni-NiO controlled redox Conditions

Powdered samples of both SYNROC and hollandite were heated to 600°C in air to remove adsorbed volatiles and then mixed with 5% Ni powder (<8μ). Heating was done in a closed silica tube fitted with a one-way valve to allow any excess pressure in the tube to escape. The powdered sample was placed in a Pt bucket and then the bucket placed on a

silica stand. The silica stand was positioned on a layer of Ni powder in a Ni crucible, and the whole assembly sealed into the silica outer tube. Temperatures were controlled to within $\pm 10^{\circ}\text{C}$, and maintained for 2 hours. Weight changes were monitored for all heating experiments, and are summarized in Table 5. Under Ni/NiO conditions the samples generally lost a small amount of weight with the 800°C SYNROC run showing a slight gain. If all the Ni powder in the sample were oxidized to NiO and no volatiles were lost a gain in weight of 1.4% would result. The weight loss found is thus a minimum loss since some of the Ni is oxidized to NiO.

Table 5

<u>Cs Hollandite</u>	<u>Temp.</u>	<u>Weight Change</u>
Ni-NiO	700°C	no change
	800°C	0.31% loss
	900°C	0.59% loss
	1000°C	0.68% loss
Fe-FeO	800°C	1.09% gain
	900°C	0.62% gain
<u>SYNROC-C</u>	<u>Temp.</u>	<u>Weight Change</u>
Ni-NiO	700°C	0.28% loss
	800°C	0.26% gain
	900°C	0.16% loss
	1000°C	0.92% loss
Fe-FeO	800°C	0.80% gain
	900°C	0.38% gain
	1000°C	0.28% gain

Concentrations of Cs were determined by atomic absorption in all powder samples after heat treatment. Since the starting material was slightly heterogeneous, results given

in Table 6 are only directly comparable within a series. There is clear evidence of Cs loss by volatilization at 1000°C for both SYNROC-C and hollandite mixtures.

Table 6. Cs analyses by atomic absorption.

SYNROC-C:

Temp.	Oxygen Buffer	Cs %
600°C	air	0.63
900°C	air	0.60
1300°C	air	0
700°C	Ni-NiO	0.51
800°C	Ni-NiO	0.53
900°C	Ni-NiO	0.53
1000°C	Ni-NiO	0.35
800°C	Fe-FeO	0.59
900°C	Fe-FeO	0.57
1000°C	Fe-FeO	0.60

Hollandite:

Temp.	Oxygen Buffer	Cs %
600°C	air	1.68
700°C	air	1.64
900°C	air	1.70
700°C	Ni-NiO	1.58
800°C	Ni-NiO	1.58
900°C	Ni-NiO	1.50
1000°C	Ni-NiO	1.42
800°C	Fe-FeO	1.58
900°C	Fe-FeO	1.49

(c) Heating experiments at Fe-FeO controlled redox conditions

Powder samples were heated to 750°C in air to remove excess volatiles and then mixed with 5% Fe powder. These mixtures were then heat-treated under the conditions

described for Ni-NiO but with an Fe crucible filled with Fe powder replacing the Ni assembly. This served to control oxygen fugacities at Fe-FeO. All samples showed an increase in weight (Table 5) indicating oxidation of Fe to FeO during heating. The largest increases occurred at 800°C for both systems. Analyses of the powders for Cs after heating (Table 6) show no loss of Cs even at 1000°C for SYNROC powders; there may have been a slight Cs loss at 900°C for the pure hollandite system.

PART III: KINETICS OF FORMATION OF SYNROC MINERALS

(a) Introduction

The experiments described in the preceding section also served to elucidate the effects of temperature and oxygen fugacity upon the reactivity of oxide mixes possessing SYNROC and hollandite bulk compositions. The SYNROC-C sample contained 10 percent .. waste elements (including 0.76% Cs₂O and 1.21% MoO₃) whilst the hollandite contained 1.84% of Cs₂O and 3.26% of MoO₃ (Table 3).

(b) SYNROC-C

The starting material prepared as described in Part II was partly amorphous but also contained anatase and poorly crystallized perovskite. Heating in air at 700°C for 2 hours caused X-ray reflections to strengthen and a trace of hollandite to appear. At 800°C, results were similar. However, after heating at 900°C, important changes occurred. Hollandite became well-crystallized, with its X-ray lines becoming stronger than those of anatase. Perovskite was also well-crystallized and weak zirconolite reflections appeared.

A further major change occurred in the run at 1000°C. Anatase reflections disappeared and were replaced by a moderately strong set of rutile reflections. Hollandite and perovskite were well-crystallized, whilst zirconolite reflections were moderately strong. Two further runs at 1250°C and 1350°C yielded essentially complete crystallization to hollandite + perovskite + zirconolite, whilst a trace of rutile remained.

An analogous set of runs was carried out at the Ni-NiO buffer. Similar results to those in air were obtained at 700°C and 800°C. However, at 900°C, the hollandite reflections were much more weakly developed than had been the case in air. Conversely, the anatase reflections were stronger in the Ni-NiO run. Corresponding differences were noted in the runs at 1000°C. At Ni-NiO oxygen fugacities, zirconolite reflections were weaker than for the runs carried out in air, whilst TiO₂ was still present as anatase rather than rutile.

Two runs were then carried out at the Fe-FeO buffer at 900°C and at 1000°C. In both cases, the sample was not as well crystallized as had been observed in the case of the corresponding run at the Ni-NiO buffer.

These experiments show that the development of SYNROC mineral assemblages is markedly affected by oxygen fugacity. The reactions proceed more readily in air than at Ni-NiO oxygen fugacities whilst reactivity at the Fe-FeO buffer is reduced compared to Ni-NiO.

It seems likely that these differences are caused by the effect of oxygen fugacity on the stability of residual oxidized species such as nitrates and molybdates, which tend to catalyse the formation of SYNROC phases. Prior to decomposition, these salts provide a low-melting point liquid or flux which increases the rate of reaction between the remaining oxide components. The decreased reactivity under the increasingly reducing conditions of the Ni-NiO and Fe-FeO buffers is believed to be due to the reduction and decomposition of the residual nitrates and molybdates. Experimental data described in Section IV of this report indeed show that molybdates are unstable at Fe-FeO and Co-CoO oxygen fugacity buffers at 1200°C, the molybdenum being reduced to the quadrivalent and elemental states.

(c) Hollandite

An analogous investigation was carried out on a synthetic hollandite composition doped with Cs and Mo (Table 3). When heated in air at temperatures up to 800°C, the main phase was anatase. At 900°C, a weak set of hollandite lines

appeared, but strong anatase reflections persisted, whilst at 1000°C hollandite was well-crystallized and was accompanied by fairly strong rutile reflections, the latter being more intense than the anatase reflections.

In runs carried out at the Ni-NiO oxygen buffer, results were generally similar to those carried out in air. However, the reactivity was definitely less, as shown by the weaker development of X-ray lines for hollandite in both runs and for rutile in the 1000°C run.

In runs carried out at the Fe-FeO buffer, a large decrease in reactivity was noted, both at 900°C and 1000°C. In particular, hollandite was poorly crystallized in both of these runs, whilst rutile did not appear at 1000°C.

(d) Discussion

The experiments on the hollandite composition are qualitatively similar to those on SYNROC-C. In both cases, reactivity decreases (especially between 900-1000°C) as oxygen fugacity decreases. There is one difference - in hollandite, the big difference in reactivity is seen between the Ni-NiO and Fe-FeO buffers, whereas in SYNROC, the largest difference occurs between samples heated in Ni-NiO buffers and in air. This difference may be related to the much larger amount of molybdenum and cesium in the hollandite sample. Experiments described in Part IV show that oxygen fugacity must be below the Ni-NiO buffer in order to reduce cesium molybdate. Thus, cesium molybdate continues to act as a "mineralizer" in the hollandite sample for runs in both air and Ni-NiO. However, the main "mineralizers" in SYNROC-C are believed to be nitrates, which are apparently decomposed above the Ni-NiO oxygen fugacity buffer.

PART IV: HOT-PRESSING OF HOLLANDITE AND SYNROC-C PREPARATIONS

(a) Introduction

A Boyd apparatus was used for hot-pressing of the various SYNROC-C and hollandite preparations, at pressures of 5kbar,

temperatures of 1250-1450°C, and for periods of 1 hour. In many preparations a small percentage of Fe or Ni metal had been incorporated, and so sample capsules of the same metal were used for hot-pressing. The product assemblages were characterized by X-ray diffraction, microprobe and electron microscopy. It should be borne in mind that if the cesium in an experimental charge occurs as cesium molybdate, then the techniques for producing polished sections commonly cause almost total loss of cesium from the sample; the molybdate dissolves during washing and polishing. However, only pristine broken surfaces of the experimental charge are used for electron microscopy, hence Cs molybdate is preserved and can be readily identified by this latter technique.

(b) Experimental results: Hollandite

(i) Hollandite mixes pre-treated in air; hot pressed in Ni capsules

After heating in air at 650°C and 700°C, 3-5% Ni metal powder was incorporated in some mixes. Electronprobe analyses of polished surfaces showed that the sample consisted of compositionally-heterogeneous hollandites with 0.22 MoO_2 but no Cs_2O , together with Mo-bearing rutile and Ni-metal (Table 7). Note that essentially all Cs and some Mo has been lost from the polished surface of the specimen.

(ii) Hollandite mixes pre-treated in air; hot-pressed in Fe capsules

With 5% Fe metal added after pre-treatment in air at 750°C, the hot-pressed product consisted of heterogeneous Fe-bearing hollandites with variable Cs and Mo contents (typically low), an Fe-Mo alloy, rare blebs of pure Mo and an uncharacterized Fe-Ti-Al phase (Table 8). Most of the Mo, rather than entering hollandite, has been reduced to the metal and alloyed with Fe. Some Cs has entered hollandite.

Table 7. Hot-pressed hollandite + 5% Ni.

Pretreatment : 700°C in air

	<u>Hollandite</u>		<u>Rutile</u>
TiO ₂	65.	70.	90.9
MoO ₂	1.3	1.1	6.7
Al ₂ O ₃	11.7	12.0	2.3
NiO	3.6	3.4	0.2
BaO	19.	14.	-
Cs ₂ O	<u><.2</u>	<u><.2</u>	<u>-</u>
Total	<u>100.6</u>	<u>100.5</u>	<u>100.1</u>

Essentially pure Ni metal also present.

Run conditions: 5kb, 1350°C, 1hr, Ni capsule.

Table 8. Hot-pressed hollandite + 5% Fe.

Pretreatment : 750°C in air

	<u>Hollandite</u>	<u>'Fe-Ti-Al-Phase</u>
TiO ₂	66.1	30.1
MoO ₂	<.1	-
Al ₂ O ₃	6.2	41.3
FeO	5.1	28.9
CaO	-	-
BaO	19.9	-
Cs ₂ O	<u>2.7</u>	<u>-</u>
Total	<u>100.</u>	<u>100.3</u>

Fe-Mo alloy and essentially pure Mo also present.

Run conditions: 5kb, 1350°C, 1hr, Fe capsule.

(iii) Hollandite mixes pre-treated at Ni-NiO; hot-pressed in Ni capsules

Pre-treatment was carried out at 700, 800, 900 and 1000°C at Ni-NiO with 5% of Ni-metal added, followed by hot-pressing in Ni canisters. The product assemblages (Table 9) were similar in all cases, consisting of heterogeneous hollandites with MoO_2 contents ranging from 1-4%, whilst Cs_2O was very low, typically below detection limits. Mo-bearing rutile and essentially pure Ni-metal were also present. A NiAl_2O_4 -rich spinel occurred in a few runs. Electron microprobe analysis established a close association of Cs with Mo, presumably as a Cs-molybdate. Electron microscopy confirmed the presence of this phase.

These results show that at Ni-NiO, Mo is not reduced to metal but exists in higher valence states (+4, +6). Cs-molybdate is stabilized, and in consequence, very little Cs enters the hollandite lattice.

(iv) Hollandite mixes pre-treated at Fe-FeO; hot-pressed in Fe capsules

For this series of experiments, pre-treatment was performed under Fe-FeO redox conditions and at 900°C. 5% Fe metal was added to the mixtures, and hot-pressing was carried out in Fe capsules at temperatures ranging from 1300 to 1450°C.

At 1400 and 1450°C, the charges melted to an assemblage of Fe-hollandite, quench hollandite, corundum and an uncharacterized R_2O_3 -type phase ($\text{R} = \text{Fe}, \text{Ti}, \text{Al}$). Some Mo was preserved as Fe-Mo alloy. At 1350° and 1300°C, the subsolidus products comprised heterogeneous Fe-bearing hollandites with variable Cs_2O contents (up to 2.6%) and low ($\leq 0.6\%$) MoO_2 contents, together with an Fe-Mo alloy and an uncharacterized Fe-Ti-Al phase (Table 10).

The above results show that whilst some Mo occurs in the quadrivalent state in hollandite, most is reduced to the metal and forms an Fe-Mo alloy. Cs-molybdate is not stable at the low oxygen fugacities of the Fe-FeO buffer and so Cs is able to enter hollandite.

Table 9. Hot-pressed hollandite + 5% Ni.
Pre-treatment : 900°C at Ni-NiO

	<u>Hollandite</u>	<u>Rutile</u>
TiO ₂	70.	92.1
MoO ₂	1.3	4.1
Al ₂ O ₃	11.8	3.4
NiO	2.4	-
BaO	15.	-
<u>Cs₂O</u>	<u>4.2</u>	<u>-</u>
<u>Total</u>	<u>100.5</u>	<u>99.6</u>

Ni metal and unanalysable Cs-Mo phase also present.
Run conditions: 5kbar, 1350°C, 1hr, Ni capsule.

Table 10. Hot-pressed hollandite + 5% Fe.
Pre-treatment : 900°C at Fe-FeO

	<u>Hollandites</u>		<u>Fe-Ti-Al-Phase</u>
TiO ₂	69.7	72.9	8.6
MoO ₂	0.6	0.2	-
Al ₂ O ₃	5.3	6.1	51.2
FeO	7.0	6.7	40.4
BaO	13.6	14.0	-
<u>Cs₂O</u>	<u>2.6</u>	<u>0.4</u>	<u>-</u>
<u>Total</u>	<u>99.8</u>	<u>100.3</u>	<u>100.2</u>

Fe-Mo alloy also present.
Run conditions: 5kbar, 1350°C, 1hr, Fe capsule.

(c) Experimental results: SYNROC-C plus simulated HLW

(i) SYNROC pre-treated in air: hot-pressed in Ni capsules

Preparations of SYNROC-C doped with 10% simulated HLW (Section I) were pre-treated by firing in air at 600°C. Approximately 3 wt.% Ni metal powder was added, and the mixture was then hot-pressed in Ni capsules for 1 hour at 5 kbar, and temperatures of 1330, 1300 and 1250°C. An example of a product assemblage is given in Table 11. These data imply that a Cs-molybdate phase may be present, since virtually no Cs and little Mo has entered hollandite. The hot-pressing redox state (approx. Ni-NiO) is therefore not sufficiently reducing to stabilize Mo in the elemental state.

The analogous experiment at 1300°C was examined by scanning electron microscope. The main phases were euhedral crystals, 1 to 3 microns in size, of hollandite, perovskite and zirconolite with some rutile and Ca-Al-Ti phase. Nickel metal contained Re, and a small Ni-Fe phase was found. The material had clearly undergone extensive partial melting, and Cs and Mo had segregated. A large (10 x 30 micron) region of a Cs₂Mo phase was identified. The grain did not show any recognizable crystal morphology.

(ii) SYNROC pre-treated in air: hot pressed in Fe capsules

About 5% Fe metal was mixed with a SYNROC-C preparation after pre-treatment in air at 750°C. The product assemblage after hot-pressing in Fe at 1300°C, 5 kbar was analysed and the results are documented in Table 12. It would appear that almost all Mo has been reduced to the elemental state, since the hollandite contains <.1% MoO₃. It follows that Cs-molybdates would not be stable under these conditions, and Cs is able to partition into hollandite according to the preferred SYNROC strategy. Electron microscopy confirmed the subsolidus nature of this experiment and further demonstrated no correlation between Cs and Mo, essentially all Mo being contained in Fe-Re-Mo alloys.

It is evident from the FeO contents of all phases in

Table 11. Hot-pressed SYNROC + waste + 3% Ni.
Pre-treatment : 600°C in air

	Hollandite	Zirconolite	Peroovskite
TiO ₂	62.	49.1	55.8
ZrO ₂	0.3	29.2	0.3
MoO ₂	0.6	0.3	0.3
UO ₂	-	1.6	0.4
CeO ₂	-	1.0	?
Al ₂ O ₃	7.1	1.9	1.3
Nd ₂ O ₃	-	0.8	4.6
Sm ₂ O ₃	-	?	1.1
FeO	0.3	0.5	<.1
CaO	0.4	15.2	35.4
SrO	-	0.2	0.7
BaO	20.	-	-
NiO	8.0	<.1	<.2
Cs ₂ O	0.3	<.2	<.2
	99.0	99.8	100.1

Rutile, Ni-metal, rare Ca-Ti-Al phases also present.

Run conditions: 5kbar, 1hr, 1330°C, Ni capsule.

Table 12. Hot-pressed "SYNROC + waste" + 5% Fe
Pre-treatment : 750°C in air

	Hollandite	Perovskite	Zirconolite	Ca-Ti-Al phase
TiO ₂	69.	55.3	46.1	28.5
ZrO ₂	0.3	0.3	30.8	-
MoO ₂	<.1	-	-	-
UO ₂	-	0.3	2.3	-
Al ₂ O ₃	4.6	0.9	2.1	45.3
REE	-	5.	2.	-
FeO	6.5	2.7	4.6	11.6
CaO	0.3	34.5	12.8	13.0
SrO	-	0.5	-	-
BaO	18.	-	-	?
Cs ₂ O	0.8	-	-	-
Total	99.5	99.5	100.7	98.4

Fe-Mo alloy also present.

Run conditions: 5kbar, 1300°C, 1hr, Fe capsule.

Table 12 that there has been some oxidation of metallic iron. The entry of ferrous iron into hollandite via the substitution $\text{Fe}^{2+} = 2\text{Al}$ serves to "displace" Al which in turn reacts with other components to form Ca-Ti-Al phases.

(iii) SYNROC pre-treated in air: hot-pressed in Co capsules

For one series of experiments, no additional metal was added to the pre-treated powder, which was hot-pressed in Co-capsules at 5kbar; 1350, 1300 and 1250°C. The assemblage produced at 1350°C is given in Table 13. Cs was observed to enter hollandite, together with 1.5% MoO_2 . However, it was not clear whether Mo was essentially totally quadrivalent or whether some had also been reduced to the elemental state.

In order to establish this, 5% Co metal was incorporated in the above preparation, and the mixture hot-pressed at 1300°C (Table 14). The existence of Mo in both quadrivalent and elemental states was observed, and the partitioning of Cs into hollandite was once again confirmed. It follows that Cs-molybdates are de-stabilized in hot-pressing is carried out near Co-CoO, and the desired partitioning of Cs into hollandite is achieved satisfactorily.

(iv) SYNROC pre-treated at Ni-NiO: hot-pressed in Ni capsules

SYNROC preparations containing 5% Ni metal were pre-treated by calcining under controlled redox conditions at Ni-NiO, at temperatures of 700, 800, 900 and 1000°C. The preparations were then hot-pressed in Ni capsules at 5kb and 1300-1350°C. Table 15 gives analyses for a typical product assemblage consisting of hollandite, perovskite, zirconolite and a Ni-rich spinel. The metal alloy, essentially Ni-Re, did not contain Mo. Note that very little Mo and essentially no Cs has been partitioned into hollandite. A preparation

Table 13. Hot-pressed SYNROC + waste; no metal added.
Pre-treatment : 750°C in air

	Hollandite	Zirconolite	Perovskite	Ca-Ti-Al phase
TiO ₂	69.	47.0	55.1	14.4
ZrO ₂	0.3	30.1	0.3	-
MoO ₃	1.5	-	-	-
VO ₂	-	1.2	0.4	-
Al ₂ O ₃	0.9	2.6	1.7	72.3
Nd ₂ O ₃	-	1.4	4.1	-
FeO	0.3	0.4	0.2	5.8
CoO	1.8	2.8	0.9	0.6
CaO	0.5	14.4	35.8	7.3
SrO	-	0.4	0.8	-
BaO	18.	-	-	-
Ce ₂ O	1.1	-	-	-
Total	99.4	100.3	99.3	100.4

Run conditions: 5kbar, 1350°C, 1hr, Co capsule.

Table 14. Hot-pressed SYNROC + waste, + 5% Co.

Pre-treatment : 750°C in air

	Hollandite	Zirconolite	Perovskite	Ca-Ti-Al phase
TiO ₂	65	48.8	54.8	20.9
ZrO ₂	0.2	29.8	0.3	-
MoO ₂	0.6	-	-	-
VO ₂	-	1.4	0.8	-
Al ₂ O ₃	7.1	2.1	1.8	64.7
Nd ₂ O ₃	-	1.0	3.5	-
FeO	0.3	0.3	0.2	0.5
CoO	5.7	1.2	1.8	4.5
CaO	0.4	15.5	35.1	5.4
SrO	-	0.3	0.8	-
BaO	19.	-	-	-
Ca ₂ O	1.4	-	-	-
Total	99.7	100.4	99.1	99.0

Co-Fe-Pu-Mo alloy also present.

Run conditions: 5kbar, 1300°C, 1hr, Co capsule.

Table 15. Hot-pressed SYNROC + waste + 5% Ni.
Pre-treatment : 900°C at Ni-NiO

	Hollandite	Zirconolite	Perovskite	Ni-spinel
TiO ₂	67.	46.9	54.8	2.5
ZrO ₂	0.2	30.8	0.2	-
MoO ₂	0.5	?	0.2	-
CaO ₂	-	0.3	1.1	-
UO ₂	-	1.1	0.2	-
Al ₂ O ₃	7.3	2.7	0.8	53.8
Nd ₂ O ₃	-	0.5	3.8	-
FeO	0.1	0.2	0.1	0.6
NiO	7.5	1.4	<.1	42.8
CaO	0.3	15.4	35.9	-
SrO	-	-	0.4	-
BaO	16.	-	-	-
Cs ₂ O	<.2	-	-	-
Total	98.9	99.3	97.5	99.7

Also present: Ni-Re alloy.

Run conditions: 5kbar, 1350°C, 1hr, Ni capsule.

pre-treated at 800°C, Ni-NiO, and hot-pressed in Ni at 1300 and 1350°C, 5kbar, was examined by electron microscopy. The 1350°C run showed evidence of partial melting, e.g. euhedral crystal morphologies, whilst the 1300°C run had the rounded-irregular morphological characteristics of a subsolidus assemblage. In the 1350°C run, Cs was found in a Ca,Ti phase which did not contain Mo. No Cs rich segregations were identified in the 1300°C run. These observations differ from the hollandite bulk composition (pre-treated and hot-pressed in an analogous manner) where Cs was observed to form a Cs-Mo phase.

(v) SYNROC pre-treated at Fe-FeO: hot-pressed in Fe

SYNROC preparations were pre-treated at 900°C and 1000°C at Fe-FeO and then hot-pressed at 5kbar; 1350, 1325 and 1300°C in Fe capsules. The product assemblage comprised heterogeneous Fe-bearing hollandite, zirconolite, perovskite, an uncharacterised Fe-bearing Ca-Ti-Al phase, and an Fe-Mo-Re alloy. Almost all Mo had been reduced to the elemental state whilst Cs was able to partition into hollandite. Atomic absorption analysis confirmed the predicted bulk Cs content of the system. No evidence for Cs segregation was found during electron microscopic examination of preparations hot-pressed at 1300°C, whilst irregular and rounded crystal morphologies and fine grain size confirmed subsolidus conditions.

A sample hot-pressed at 1350°C was finely crushed and leached in H₂O and acetone at room temperature. Atomic absorption analysis showed that this procedure had resulted in loss of ~60% total cesium. Since Mo has been reduced to quadrivalent and elemental states, the cesium cannot have been present as Cs-molybdate. We conclude that incipient partial melting has occurred at 1350°C, allowing partial segregation of Cs into an interstitial melt where it is potentially leachable.

PART V: TECHNOLOGICAL SIGNIFICANCE

(a) Preferred redox conditions for SYNROC processing

Prior to this study, the preferred redox conditions for SYNROC production were near the nickel-nickel oxide oxygen fugacity buffer. It had been found that under these conditions, molybdenum (when introduced separately) became reduced to the Mo^{4+} state and entered hollandite. Likewise, cesium, when introduced separately, entered hollandite and was highly resistant to leaching. More recently, it was found that when both Cs and Mo were introduced into SYNROC simultaneously and processing was carried out near the Ni-NiO buffer, most of the Cs and Mo failed to enter hollandite and Cs was readily leachable.

The present experiments clearly show that near the Ni-NiO buffer, Cs and Mo become associated in a minor phase which is readily leachable (probably in part Cs_2MoO_4). This is apparently due to the effect of Cs which stabilizes molybdenum in the hexavalent state. It is clear that processing of SYNROC containing Cs and Mo-bearing waste must be conducted under more reducing conditions. An extensive set of experiments carried out at the Fe-FeO oxygen fugacity buffer showed that cesium entered hollandite whilst most of the molybdenum was reduced to the metallic state (alloying with iron). No trace of Cs-Mo phases was seen on fresh surfaces studied under an SEM equipped with energy dispersive detector. Subsequently, it was found that this treatment at Fe-FeO had greatly reduced the leachability of cesium.

Another set of experiments at the Co-CoO buffer produced similar results, except that a larger proportion of Mo enters hollandite as Mo^{4+} , due to the more oxidizing conditions. We conclude, therefore that final heat-treatment and equilibration of SYNROC mixtures should be carried out under conditions which are more reducing than Ni-NiO buffers and preferably, in the vicinity of the Co-CoO and Fe-FeO buffers.

(b) Preferred hot-pressing temperatures

In runs carried out at the Fe-FeO buffer, it was found

that the leachability of cesium increased drastically in runs carried out above the solidus. Apparently, cesium preferentially becomes partitioned into the liquid phase, which is produced by incongruent melting. When the liquid is quenched, one or more metastable cesium titanate phases are apparently formed. These quench phases are apparently much more easily leachable than the cesium which is locked up in the primary hollandite crystals. It is clear, therefore, that hot-pressing and/or sintering should be carried out appreciably below the solidus.

The solidus temperature in SYNROC containing 10% HLW appears to lie between 1260°C and 1300°C. In some cases, where excess FeO was introduced during processing, the solidus was reduced below 1250°C. In order to provide a margin of safety during processing, it is recommended that hot-pressing should not be carried out above 1200°C.

In order to sinter SYNROC to near-theoretical density without application of pressure, it is necessary to heat samples very close to the solidus, or even slightly above the solidus. It does not seem likely that this will lead to optimum leachability. Even if sintering to high density can be achieved just below the solidus, there will be little margin for error in temperature control during large-scale processing. Accordingly, it is believed that hot-pressing, which can achieve theoretical density well below the solidus, will be superior to sintering in a large-scale processing operation.

(c) Cesium volatility

Apart from a single anomalous result at the Ni-NiO buffer, all experiments so far carried out indicate negligible volatility of cesium from fine SYNROC powders at temperatures up to 900°C and at oxygen fugacities ranging from air to Fe-FeO. However, substantial volatility of cesium was encountered at 1000°C on two occasions. It seems desirable, therefore, that calcining of SYNROC powders prior to hot-pressing be carried out at temperatures below 1000°C.

(d) Calcination

The SYNROC composition calcined in the experiments described herein was fully nitrated and contained no carbonate. The following results may not necessarily be applicable to initial SYNROC mixtures containing carbonates.

When calcined in air, decomposition of nearly all nitrates occurred around 700°C, to form a highly reactive, fine grained, homogeneous mixture of oxides. This mixture showed very little tendency to react further to produce SYNROC phases until heated above 900°C. Reactivity was greater when heated under oxidizing conditions (in air) possible because of the presence of residual molten molybdates and a small amount of nitrate, which functioned as mineralizers, or fluxes. It would be undesirable to calcine SYNROC powders under oxidizing conditions at temperatures high enough to form hollandite (>1000°C) since cesium will preferentially react to form a molybdate. Subsequent entry into hollandite under more reducing conditions would be very difficult owing to kinetic factors.

Accordingly, it seems that two alternatives exist for calcination (i) heat to 750-900°C in air, and carry out subsequent hot-pressing under reducing conditions to achieve the correct redox state and oxygen content. (ii) Heat to 750-850°C under reducing conditions (e.g. in an Ar-H₂-H₂O atmosphere) and achieve the correct redox state and oxygen content at this stage. The second alternative seems preferable. If this control of redox-state is to be achieved during the hot-pressing step, it will probably be necessary to mix in a condensed phase such as Fe metal powder. While this produces the correct redox state, the oxygen consumed by reducing molybdates and unreacted nitrates forms an excessive amount of FeO. This enters the hollandite, displacing Al₂O₃ and leads to the formation of substantial amounts of Ca-Ti-Al phases. We suspect that these phases may sometimes take up significant amounts of Sr and possibly Cs which are thus more leachable than when incorporated in normal SYNROC minerals.

Accordingly, it is recommended that calcination of SYNROC feedstock be carried out in a controlled gaseous atmosphere at 750-850°C, thereby producing a homogeneous powder with the desired redox state and oxygen content. Subsequent hot-pressing may then be carried out in a closed system at 1100-1200°C.

Abstract

Zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3) are key minerals in SYNROC, a ceramic material developed for the immobilization of high level nuclear reactor wastes. When these are incorporated in SYNROC, the long-lived radioactive actinide elements are preferentially partitioned into zirconolite and perovskite which are therefore subjected to strong alpha-particle irradiation resulting from the decay of these elements. The effects of alpha irradiation have been studied via X-ray and electron diffraction investigations of natural samples of zirconolite and perovskite of varying ages and varying uranium and thorium contents. The samples studied have received cumulative alpha doses varying from 1.0×10^{18} to 1.1×10^{20} α/gr . The upper limit corresponds to the alpha irradiation which would be received by the zirconolite in SYNROC containing 10 percent of high level waste over a period of 5×10^8 years.

These studies show that zirconolites remain crystalline up to and beyond alpha doses of 2×10^{19} alphas/gm. This dose would have accumulated in such a SYNROC zirconolite after a million years of storage. Electron microscopy revealed that the grains were composed of small crystalline domains which possessed the defect fluorite-type structure. After a dose exceeding that which would be received by SYNROC in 100 million years, zirconolites appeared metamict when studied by X-ray diffraction. However, the electron micrographs and diffraction patterns clearly demonstrate that the mineral continues to retain a large degree of short range order and in no way resembles a glass. The density changes produced in these zirconolites by irradiation are small and range from 1% to 3% at saturation. Perovskite samples which have SYNROC ages up to 20,000 years decrease in density by 1.8%. Their X-ray

powder patterns are essentially unaffected. Comparative studies show that the perovskite lattice is even more resistant to the effects of alpha irradiation than the zirconolite lattice. The results demonstrate that zirconolite and perovskite are extremely resistant to the effects of nuclear radiation and will provide stable crystal structures for the containment of the radioactive waste elements during the time required for the radioactivity to decay to safe levels (typically 10^5 - 10^6 years).

1. Introduction

Zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3) are used in the SYNROC process for the immobilization of elements occurring in high-level nuclear wastes (Ringwood et al., 1979). The radioactive wastes are incorporated into the crystal structures by forming dilute solid solutions with the SYNROC phases. The waste elements are tightly bound within the crystal lattices and are extremely resistant to leaching by hydrothermal solutions.

These experiments, however, do not take into consideration the important effects of nuclear radiation arising mainly from alpha-decay of the actinide elements. Alpha particles emitted by these elements, notably neptunium, plutonium, americium, and curium isotopes, are associated with a recoil of the nucleus. The displacements due to the recoil may cause considerable damage to the lattice and decrease the stability of the synthetic phases. The alpha emitting elements are strongly partitioned into zirconolite and perovskite and these crystals will therefore be subjected to most of the alpha recoil damage.

We have assembled a collection of naturally occurring samples of zirconolite and perovskite containing the alpha-emitting elements uranium and thorium. The cumulative radiation doses received by these minerals have been calculated and cover a considerable range from 1.0×10^{18} to 1.1×10^{20} alphas per gram (Oversby and Ringwood, 1980). In this paper we describe the effects of increasing doses of alpha radiation on the crystal structures of these minerals using X-ray diffraction and electron microscopy techniques.

Reeve and Woolfrey (1980) have approached the same problem by irradiating SYNROC mineral assemblages with fast neutrons to simulate alpha particle and actinide recoil damage. Their results form a complementary study and will be discussed later.

2. Previous Studies of Radiation Damage in Minerals

Many other phases have also been examined for the effects of radiation damage. Pyatenko (1970) has suggested that as minerals

(including zirconolite) become metamict there is a breakdown of the crystal structure leading to a segregation of new phases on a very small scale. These new phases may represent component oxides or a more complex configuration of ions.

Extensive studies previously carried out on zircons (ZrSiO_4) have led to several differing conclusions. Holland and Gottfried (1955) and Pellas (1965) invoked a multistage process occurring with increasing radiation dose. In the model of the former authors, it was proposed that zircon breaks down into small crystallites of ordered zircon plus a new phase, which ultimately transform to a glass. Bursill and McLaren (1966) have supported this multistage process and have provided evidence from electron microscopy for the existence of small crystallites of zircon, even in the metamict state. Pellas (1965) concluded that zircon ultimately decomposes to a mixture of its component oxides, $\text{SiO}_2 + \text{ZrO}_2$. Wasilewski et al. (1973) have supported these conclusions from infrared absorption spectral studies.

More recently, Vance and Boland (1975) and Vance (1975) have suggested a progressive disordering of the lattice with increasing radiation dose. These authors did not find a second new phase for zircons as suggested by Holland and Gottfried (1955) nor the breakdown of the lattice into its component oxides. The conclusion of progressive lattice disorder was also made by Vance and Boland (1978) in studies of ZrO_2 . In the studies of Vance and Boland (1975, 1978), however, alpha particle damage was simulated using fission fragments produced by the bombardment of uranium impurities with neutrons. The results must therefore be treated with some caution since fission fragments are associated with much higher kinetic energies (~ 160 MeV) than that involved in α -recoil (~ 0.1 MeV).

In a study by Cartz and Fournelle (1979) it was also shown that ZrSiO_4 did not break down into its component oxides in the metamict state. Furthermore, the authors supported the conclusion that the ability for a material to become metamict was strongly dependent on the crystal structure. After irradiating a mixture of Si_3N_4 and ZrSiO_4 with Krypton ions (3MeV), the former compound was found to remain unchanged while zircon had completely transformed to the metamict state. Aluminium nitride and other nitrides were also reported to remain undamaged while α -quartz became metamict when irradiated with heavy ions. The behaviour was attributed to the variability of the Si-O-Si bond angle in silicates in contrast to nitrides where the A-N-A (where A = Si, Al) bond angle remains fixed. The fact that the mineral zirconite ThO_2 (whose fluorite-type structure is the parent structure of zirconolite) is not found to be metamict in the natural state was said to be explained by this hypothesis.

Comes et al. (1967) have reported the effects of fast neutron irradiation on single crystal quartz. These authors observed from X-ray diffraction techniques, a gradual breakdown of the structure into a heterogeneous mixture of crystalline and metamict areas. After very strong irradiation ($>10^{20}$ n/cm²) the crystal becomes entirely metamict and exhibits a diffuse diffraction ring on X-ray photographs. They concluded that the SiO_4 tetrahedra remain nearly undamaged during irradiation. The arrangement of these units is modified due to the flexibility of the bonding between the tetrahedra. In contrast, the ionic crystal LiF remains nearly undistorted when subjected to radiation damage.

3. Present Investigation

In view of the variety of conclusions existing in the literature, it seemed possible that an independent detailed study on new mineral types such as zirconolite and perovskite may provide the necessary

information to resolve the effects of large doses of nuclear radiation. Moreover, since these minerals are key components of SYNROC, the information so obtained should have an important bearing on the long-term behaviour of SYNROC after incorporation of high-level nuclear reactor wastes.

Zirconolite, $\text{CaZrTi}_2\text{O}_7$, is closely related to the defect fluorite-type (CaF_{2-x}) structure (Pyatenko and Pudovkina, 1964; Russell, 1980a). It can be derived from the simple lattice by distortion of the parent cubic cell and ordering of the cations. The structure so derived is monoclinic and has eight times the volume of the original cube. The compound $\text{CaZr}_{1+x}\text{Ti}_{2-x}\text{O}_7$ exists in a range of stoichiometries with x varying from -0.09 to 0.30 (Russell, 1980b). Both natural and artificial zirconolite take into solid solution a wide variety of elements and can contain up to twenty weight percent ThO_2 and UO_2 and ten weight percent rare earth elements in the natural state.

Zirconolite occurs in trace amounts in a variety of environments and is usually found as small grains up to several millimeters in dimension. At Jacupiranga, Brazil, it occurs in the magnetite-pyroxenite rock which intrudes the carbonatite complex (Hussak and Prior, 1895). In Germany, zirconolite has been found in several dikes which intrude the Kaiserstuhl carbonatite (Keller, pers. comm.).

The mineral has been reported in several locations in the USSR (Vlasov, 1966). Samples from Arbarastakh in Aldan are contained in the central regions of pyroxenite massifs. The pyroxenites outcrop in a group of ultrabasic alkali rocks and have been subjected to intense metasomatic alteration (Borodin et al., 1960). A niobium-rich variety of zirconolite from the apatite-magnetite rocks of the Vuoriyarvi massif has also been reported by these authors. Zirconolite from the Kola Peninsula occurs in the coarse grained pyroxene-amphibole rock of the Afrikanda massif.

In Sri Lanka, zirconolite occurs as large pebbles weighing up to 60 grams. They are found in sea gravels at several localities

(Blake and Smith, 1913).

The oldest known specimens on earth have been found in the Jimberlana intrusion, Western Australia. The intrusion consists of a layered horizontal mafic complex and has been dated at about 2500 m.y. old (Turek, 1966; Oversby and Kingwood, 1980). Recently, Williams (1978) has reported an occurrence of zirconolite in the Rhum ultrabasic layered intrusion. The zirconolite is interpreted to be a late stage mineral containing the remaining incompatible elements of the original magma.

Samples from Norway are known as polymignite (Dana and Dana, 1944; Vlasov, 1966). This mineral is found in Norway in a pegmatite with ka-orthoclase, magnetite, nepheline, zircon and pyrochlore. It has also been found in augite-syenite rocks.

Perovskite (CaTiO_3) is much more abundant than the zirconolite with which it is commonly associated. The structure is orthorhombic consisting of a 3-dimensional framework of corner-joined TiO_6 octahedra which Ca atoms occupying the spaces between them. The structure is distorted from the ideal cubic modification mainly by rotations of the octahedra. In nature, perovskite shows a considerable range of ionic substitutions. The rare earths and alkalis common, replace calcium while small sized cations such as niobium and tantalum replace titanium.

The ability of these minerals to accommodate a large range of elements in their crystal structures is of primary importance to their inclusion in the SYNROC process.

4. Experimental

A suite of natural samples was examined using X-ray diffraction and electron microscopy. The X-ray diffraction techniques

included single crystal precession, rotation and Weissenberg photography, and Debye-Scherrer and Guinier powder photography. The minerals were analysed using the electron microprobe by Mr. N. Ware and the analyses are given in Tables 1 and 2.

The natural crystals were first examined under a binocular microscope for any sign of impurities. These were sometimes difficult to detect as zirconolite was often associated with phases of similar appearance, such as calzirtite (CaZr_3Ti_2) and baddeleyite (2ZrO_2). The presence of calzirtite was particularly troublesome as its powder diffraction pattern has a similar appearance to the main subcell reflections of zirconolite. Calzirtite is, in fact, a closely related phase of similar chemistry, being derived from the same cubic CaF_{2-x} -type structure as zirconolite (Pyatenko and Rudokina, 1961). In these cases the crystal or fragment was examined by mounting either on a silica glass fibre or on adhesive tape and examined under the microprobe. This quickly established the identification and purity of the crystal concerned. These time-consuming analyses were also performed by Mr. N. Ware.

The samples were then heated at 400°C and $700-800^\circ\text{C}$ for periods of 1 to 2 hours. Again both powder and single crystal patterns were recorded. Above 800°C , heating intervals varied and were dependent on the results obtained at lower temperatures. The heating experiments were all carried out in air in unsealed platinum capsules. All zirconolite samples, except for the Kaiserstuhl crystals, changed to a brown colour when heated. This was associated with a change from isotropic (metamict state) to anisotropic when viewed with crossed nicols under the optical microscope.

In order to detect any changes in lattice parameters of these samples, particularly the perovskites, powder patterns were obtained from a Guinier-Hägg focussing camera using strictly monochromated $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54060 \text{ \AA}$). The photographs were internally calibrated with silicon powder (SRM640 , $a = 3.5696 \text{ \AA}$). A listing of structure factors for a synthetic zirconolite was kindly made available by Dr. R.J. Hill of the CSIRO, to aid in indexing the complicated powder patterns. The cell parameters were refined by the method of least squares using a computer program written by Dr. R.A. Eggleton for a Hewlett-Packard 9825A desktop calculator. Cell parameters calculated for natural zirconolites were obtained from precession photographs. The diffraction patterns were generally of poor quality giving comparatively large errors in the cell dimension. In one case, however, a faint diffraction pattern of a natural zirconolite from Russia was obtained from a 57.3 mm diameter Debye-Scherrer camera internally calibrated with Si using $\text{Fe K}\alpha$ radiation. Diffraction patterns from natural Kaiserstuhl zirconolites showed little evidence of damage and accurate lattice parameters were obtained from these samples. The final results are given in Tables 3 and 4.

Electron microscope studies were carried out under the guidance of Dr. John Fitzgerald using a 200 keV JFOL instrument. The samples were first roughly thinned by manual polishing to about 40 μm and were then ion-thinned with 5 keV Ar ions. Other samples were crushed and placed onto a carbon grid. Density measurements were determined by the method of Archimedes, using toluene as the immersion liquid.

5. Radiation Dose as a Function of SYNROC Age

The radiation dose received by the natural samples can be calculated from their age and U and Th concentrations. The dose,

in alphas per gram, can then be directly related to the age of a SYNROC sample containing 10% high level waste which would have received a similar radiation dose. This relationship is shown in figures 1 and 2. The figures have been taken from Oversby and Ringwood (1980).

The samples described in the following sections have been placed on the curve. The perovskite radiation doses range from 1.3×10^{18} α /gm for the loparite samples to 2.2 and 2.6×10^{18} α /gm for the perovskite specimens from Lake Baikal. These latter samples have SYNROC ages of 1×10^4 yr and 1.7×10^4 yr respectively. Zirconolite samples cover a much wider range of radiation doses. The zirconolites from Sri Lanka have received very large doses of alpha radiation. These doses would only accumulate in SYNROC after a period of time of 4×10^8 yr.

6. Results

(a) Kaiserstuhl zirconolite

The Kaiserstuhl (Germany) carbonatite complex contains traces of zirconolite in a late stage vein. The estimated age of these samples is 16 m.y. The grains of zirconolite vary in their U and Th contents from a low of 0.8% UO_2 , 1.7% ThO_2 to a high of 1.5% UO_2 , 2.9% ThO_2 . The accumulated alpha dose received by the high uranium sample is 1.3×10^{18} alphas per gram. The age of SYNROC which would have received an alpha dose equivalent to this sample would be about 10^3 years (Fig. 1). X-ray diffraction of powders and single crystals shows this zirconolite to be well-crystallized. The X-ray powder data for these samples show that the fluorite-type subcell reflections remain constant while the reflections from the zirconolite superstructure decrease slightly in intensity with increasing alpha dose. This effect is noticeable at high 2θ values, where slight broadening of spots is also seen. Based on these observations, we would expect that the zirconolite super-structure

lines would still be present at twice the alpha dose. This would correspond to a SYNROC age of about 10^4 years. After annealing at 1200°C , a slight decrease in volume of less than 1% is noted (Table 3).

(b) Brazilian zirconolite

A small grain of zirconolite from Jacupiranga, Brazil, with an age of 133 m.y. contains 0.4% UO_2 and 6.6% ThO_2 . The cumulate alpha dose for this sample is 7.6×10^{18} alphas per gram, which corresponds to a SYNROC age of 4×10^5 years (Fig. 1). Zirconolites from this locality were first reported by Hussak and Prior (1895). The rare mineral, which they named zirkelite, occurs in the decomposed magnetite-pyroxenite of Jacupiranga, S. Paulo, Brazil. Our specimens were also obtained from the same area by Dr. V. Oversby. The minerals received little attention until Pudovkina et al. (1974), using Hussak's samples obtained from the British Museum, carried out chemical analyses and X-ray studies of heated specimens in order to establish their relationship to zirconolite. These authors found that in the natural state the crystals were metamict, although one specimen showed a faint, diffuse reflection from Laue photography. When heated to 800°C the samples produced cubic defect fluorite-type patterns with $a = 5.08 \text{ \AA}$. At 1200°C the X-ray diffraction pattern of the heated crystals was identified as the monoclinic zirconolite.

The latter results have been confirmed by our analyses. However, several significant additional observations were also made. Firstly, the natural samples in this investigation gave cubic defect fluorite-type diffraction patterns unlike the samples studied by Pudovkina et al. (1974) which were metamict. Secondly, the grains continued to display single crystal diffraction patterns when reconstituted at temperatures up to 1100°C .

X-ray precession photographs from natural single crystals of Jacupiranga zirconolite show a cubic cell typical of the defect fluorite-type structure. However, the diffraction spots are broader and much weaker than in annealed, crystalline zirconolite. The broadening indicates an extensive degree of metamictization according to accepted criteria. A standard Debye-Scherrer photo-

-graph of the powder of this specimen does not show distinct reflections. Broadening of the diffraction spots considerably reduces the accuracy of the measured cell dimension of 5.06 ± 0.04 Å. Weak zirconolite supercell reflections which are present in the monoclinic structure have completely disappeared. Thus, it would appear that a basic effect of the high radiation dose received by these crystals has been to cause a degree of disorder of the cations. It is important to note that these crystals remain sufficiently coherent to give single crystal patterns in their natural state.

After heating to 400°C, the intensities of the broadened reflections substantially increase. The lattice remains cubic, and supercell reflections are absent. At 700°C, the structure continues to order. The cubic lattice remains intact and the diffraction spots become more intense and well defined. After heating to 950°C the basic fluorite-type cell begins to distort and ordering of the cations onto the monoclinic zirconolite atom positions takes place and weak supercell reflections appear. Although the samples have now been reconstituted to their pre-metamict monoclinic lattice, the crystals continue to produce single crystal diffraction patterns. This observation provides us with evidence that even after receiving a radiation dose of 8×10^{18} alphas per gram, equivalent to a SYNROC age of 4×10^5 years, the cations of this extensively metamict zirconolite remain structurally close to the original monoclinic atomic positions. This finding is of considerable significance, showing that after intense radiation damage and suffering extensive metamictization, the lattice retains a large degree of order.

At 1200°C the original cubic defect fluorite-type cell has now completely transformed. Diffraction patterns taken of single

crystals heated to this temperature display sharp powder lines. This indicates complete recrystallization and the formation of a polycrystalline aggregate. An optical analysis confirmed this interpretation. The patterns obtained seemed at first much simplified in comparison to synthetic zirconolite and to samples which had been heated at temperatures between 1000 and 1100°C. Pudovkina and Pyatenko (1966) were able to describe the simplification of X-ray patterns from Aldan zirconolites in terms of a distortion along the 3-fold axis of a cube. The resultant X-ray pattern displays a strong hexagonal appearance while at the same time appears pseudo-cubic. The "hexagonalisation" of the X-ray patterns were also encountered by Pudovkina et al. (1974) for zirconolites from Brazil. In comparing the volume change, if any, of the radiation damaged natural zirconolite and the same crystal reconstituted at 1200°C, an upper limit only will be given due to the inaccuracy in measurement of the natural sample. Using the maximum value of $a_{\text{cubic}} = 5.1 \text{ \AA}^*$, a volume increase of 2.9% is obtained; using the most probable value of $5.06 \text{ \AA}$, the volume increase would be only 0.5%.

Preliminary electron microscopy of a natural unheated Brazilian zirconolite revealed that the specimen was composed of a number of regions with different properties. The appearance of these regions were similar to those described by Bursill and McLaren (1966) for zircon. One area of the zirconolite samples was still highly crystalline and gave strong extinction contours (Fig. 3). The corresponding diffraction pattern displayed sharp reflections of the defect fluorite-type cell and extra weak diffuse reflections. Another area is similar to the samples of stage III

---

*The monoclinic zirconolite cell is 8 times the volume of its defect fluorite subcell (Pyatenko and Pudovkina, 1964).

(Bursill and McLaren, 1966). This region, figure 4, exhibited a spotty contrast on the scale of less than $50 \text{ \AA}$ in diameter and was tilt dependent. No extinction contours were present. The single crystal electron diffraction pattern gave strong slightly diffuse reflections of the cubic defect fluorite-type cell observed by X-ray diffraction. The patterns also show a few very weak reflections, and are associated with several diffuse powder rings. The innermost intense ring corresponds to the d-spacing of the (111) fluorite-type reflection. It was noted that only the areas of low contrast between the small domains contributed to this ring (Fig. 5). Still other areas of the Brazilian specimen gave only the diffuse powder rings already reported, and were of low contrast. These areas, are interpreted to be the final state of radiation damage.

The d-spacing of $\sim 2.92 \text{ \AA}$ of the inner ring corresponds to the distance between the metal-only (111) planes of the fluorite-type structure. In the zirconolite structure the planes which alternately contain Ti and $\text{Ca} + \text{Zr}$ are derived from these close-packed (111) fluorite-type planes. Thus, even in the metarict state the cations within these planes still retain a short range periodic arrangement. It is now obvious that the Brazilian zirconolite crystals break down into domains possessing an orthogonal lattice. These domains become smaller and only the cubic defect fluorite-type subcell reflections remain visible. The domains then grade into regions of featureless material. These areas retain a degree of short range order and continue to display a strong (111) fluorite-type reflection.

To check to see if the crystal had segregated into several new phases such as its component oxides as suggested by Pyatenko (1970), large areas of the specimen were moved under the electron

beam. The cubic subcell did not change and remained orientated throughout the procedure. No other phases were observed to be present.

(c) Norwegian zirconolite

Two samples of polymignite (Lima de Faria, 1964) were obtained from Norway. They are distinguished by their localities, one being labelled Knapliveien, Stavern and the other Skneppestad, Larvik. Both specimens have received similar radiation doses of 1.7×10^{19} alphas per gram. This is equivalent to just greater than 10^6 SYNROC years (Fig. 2). Single crystal diffraction studies of the natural Stavern crystals gave the defect fluorite-type pattern. On heating to 880°C , it became apparent that two types of crystals were present. One variety was translucent, reddish in colour and had a vitreous lustre while the other was golden brown. The electron-probe analyses also showed a small difference in composition (Table 1). Single crystal X-ray patterns of crystals which were reddish in colour, gave a new orthorhombic cell with the following approximate dimensions: $a = 10.08$, $b = 14.28$, $c = 7.40$ Å. The space group of this mineral is either Aba_2 or Cmca . The new phase is closely related to monoclinic zirconolite and is obviously another distortion of the CaF_{2-x} -type parent structure. Further studies of this mineral are at present being undertaken.

At 1200°C , the orthorhombic lattice transforms to the 'hexagonalized' zirconolite and continues to give a single crystal pattern. The presence of weak superstructure reflections within a defect fluorite sublattice of the low temperature intermediate phase suggests that the cations remain close to their ordered atomic positions in the metamict state. Presumably, a similar process to that found for the Brazilian sample occurs. The crystal transforms to domains of an ordered orthorhombic structure. The domains become smaller and fewer and thus produce weaker X-ray diffraction patterns.

The X-ray photographs from fragments of the brown material heated to 880°C produced only powder patterns. The pattern was identified as the cubic CaF_{2-x} -type. At 1100°C the crystals gave a 'hexagonalized' zirconolite pattern identical to the red crystals plus several extra strong lines. These lines could not be indexed on the zirconolite monoclinic cell. The mean volume change of the red crystals is 2.8%. This value is close to the maximum volume expansion measured for the Brazilian zirconolite.

Single crystal patterns of the Larvik minerals produced only diffuse powder rings. The crystals obtained after heating at 800°C were similar in appearance to the red translucent minerals described above. Guinier patterns taken after heating to 1200°C for 2 hours gave a 'hexagonalized' zirconolite pattern. It is therefore assumed that polymignite is in fact zirconolite containing a high amount of rare earth elements.

(d) Russian zirconolite

Several Russian zirconolite samples were also examined. At the present time the origin of these crystals is unclear although their chemical and X-ray properties suggest they originate from the Arbarastakh Massif, Aldan. Lead isotopic studies (Oversby and Ringwood, 1980) show an age of 650 m.y. These samples (Russian A, fig. 2) have accumulated a dose of 1.8×10^{19} alphas per gram which is slightly more than the total alpha dose received by SYNROC in 10^6 years. Precession photographs of these single crystals show the same cubic defect fluorite-type diffraction pattern as displayed by the natural Brazilian zirconolites. Heating these samples we note similar changes to their single crystal diffraction patterns as already described for the Brazilian samples. This sequence of events, including diffraction in the natural state, was also observed by Borodin et al. (1960) and Pudovkina and Pyatenko (1966) on samples from Aldan.

The lattice parameter given in the natural state was obtained from a 57.3 mm Debye-Scherrer camera. On comparison with the same sample heated, a maximum of 1.7% increase in volume is noted. Diffraction lines and spots from these crystals were unusually sharp although very weak. Pudovkina and Pyatenko (1966) observed similar patterns and made the following comment: "We then can assume that the reflections are not due to highly dispersed crystalline particles, but to a small number of rather large sections with crystalline structure". Thus, the very high alpha dose is still not sufficient to cause these samples to become metamict. (e) Sri Lanka zirconolite

Zirconolites from Sri Lanka were first described by Blake and Smith (1913). These crystals had typically accumulated large radiation doses in excess of 8×10^{19} a/gm. This is equivalent to a SYNROC age greater than 4×10^8 years (Fig. 2). X-ray photographs indicated that these minerals were completely metamict. The powder patterns gave only diffuse rings. Electron microscopy of sample 83800 displayed regions similar to those of the Brazilian zirconolite. One grain (Fig. 6) contained small crystallites of about $140 \text{ \AA}$ in diameter, in random orientations. The corresponding diffraction pattern gave a sharp spotty powder photograph identified as the cubic defect fluorite-type pattern. This observation is of considerable significance. The radiation dose accumulated by the sample is 6 times higher than the expected dose received by zirconolites in SYNROC containing 10 percent high level waste and stored for 10^6 years. The specimen, however, still contains areas of crystalline material. Other grains (Fig. 7) were composed of featureless regions and the corresponding diffraction patterns (Figs. 7 and 8) contained only diffuse powder rings. The innermost ring (I) is equivalent to the combination of the (111) and (200) reflections of the cubic defect fluorite-

type structure. Similarly, the next ring further away (M) from the centre corresponds to the (220), (311) and (222) defect fluorite-type reflections. The rings were broader than those obtained from similar areas of the Brazilian sample. Thus, there is a decrease in the short range order in metamict areas of the Sri Lanka sample.

Heating to 700-800°C for two hours caused the cubic defect fluorite-type powder pattern to appear. After further heating to 1100-1200°C the X-ray patterns corresponded to the monoclinic zirconolite. Two samples, numbers 83800 and 820392, gave the 'hexagonalized' zirconolite pattern while sample SL3/12 produced a monoclinic pattern similar to a pure synthetic zirconolite. All of the specimens reconstituted as polycrystalline material.

The value obtained from the density measurement of sample SL3/12 in the natural state was 4.39 gm/cc. After reconstituting the specimen at a temperature of 1300°C, a value of 4.50 gm/cc was measured. This represents a 2.5% decrease in density and is quite small considering the extremely high alpha dose this mineral has received. The density change calculated here is also close to the highest value obtained from the Jacupiranga zirconolites using X-ray methods.

(f) Perovskite

Small samples of loparite, and three perovskite samples have also been studied by X-ray diffraction and electron-probe. The samples of loparite, a perovskite-type mineral containing large amounts of cerium and niobium, were obtained from the Lovozero alkaline massif of the Kola Peninsula. The U and Th contents of the loparite samples are 30 ppm and

2000 ppm respectively.

For an age of 300 m.y. (Komlev et al., 1961), an alpha dose of 1.3×10^{18} α /gm would have accumulated for the loparite sample. The corresponding age for SYNROC at this dose would be 10^3 years (Fig.1). X-ray powder photographs reveal that the loparite crystals have not suffered any perceptible radiation damage to their crystal structure. The powder lines are sharp, and at angles of high 2θ , the α_1 and α_2 peaks are clearly resolvable. Comparison of these X-ray observations with those on Kaiserstuhl zirconolite indicates that the perovskite mineral is even more resistant to radiation damage than zirconolite. On annealing loparite at 1200°C , a slight decrease in "d" spacings occurs, equivalent to an increase in density of 1.6% (Table 4).

The two perovskite samples A and B, from Lake Baikal, Tazheran, contained the following amounts of U and Th; A, U = 1280, Th $\approx$ 500 ppm and B, U = 1530 ppm, Th $\approx$ 500 ppm. The age of these minerals reported by Oversby and Ringwood (1980) is 500 m.y. They have received an alpha dose of 2.2×10^{18} and 2.6×10^{18} alphas per gram respectively. This is equivalent to a SYNROC age of 1×10^4 yr and 1.7×10^4 yr (Fig. 1). Although these minerals have received higher alpha doses than the loparite, their X-ray patterns are extremely sharp with no observable sign of structural damage to the lattices. After annealing the perovskites at 1200°C , a slight decrease in volume occurs in both samples, equivalent to 1.8 ± 0.1 for A and $1.82 \pm .04\%$ for B. The percentages compare favourably with the results of Reeve and Woolfrey (1980). These workers reported an increase in volume of approximately 2.6% for synthetic perovskites irradiated with fast neutrons for a period of time equivalent to a SYNROC age of 10,000 years. Although this dose was accumulated in 22 days, the above results support the relevance of accelerated irradiation testing.

The Jacupiranga perovskites (not shown on the figure) contain concentrations of uranium and thorium which range from a high of 0.3% UO_2 and 1.6% ThO_2 to a low of 0.1% UO_2 and 0.5% ThO_2 . Using the average values of 0.2% UO_2 and 1.0% ThO_2 , the calculated dose for these samples is 1.6×10^{18} alphas per gram. This corresponds to a SYNROC age of 5×10^3 yr. The X-ray powder pattern reflections of this mineral were only slightly broadened in the natural state. After heating at $1200^\circ C$ for two hours a small decrease in volume of $1.03 \pm 0.06\%$ occurs.

The volume changes reported here are quite small in relation to the alpha dose received and demonstrates the structural stability of perovskite. These results suggest that both for zirconolite and perovskite most of the lattice expansion occurs after a relatively small radiation dose. After lattice expansion of less than 3 percent there is little further expansion even for very large alpha doses.

7. Relationship between Calculated and Measured Density

Most of the density changes reported within this paper are based on values calculated from X-ray volumes. It is known that the calculated density (X-ray) does not always agree with the measured density (Archimedes method) of some irradiated materials (Budylin and Vorob'ev, 1964; Hickman et al., 1965). The following examples, however, show that the calculated density changes of zirconolite and perovskite should reflect the measured densities within the range of values reported.

Howard and Sabine (1974) have described the difference between the densities of ionic compounds obtained from these different techniques by closely studying the behaviour of irradiated MgO . They found that with increasing radiation dose, the (200)

bragg peak of MgO initially shifts to a lower 2θ angle in agreement with the corresponding directly measured density. At higher doses the reflection is associated with a diffuse component skewing the peak profile on the high angle side. The diffuse component is caused by defects which occur on irradiation and eventually it dominates the powder profile.

The value of the X-ray density at this stage is close to that of the unirradiated crystal. Hence, the use of diffuse peak positions for calculating the density of highly irradiated simple ionic compounds would lead to incorrect values.

Calculated and measured densities of complex compounds containing a degree of covalent bonding appear to behave differently to those of the simple ionic materials. Results of Comes et al. (1966) and Wittels (1957) from neutron irradiated α -quartz show that the X-ray volume agrees with the measured volume after receiving a radiation dose of approximately 3×10^{19} neutrons/cm². This corresponds to a 2% reduction in density. At higher doses the volume determined by X-rays is found to be greater than the measured volume. Pronounced skewing of certain bragg reflections towards the high angle side is evident from the figures presented by Wittels (1957). The author notes, however, that if the mean positions rather than the peak positions of a sample irradiated with 8×10^{19} neutrons/cm² are used to determine the lattice constants, then the ratio of X-ray to directly measured volume is reduced from 1.42 to 1.14. Thus, the deviation of the calculated X-ray density from the measured density will start to occur after a volume increase of somewhere near 6%. This value represents the amount of expansion in volume of the sample after being irradiated by 8×10^{19} neutrons/cm².

In the case of zircon the (112) bragg peak becomes associated

with a second more diffuse peak on the high angle side with increasing alpha dose (Holland and Gottfried, 1955). The Bragg diffraction line eventually disappears leaving only the second peak at a 2 θ angular position similar to the unirradiated (112) value. The development of this second diffuse peak indicates that a process similar to that outlined by Howard and Sabine (1974) for ionic compounds may be occurring. A plot by Holland and Gottfried (1955) of the reciprocal of the X-ray volume versus measured density for zircon shows initially a straight line relationship until at a dosage of 0.3×10^{19} /gm the curve begins to deviate. The deviation occurs after zircon has undergone a 5% expansion in volume. This value is similar to that encountered for α -quartz. It is interesting to note that the deviation of the curve for zircon is in the opposite direction to that given for α -quartz by Wittels (1957).

From the above examples, the calculated and measured density values seem to remain equivalent until the compounds have expanded by about 5% in volume.

The X-ray volume changes of zirconolite and perovskite (43) are well within the above value and are therefore assumed to reflect the density change of the material. Further support is given by the work of Reeve and Kodifrey (1960). These authors reported that synthetic perovskite underwent an expansion of about 2.6% after receiving a radiation dose estimated to be equivalent to 10,000 SYNROC years. This figure is in good agreement with the volume change calculated from the natural perovskites which have accumulated a similar dose. The value of 2.5% obtained for the density change of zirconolite sample SL3/12 from measurements made by the Archimedes method is also close in value to the higher volume changes calculated from X-ray measurements of the other

zirconolite samples (Table 3).

6. Discussion

X-ray diffraction and electron microscopy studies suggest that zirconolites retain a high degree of lattice order even after they have received a radiation dose equivalent to 10^6 Sr-90 years. The very small volume changes observed for the samples which have received large doses of radiation indicates that only a small degree of internal rearrangement has occurred. Moreover, the zirconolite samples reconstituted, as single crystals, to their original undamaged state after being heated for less than one hour at temperatures as low as 950°C . Even the highly damaged Sri Lanka zirconolites reconstituted to a single phase of polycrystalline material. This is in contrast to the behaviour of heavily damaged zircons. These minerals, when heated, reconstitute to a complex mixture of the oxides (Cartz and Fournelle, 1979).

The effects of nuclear radiation on the properties of inorganic compounds are highly variable. As early as 1924, however, Goldschmidt (1924) suggested that those crystals which contain a high degree of ionic binding were more resistant to the effects of radiation. This same observation has since been made by many authors (e.g. Wittels and Sherrill, 1959; Billington and Crawford, 1961; Budylin and Vorob'ev, 1962 and Kanuib and Kelly, 1975). Close packing of the atoms within the structure is another desirable characteristic of the compound.

The fluorite-type structure exhibits these characteristics. It possesses a high ionicity, Kanuib and Kelly (1975), and its atoms are arranged in cubic closest-packing. Thorianite adopts this structure and, in nature, is not found in the metamict state.

Several other simple oxides with the fluorite-type structure have also been found to remain crystalline when bombarded with high doses ($\approx 10^{17}$ ions/cm²) of energetic heavy ions (Naguib and Kelly, 1975).

The close relationship between the zirconolite structure and the fluorite-type structure has already been mentioned in a previous section. The fluorite-type subcell, upon which zirconolite is based, is only slightly deformed from an undistorted face-centred cubic lattice. A rhombohedron results with an angle of about 92° (Pudovkina and Pyatenko, 1966). The ability of natural zirconolite to withstand the damaging effects of large doses of alpha radiation is probably due to this association.

The perovskite structure, like that of zirconolite, is based upon a cubic lattice. In this structure the oxygen and calcium atoms are arranged approximately in cubic close-packing, i.e. a face-centred cubic array (Bloss, 1971). The distortion to the observed orthorhombic structure involves a very small degree of shearing ($.48^\circ$) of the cubic pseudo-cell (Kay and Bailey, 1967). Wittels and Sherril (1959) irradiated a number of perovskite-type crystals. These included BaTiO_3 , KNbO_3 and PbTiO_3 . They demonstrated that the above compounds transformed to their high-temperature cubic modification when irradiated with fast neutron dosages in excess of 10^{19} n/cm². The a and c axial lengths of tetragonal BaTiO_3 increased by approximately 1.9 and 0.9 respectively after receiving a neutron dose of 1.2×10^{20} n/cm². At this stage, all axes were equivalent (cubic) and after 1.6×10^{20} n/cm² the value of the cubic axis increased by a further 0.3%. This radiation dose is close to three times the dosage received by the perovskites used in the experiments of Reeve and Woolfrey (1980). The BaTiO_3 crystals remained single throughout the entire irradiation.

Recently, loparites containing greater than 1% UO_2 have been found in the Lovozero intrusion, Kola Peninsula. Although these minerals have accumulated a dosage of 8.9×10^{18} α/gm they still continue to produce sharp diffraction patterns (Kogarko, pers. comm.). The radiation dose exceeds that received by the zirconolites from Jacupiranga.

In contrast to the titanate perovskites discussed above, the rhombohedral perovskite-type compound CaAlO_3 became metamict after it had received a dose of 1.6×10^{18} α/gm . This dose was derived in 8 days from the decay of ^{244}Cm , and is equivalent to a SYKROC age of 1000 years. The effect of nuclear radiation caused a small increase in volume (3.2% at saturation) and a phase transformation to the cubic modification before the compound became amorphous to X-rays (Mosley, 1971).

The behaviour of CaAlO_3 to nuclear radiation may be a consequence of its differing chemical composition and reflects the nature of the bonding and type of distortion from the ideal cubic perovskite-type compound. Moreover, the extremely high dose rate may have been a contributing factor. In contrast all titanate perovskites which have received much larger doses, but over longer periods of time, have been shown to remain highly resistant to the effects of large doses of nuclear radiation. Furthermore, the volumes of all the perovskite-type compounds mentioned increase by only small amounts.

9. Nature of the Metamict State

The term metamict is usually applied to minerals which have lost their crystallinity due to the action of nuclear radiation arising from the radioactive elements contained within them.

Rabst (1952) and German (1955) have given a detailed discussion of the term and some of the characteristics associated with such minerals. There are many degrees of the metamict state and the physical properties usually change continuously in response to the amount of radiation dose. With the use of electron microscopy, minerals that were once thought to be metamict and now found to display strong diffraction patterns typical of well-crystallized materials.

Recently, several authors (Cartz and Turner, 1973 and Swinn, 1976, 1978) have suggested that minerals in the metamict state have a disordered atomic arrangement. However, the atomic structure of the fluorite-type minerals, which are metamict, has been determined by x-ray diffraction. These minerals have received extremely high doses of alpha radiation and it has been found that the atoms remain sufficiently ordered to display ordered powder rings. The rings are identifiable with a cubic fluorite-type pattern. The Mössbauer study of Cartz (1975) on a sample of X-ray amorphous thore-steenströmine $(\text{U}_{0.5}\text{Th}_{0.5}\text{Fe}_2\text{Ti}) (\text{Si}_2\text{P}_2\text{O}_{11})_3 \cdot 2\text{H}_2\text{O}$ also supports an ordered atomic arrangement in the metamict state. The author has shown that Fe^{3+} occurs in two different distinct sites and that the Mössbauer spectrum has not been affected by the radiation damage.

10. Conclusions

Results described in previous sections have elucidated several of the effects of increasing doses of nuclear radiation on the crystal structures of naturally occurring zirconolite and perovskite minerals. When subjected to an alpha dose of 8×10^{18} μ /gm equivalent to a SYNROC age of 4×10^5 yr, zirconolite transformed to the cubic defect fluorite-type structure. Despite the very large radiation doses received, these crystals continued to display single crystal X-ray diffraction patterns. Electron microscopy of these zirconolites revealed that the mineral was mainly composed of crystalline domains coherently orientated.

Sri Lanka crystals which had received a radiation dose exceeding that which would be experienced by SYNROC in 4×10^8 yr were apparently metamict when studied by X-ray diffraction. However electron diffraction investigations demonstrated that they contained areas of crystalline domains. These, however, were in random orientations and gave a spotty cubic defect fluorite-type powder pattern. The micrographs of other areas of this sample studied by electron microscopy were of low contrast but the diffraction patterns exhibited diffuse powder rings also identifiable with the defect fluorite-type pattern. These apparently metamict areas have suffered an extremely large radiation dosage and yet the atoms retain a large degree of short range order.

These results have a direct bearing upon alternative hypotheses dealing with the effect of radiation damage in crystals. In particular, they are best explained by progressive disordering of the structure with increasing radiation dose, as suggested by Vance (1975) and Vance and Boland (1975, 1978). There is no evidence that the minerals become segregated into simple oxide phases even after receiving extremely large doses of radiation as proposed by Pyatenko (1970), Wasilewski et al. (1973) and Pellas (1965).

The atomic arrangement of zirconolite in a state which would be classed as metamict when investigated by X-rays has nevertheless been found to retain a high degree of short range order when studied by electron diffraction. This state in no way resembles a true glass as suggested by Ewing (1975,1976) and Caraz and Fournell (1979). The electron diffraction pattern of the metamict areas of highly irradiated zirconolite gave distinct powder rings and could be identified with the cubic defect fluorite-type pattern.

11. Implications for Long-Term Stability of SYNROC

One of the primary concerns expressed about proposals to incorporate nuclear waste into a crystalline ceramic waste form, has been the possibility that radiation damage could destroy the crystal structures and seriously impair their ability to immobilize the waste elements (e.g. Ross et al., 1979). It has been suggested that because radiation damage ultimately leads to metamictization, the ability of these metamict minerals to retain the waste elements may be no greater than that of glass. Our results on zirconolite and perovskite effectively dispel these concerns, at least, for these particular minerals. They show that the atomic structures of the irradiated minerals are still essentially those of the crystalline state and are in no way analogous to those of silicate or borosilicate glasses. Further support for this conclusion is provided by the results of Oversby and Ringwood (1980) on the Pb/U isotopic systematics and leachability of the natural zirconolites and perovskites used in their study. They demonstrated that the minerals display a remarkable ability to immobilize U and Pb under geological conditions. Moreover, the Sri Lanka zirconolites which have suffered the most extensive radiation doses were found to be less leachable than borosilicate glasses in water and brines at 200°C by a factor

exceeding one thousand (Oversty and Ringwood, 1980).

For SYNROC containing 10 percent of high level waste, it is usually estimated that a storage period of 10^5 - 10^6 yr would be required for the wastes to decay to a safe level. The natural samples described here provide us with a suitable model with which to assess the crystalline integrity of SYNROC phases during this storage interval. After 1000 years the crystal structures of zirconolite and perovskite in SYNROC containing 10% high level waste are essentially unaffected by the nuclear radiation received (chiefly from alpha particle recoils). After receiving a radiation dose equivalent to a SYNROC age of one million years zirconolite is still crystalline but undergoes a change in structure to the defect fluorite-type lattice. The volume increase is less than 3%. After a radiation dose equivalent to 100 million years SYNROC age zirconolite appears metamict. Electron diffraction, however, shows that the atoms still maintain short range order, as previously described. The volume increase after this period of time has already reached saturation level and remains smaller than 3%.

At a radiation dose equivalent to that which SYNROC would accumulate in 10,000 years of storage, perovskite expands in volume by less than 2% but the crystallinity remains unaffected. After receiving a radiation dose equivalent to a SYNROC age of half a million years, perovskite is still crystalline. Comparison of X-ray diffraction photographs of perovskites and zirconolites which have received similar radiation doses indicates that perovskite is even more resistant to nuclear radiation than zirconolite. Thus, the basic properties of the crystalline state of these phases are not affected over the time period required for the waste to decay to a safe level.

The volume change of SYNROC containing 25% perovskite, 35%

zirconolite and 40% Ba-hollandite*, buried for 10^5 - 10^6 yrs would be less than 2%. Because of the very slow strain rate in the presence of confining pressure when buried at depth in a geological repository it is expected that this expansion will cause SYNROC to deform by plastic flow rather than by brittle fracture. Indeed, this behaviour is displayed by large (~60 gram) single crystals of Sri Lanka zirconolite which are found as resistate minerals in the gem gravels.

Results of fast neutron damage produced on a rapid time scale (1 month) and the damage caused by alpha-particles over periods of geological time (up to 10^8 yrs) were found to be in good agreement. Although there is a factor of 10^9 difference between the two time scales, these results support the relevance of accelerated irradiation testing. The rate of accumulation of radiation damage in SYNROC containing high level waste is intermediate between the above dose rates. In view of these results we conclude that the responses to nuclear radiation observed on the natural minerals over much longer time scales are directly applicable to the long term behaviour of these phases in SYNROC.

---

* Ba-hollandite expanded by less than 2% after being irradiated for a period of time equivalent to 10^6 yr SYNROC age (Keeve and Woolfrey, 1980).

Acknowledgements

We wish to record our appreciation of the persons and institutions who made it possible to obtain the samples of minerals used in this investigation. In this respect, we are particularly indebted to Jörg Keller, Gene Kaula, Carl Francis, Brian Mason, Arne Råheim, Andrew Graham, Andrew Clark, Geraldo Melcher, Monica Cassola, T.R. Cuttlan, H.D.N. Sathirana, and to the British Museum (Natural History), the Smithsonian Institution, Harvard University, Mineralogisk-Geologisk Museum (Oslo), University of Freiburg, Serrana S/A de Mineracao, Sri Lanka Geological Survey, and the USSR Academy of Science.

We are also indebted to Dr. R.A. Eggleton of the Department of Geology, and Professor B.G. Hyde and Dr. G.B. Robertson of the Research School of Chemistry, Australian National University for the use of the X-ray equipment. One of us (W.S.) would like to thank Dr. Eggleton for critically commenting on sections of the manuscript. The researches described in this paper were supported by grants provided by the National Energy Research Development and Demonstration Program of the Commonwealth Department of National Development and by the Australian Atomic Energy Commission. This support is gratefully acknowledged.

- Ewing, R.C. (1975) The crystal chemistry of complex niobium and tantalum oxides. 1V. The metamict state: Discussion. *Am. Mineral* 60, 728-733.
- Ewing, R.C. (1976) Metamict mineral alteration: an implication for radioactive waste disposal. *Science* 192, 1336-1337.
- Goldschmidt, V.M. (1924) Über die umwandlung krystallisierter Minerale in den metamikten zustand (Isotropisierung). *Norsk. Ak. Skr. I. 1*, No. 5, Geochemische Verteilungsgesetze der Elemente, III (Anhang) 51-58.
- Hickman, B.S., Walker, D.G. and Sabine, T.M. (1965) The behaviour of defects in neutron irradiated magnesium oxide. *International Conference on Electron Diffraction and Crystal Defects*, Melbourne.
- Holland, H.D. and Gottfried, D. (1955) The effect of nuclear radiation on the structure of zircon. *Acta Crystallogr.* 2, 291-300.
- Howard, G.D. and Sabine, T.M. (1974) X-ray diffraction profiles from neutron-irradiated magnesium oxide. *J. Phys. C: Solid State Phys.* 7, 3453-3466.
- Hussak, E. and Prior, G.T. (1895) Lewisite and zirkelite, two new Brazilian minerals. *Mineral. Mag.* 11, 80-88.
- Kay, H.F. and Bailey, P.C. (1957) Structure and properties of CaTiO_3 . *Acta Crystallogr.* 10, 219-226.
- Komler, L.V., Mikhalevskaya, A.D. and Danilevich, S.I. (1961) The age of the alkaline intrusions of the Chibina and Lovozero Tundras (Kola Peninsula). *Dokl. Akad. Nauk. SSSR* 136, 31-33 (Earth Sciences Trans.).
- Lima de Faria, J. (1964) Identification of Metamict Minerals by X-ray Powder Photographs. Junta de Invest. do Ultramar, Portugal; *Estud., Ensaio and Documentos* 112, 130 pp.

- Mosley, W.C. (1971) Self-radiation damage in curium-244 oxide and aluminate. *J. Amer. Ceram. Soc.* 54, 475-479.
- Naguib, H.M. and Kelly, R. (1975) Criteria for bombardment-induced structural changes in non-metallic solids. *Rad. Effects* 25, 1-12.
- Oversby, V.M. and Ringwood, A.E. (1980) Lead isotopic studies of zirconolite and perovskite and their implications for long range SYNROC stability. (in preparation).
- Pabst, A. (1952) The metamict state. *Am. Mineral.* 37, 137-157.
- Perias, P. (1965) Etude sur la recristallisation thermique des zircons métamictes. *Mém. Mus. Natl. d'Histoire Nat., Series C*, 12, 227-253.
- Pudovkina, Z.V., Dubakina, L.S., Levedeva, S.I. and Pyatenko, Yu. A. (1974) Study of Brazilian zirkelite. *Zap. Vses. Mineral. Obshch.* 107, 368-372 (in Russian).
- Pudovkina, Z.V. and Pyatenko, Yu.A. (1966) On zirconolite and its crystallographic features. *Tr. Mineral. Muzeiya Akad. Nauk. SSSR* 17, 124-133 (in Russian).
- Pyatenko, Yu.A. (1970) Behaviour of metamict minerals on heating and the general problem of metamictization. *Sockol'nikiya* 9, 1077-1083 (in Russian).
- Pyatenko, Yu.A. and Pudovkina, Z.V. (1961) The crystal structure of calcitite: a new derivative structure of $\text{CaF}_2\text{-CaO}_2$ type. *Kristallografiya* 6, 196-199 (in Russian).
- Pyatenko, Yu.A. and Pudovkina, Z.V. (1964) The lattice metric of $\text{CaZrTi}_2\text{O}_7$ crystals. *Kristallografiya* 9, 96-100 (in Russian).
- Reeve, K.D. and Woolfrey, J.L. (1980) Accelerated irradiation of SYNROC using fast neutrons I. First results on barium hollandite, perovskite and undoped SYNROC B. *J. Aust. Ceramic Soc.* (in press).

- Ringwood, A.E., Kesson, S.E., Ware, R.G., Hibberson, W. and Major, A. (1979) Immobilization of high level nuclear reactor wastes in SYNROC. Nature 277, 219-223.
- Ross, W.A., Mendel, J.E., Turcotte, R.P. and Rusin, J.M. (1979) A comparison of glass and crystalline waste materials (abs). in Extended Abstracts International Symposium on Ceramics in Nuclear Waste Management, Cincinnati, April 30 - May 2.
- Russell, H.J. (1980a) Zirconolite - a fluorite-related super-structure. Nature 283, 282-283.
- Russell, H.J. (1980b) Cation substitution in zirconolite. Presented at CRYSTAL XII the Twelfth Meeting of Crystallographers in Australia, Canberra, January 30 - February 2.
- Turner, G. (1966) Rubidium-strontium isotopic studies in the Pilgarrlie-Margheran area, Western Australia. Univ. of W. Austr., B.S. Thesis.
- Varley, E.R. (1975) α -recoil damage in zircon. Rad. Effects 24, 1-6.
- Varley, E.R. and Boland, J.N. (1975) Fission fragment damage in zircon. Rad. Effects 26, 135-139.
- Varley, E.R. and Boland, J.N. (1978) Fission fragment irradiation of single crystal monoclinic ZrO_2 . Rad. Effects 37, 237-239.
- Vlasov, K.A. (ed.) (1966) Geochemistry and Mineralogy of Rare Elements and Genetic Types of their Deposits. (Israel Program for Scientific Translations, Jerusalem). Vol. 2.
- Wasiilewski, P.J., Senftle, F.E., Vaz, J.E., Thorpe, A.N. and Alexander, C.C. (1973) A study of the natural α -recoil damage in zircon by infrared spectra. Rad. Effects 37, 191-199.
- Williams, C.T. (1978) Uranium-enriched minerals in Mesostasis areas of the Rhum layered pluton. Contrib. Mineral. Petrol. 66, 29-39.

Wittels, M.C. (1957) Structural behaviour of neutron irradiated quartz. *Phil. Mag.* 2, 1445-1461.

Wittels, M.C. and Sherrill, F.A. (1959) Some irradiation effects in non-metallic crystals. in Advances in X-ray Analysis (ed. Mueller, W.M.), Pitman, London, 3, 269-288.

Table 1. Chemical analyses ZIRCONOLITES

	Stavern (Brown)	Stavern (Red)	Larvik	Jadunthorpa	Aldar (1)	Reinert-Dahl	Gr. 15084 (84-392)	Gr. 15085 (84-393)	Gr. 15086 (84-394)
Nb ₂ O ₅	18.9	15.6	3.03	11.3	4.6	15.7	3.6	2.7	10.2
Ta ₂ O ₅	0.4	<0.2	0.69	0.2	<0.1	1.2	-	-	<0.1
TiO ₂	16.7	22.4	27.00	24.3	35.4	20.9	20.9	17.0	36.5
ZrO ₂	32.0	35.3	31.40	35.2	36.5	31.8	36.5	33.4	38.6
ThO ₂	3.7	0.6	4.11	7.4	1.2	2.9	20.5	21.0	0.9
UO ₂	1.9	0.3	1.27	0.5	0.5	1.5	1.1	1.7	4.6
FeO	9.3	8.4	6.88	7.2	5.0	7.5	3.1	3.0	3.4
MnO	.5	0.4	0.48	0.2	<0.1	0.2	-	1.2	0.2
MgO	-	-	-	0.4	-	0.3	2.4	2.5	0.6
CaO	7.7	10.0	9.15	11.5	15.1	12.1	7.9	7.7	12.1
Y + REE	6.6	4.3	9.34	2.6	1.9	2.9	-	-	-

Data for Larvik supplied by A. Gineim.

Data for other samples are electron microprobe analyses (R.G. Ware, analyst).

Table 2. Chemical analyses PEPOVSKITES

	Lovchoro (leparite)	Bafkal	Lacopiranga
Na ₂ O	6.7	6.9	3.4
CaO	0.1	0.1	0.1
TiO ₂	48.1	54.6	53.3
FeO	0.1	-	1.0
Al ₂ O ₃	<0.1	0.12	0.2
FeO	-	1.1	1.6
CaO	5.9	41.0	37.2
FeO	7.6	-	-
Na ₂ CO ₃	9.1	<0.1	0.3
SiO ₂	23.2	2.2	-
Y + other PEE	3.1		1.6

Electron microprobe analyses; N.G. Ware, analyst.

Table 3. Unit cell dimensions of natural zirconolites.

Sample	Temperature (°C)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Vol. Change (mean value)
Kaiserstuhl	R.T. ^a	12.554 (1) ^c	7.289 (1)	11.600 (1)	101.29 (2)	1000.1 (1)	0.7
	1200	12.541 (1)	7.280 (1)	11.585 (1)	101.30 (2)	1000.4 (1)	
Jacupiranga	R.T.	5.06 (1)	-	-	-	10.00 (1) ^d	0.5
	1200	12.5924 (5)	7.2701 (2)	11.5512 (6)	100.591 (3)	1000.6 (1)	
Stavern	R.T.	5.10 (1)	-	-	-	10.01 (1)	2.8
Stavern (red)	1200	12.6160 (9)	7.285 (1)	11.427 (13)	100.800 (7)	1001.8 (3)	
Larvik	R.T.	-	-	-	-	-	
	1200	12.5407 (6)	7.1637 (3)	11.5159 (6)	100.507 (4)	1025.5 (2)	
Russian (Aldan?)	R.T.	5.01 (1) ^e	-	-	-	10.18 (1)	0
	1200	12.5486 (4)	7.2449 (2)	11.5041 (3)	100.507 (3)	1019.2 (1)	
Sri Lanka ^b B20392	1200	12.5659 (5)	7.2543 (1)	11.5321 (9)	100.526 (5)	1021.6 (2)	
Sri Lanka 83800	1140	12.5678 (7)	7.2560 (4)	11.4352 (9)	100.558 (6)	1025.1 (2)	
Sri Lanka SL3-12	1200	12.5509 (18)	7.2427 (9)	11.3865 (16)	100.54 (2)	1000.5 (4)	2.5 ^f

a Room Temperature.

b Sri Lanka samples gave diffuse patterns at room temperature.

c Errors are given in parentheses.

d The monoclinic zirconolite cell is 8 times the volume of its fluorite subcell.

e Cell edge derived from a 57.3 nm diameter Debye-Scherrer pattern with an internal Si standard.

f Volume change obtained from density measurements using the Archimedes method.

Table 4. Unit cell dimensions of natural perovskites.

Sample	Temperature (°C)	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Volume Change
Leperite	R.T.	3.8839 (5) ^a			58.59	1.56
	1200	3.8636 (5) ^b			57.67	
Jacupiranga	R.T.	5.4791 (6)	7.6873 (15)	5.4066 (8)	227.72 (8)	1.03 ± 0.06
	1200	5.4517 (3)	7.6617 (10)	5.3956 (5)	225.37 (6)	
Baikal A	R.T.	5.4889 (7)	7.6906 (10)	5.4005 (8)	227.97 (9)	1.8 ± 0.1
	1200	5.472 (1)	7.644 (2)	5.382 (2)	223.9 (2)	
Baikal B	R.T.	5.4926 (2)	7.6972 (5)	5.4049 (3)	228.51 (4)	1.82 ± 0.04
	1200	5.4586 (3)	7.6475 (7)	5.3844 (4)	224.35 (5)	

a Pseudo-cubic cell edge.

b Errors are given in parentheses.

Figure Captions

- Figure 1. Total alpha dose vs. age for SYNROC samples between 10^3 and 10^6 yrs. (After Oversby and Ringwood, 1980).
- Figure 2. Total alpha dose vs. age for SYNROC samples between 10^6 to 10^9 yrs. (After Oversby and Ringwood, 1980).
- Figure 3. Dark field image and diffraction pattern of a well crystallized area of natural Brazil zirconolite. Beam direction along $[0\bar{1}1]$ fluorite.
- Figure 4. Dark field image illustrating the domain structure of natural Brazil zirconolite. The contrast is speckled on a scale of about $50 \text{ \AA}$. The beam direction of the diffraction pattern is along $[0\bar{1}1]$ fluorite.
- Figure 5. Dark field image of a sector of the $\{111\}$ powder ring of Figure 4. Only areas of low contrast in Figure 4 contribute to the powder ring.
- Figure 6. Bright field image of sample 83800. The crystallites ($\sim 140 \text{ \AA}$ in diameter) are randomly orientated giving rise to the sharp defect fluorite-type powder pattern.
- Figure 7. Electron micrograph of the featureless areas of sample 83800. The corresponding diffraction pattern displays diffuse rings which approximate the cubic defect fluorite-type pattern. The centre rings have been over-exposed in order to show the outer ring (0).
- Figure 8. Densitometer trace across the diffraction pattern in Figure 7. The three rings marked I, H and O correspond to combinations of defect fluorite-type powder rings.

FIGURE 1

α Dose vs SYNROC Age
for Zirconolite & Perovskite

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

Lead Isotopic Studies of Eironselite
and Perovskite and their Implications
for long range SYSTEM stability

A.M. Oversby and A.E. Ringwood

Research School of Earth Sciences
Australian National University
Canberra, A.C.T. 2600, Australia

Abstract

The minerals zirconolite and perovskite are used in SYNROC to immobilize the fissionable actinide elements present in high level nuclear waste. Natural samples of these minerals have been studied by Pb isotopic methods to estimate the effect of alpha irradiation on the ability of the minerals to retain actinides and their decay products. We have related the alpha dose received by the minerals to the length of time required before minerals in SYNROC containing ^{235}Pu would reach this dose. Perovskite samples with alpha doses equivalent to 30,000 storage years (i.e. 10^7 years) show excellent retention of U, Th and Pb. Zirconolite samples with half-lives ranging from 1×10^5 yr to 5×10^8 yr show quantitative retention of U, Th and Pb, even when the mineral is metastable. These results show that SYNROC will provide the means of disposing of the actinide elements in high level reactor waste during the time required for waste radioactivity to decay to safe levels.

SYNROC

The basic objective of the SYNROC method of immobilizing high level nuclear reactor wastes (HLW) is to incorporate the fission products and a number of dilute solid solutions in the crystal lattices of synthetic minerals. These minerals are closely related to natural minerals known to have been stable in a wide range of geological and geochemical environments for periods of more than 10^9 years. The minerals employed in SYNROC technology are designed to immobilize HLW from reprocessed fuel rods of power reactors are bellowsite ($\text{BaAl}_2\text{Si}_2\text{O}_{10}$), zirconosilicate (ZrSiO_4), and titanite ($\text{CaTiSi}_3\text{O}_{10}$). It has been demonstrated that these minerals have the capability to accept nearly all HLW fission products and diluents into solid solutions in their crystal lattices.

It is well established to demonstrate that these minerals are capable of immobilizing the HLW safely for periods sufficient to allow the radioactive fission products and actinides to decay to safe levels. The required minimum immobilization period is currently estimated to lie between 10^5 and 10^6 years, because this time lies beyond human experience, there has been a great deal of concern within society as to whether safe immobilization of HLW can be firmly guaranteed by existing technologies. One of the major advantages of the SYNROC approach is that natural minerals themselves provide the key evidence that safe immobilization is possible for these long periods. This factor may well prove to be of critical importance in determining the public acceptability of waste immobilization technologies. Indeed, in some countries, the public concern with the long term safety of nuclear waste disposal is so intense that the very future of nuclear power may rest upon an acceptable answer to this problem.

A key technical question is the effect of radiation damage on the structures of minerals proposed for waste immobilization. How much accumulated radiation damage is necessary to cause metamictization of these minerals? Do radiation damage and metamictization impair the capacity of the minerals to immobilize wastes? In this paper we will describe the results of isotopic studies carried out using natural samples of zirconolite in perovskites. The natural minerals have accumulated large radiation doses from the uranium and thorium contained in their crystal structures. The ability of the natural minerals to retain U, Th and their decay products will provide evidence of the long-term stability to be expected of SYNROC minerals containing high level radioactive waste.

Sample Descriptions

Zirconolite was first identified by Hussak and Brier (1975) in the decomposed magnetite - pyroxenite at Jacupiranga, Brazil. They named the mineral zirkelite; however, crystallographic studies have shown that zirkelite and zirconolite are the same mineral (Padovkina and Platenko, 1966). Since the original discovery, only a few occurrences of zirconolite have been documented. We have obtained samples from six of the eight known terrestrial localities where zirconolite occurs. The two localities not included in this study are the Rhum Pluton (Williams, 1978) and the Jimberlana intrusion, Western Australia (Lovering, personal communication). At both of these localities zirconolite grains are small, typically 10 to 15 μm , which would make it difficult to obtain suitable samples for isotopic work.

The samples used in this study are:

I. Jacupiranga, Brazil

Zirconolite occurs as a trace phase in the magnetite-pyroxenite of δ which underlies the carbonite at Jacupiranga. The zirconolite is always associated with phlogopite, titanite and magnetite.

Samples 1 and 2 were single grains, weighing 0.05 and 4 mg, respectively. They were separated from fresh rock material which had been collected from the same pit at Jacupiranga. Both samples came from the same hand specimen.

We have analyzed by electron microprobe over thirty individual grains of Jacupiranga zirconolite. The data in Table 1 are an average of analyses with 1000 μ and 10 μ concentrations of these grains. Zirconolite from Jacupiranga has Nb always greater than 10%, Ta always in excess of 10%, Th is generally at 1%, and U is generally less than 0.1% in most grains (Table 1).

Sample 3 (17-19) is a single grain extracted from a sample of weathered Jacupiranga. The whole rock sample was trilled as the result of extensive surficial weathering. The zirconolite extracted from this sample had a thin surface suggesting a weathered skin. The grain used for Th analysis was crushed gently and hand-picked to remove as much of the surface material as possible.

II. Russian A

A sample of purified zirconolite was supplied to us by the Academy of Science, USSR. The material is believed to be from the Aldan alkaline ultrabasic rocks of the Arbarastrakh Massif.

Chemical analysis (Table 1) shows this zirconolite to be low in Nb, REE, U and Th.

111. - La Termitière

A specimen of a fine specimen of carbonate rock containing zirconite was supplied by the Academy of Science, 1937. We were able to extract 2.5 g. of hand-picked, 99% pure, zirconite from the sample. The sample is very high in Th (see Table 1) and is also high in U. The Th/U ratio is high, while the Th/U ratio is moderately high.

112. - La Termitière

A specimen of a fine specimen of carbonate rock containing zirconite was supplied by the British Museum, Natural History, 1937. The sample was a single crystal with well developed prisms. Total weight was approximately 10 mg.

A specimen of a fine specimen of carbonate rock containing zirconite was supplied by the National Museum of Natural History, 1937. The sample was a single crystal with well developed prisms. Total weight was approximately 10 mg.

A specimen of a fine specimen of carbonate rock containing zirconite was supplied by the Geological Museum, Harvard University. The sample was a large, well-developed piece weighing approximately 10 mg.

14-11-12 - Purchased from a private collector in Sri Lanka. The sample is a large, well-rounded pebble, weighing 60 g, or nearly pure zirconite.

23-8.-1. - Purchased from a private collector in Sri Lanka. The sample was a rounded pebble of approximately 20 g, containing a fine grained mixture of zirconite, baddeleyite and ilmenite. Typical grain size for zirconite is 20 μ m. Electron probe analysis of a typical grain of this zirconite is given in Table 1. Comparison of the U and Th values measured by microprobe with those determined on the 1 mg sample of mixed phases used for Pb isotopic work (Table 3) suggests that only 1/3 of the bulk

showed ThO_2 content as high as 1.0% (von Laskemann, 1968). However, samples of Al_2SiO_5 kyanite supplied to us by several independent sources had ThO_2 generally less than 0.1%.

Two localities from which we obtained samples had perovskite which contained sufficient U and/or Th to make Pb isotopic analysis worthwhile. They are:

I. Lake Baikal

The sample consisted of approximately 15 grams of perovskite extracted from skarn at Iakhernan, Baikal Lake area.

The crystals are 2 to 4 mm on a side and contain various inclusions of calcite and other minerals.

Single cubes were prepared for analysis by crushing and sizing into fractions; the fraction used for analysis was 200 to 250 μ size. The sample was purified using methylene iodide heavy liquid and hand-picked to remove impurities.

Samples A and B are two different cubes. Chemical analysis (Table 2) shows that the samples are relatively pure CaTiO_3 , with small amounts of Nb, Fe^{+2} and RBE.

II. Lovozero

Loparite, a perovskite-type mineral with large amounts of sodium and cerium, was separated from an urtite occurring in the Lovozero alkaline massif in the Kola Peninsula.

The loparite occurs as euhedral interpenetrating twins, ranging in size from 100 to 500 μ . Loparite from this area has been shown by Komlev et al. (1960) to be approximately 300 m.y. old.

The chemical analysis (Table 2) shows that the loparite contains a substantial amount of Nb and Sr. The Ca site is occupied mainly by Ce and Na.

Alpha Dose as a Function of Age for SYNROC

By far the most important source of lattice damage in SYNROC minerals would arise from recoil of the parent nucleus during alpha decay. We have used the fuel compositions calculated by Cohen (1977) to estimate the actinide composition of the waste material. The fuel type is U-enriched with 37% of ^{235}U , a burn-up of 1000 MWD/THU, and a cooling time of 150 days before reprocessing. Reprocessing of one metric ton of this fuel would generate approximately 35 kg of HLW calcine. We plan to incorporate this waste calcine as 10% of the SYNROC mixture.

In SYNROC, the quadrivalent and trivalent actinides are partitioned into zirconolite and perovskite phases. These represent about 60% of the total SYNROC, and will absorb most of the alpha recoil damage. To evaluate the effect of alpha decay on mineral structures, we have calculated the cumulative alpha dose per gram of mineral as a function of SYNROC age. The dose rate is initially very high due to decay of ^{242}Cm and ^{244}Cm . After about 50 years, decay of americium isotopes dominates until 10^3 years. From 10^3 to 10^4 years, ^{241}Am is dominant. Half the total activity and ^{239}Pu and ^{240}Pu take up most of the remainder. Total alpha dose per gram for zirconolite and perovskite would be 5×10^{17} at 100 yrs, 1.1×10^{18} at 1000 yrs and 1.2×10^{18} at 10,000 yrs. During this period, the cumulative dose doubles for each factor of 10 increase in age of SYNROC.

The period from 10^4 to 10^5 years is transitional. ^{241}Am decreases in importance while ^{239}Pu (produced from ^{243}Am) decay dominates most of the period. Decay of ^{237}Np and its short lived daughters begins to make an important contribution. Cumulative dose absorbed by 10^5 yrs is 4.2×10^{18} alphas per gram of zirconolite plus perovskite. The dose rate is still roughly a factor

of two increase for a factor of ten increase in age.

From 10^5 to 10^7 years, ^{237}Np and its daughters completely dominate the alpha activity. Because the ^{237}Np daughter products are all short-lived, the alpha dose increases during the time while Np decays. For each factor of ten increase in SYNROC age from 10^5 to 10^7 years, the cumulative alpha dose increases by roughly a factor of three. At 10^6 years, the total is 1.5×10^{19} alphas per gram and at 10^7 years the total is 4.9×10^{19} . After 10^7 years the system is essentially zirconolite and perovskite with an average U content of 2.4% and inert hollandite. The activity is then nearly constant over periods of 10^8 years at 7.5×10^{18} alpha events per year per gram of zirconolite or perovskite. For a SYNROC age of 10^5 years, total alpha dose received would be 1.5×10^{19} per gram. This is an increase of less than 20% for a factor of ten increase in age.

To study the effects of radiation damage in zirconolite and perovskite we have examined naturally occurring samples of these minerals. The samples are described with chemical analyses in the previous section. The samples cover a range of radiation dose from 5×10^{17} a/gm to 1.1×10^{20} a/gm. For samples which have known age and measured U and Th concentrations we can calculate the total radiation dose received by the sample. This dose can then be directly related to the age of a SYNROC sample containing 10% HfW which would have received a similar radiation dose.

Figures 1 and 2 show the variation of radiation dose vs. age for SYNROC. These curves are obtained by the calculations described above. We may then locate the natural samples of perovskite and zirconolite on the SYNROC curves. Perovskite samples from Lake Baikal have radiation doses of 2.2×10^{18} and 2.6×10^{18} a/g. This corresponds to SYNROC ages of 1×10^4 yr and 1.7×10^4 yr respectively.

We have zirconolite samples which cover a range of radiation doses from less than 1×10^{18} α/g up to 11.2×10^{19} α/g . The Jacupiranga zirconolites have received an average dose of 8.2×10^{18} α/g , corresponding to a SYNROC age of 4.5×10^5 yr. The Russian A and Norwegian samples have SYNROC dose ages of about 1×10^6 yr, while the Sri Lanka zirconolites have received radiation doses that would only accumulate in SYNROC after times in excess of 5×10^3 yr.

Figure 2 also shows the alpha dose accumulated by zirconolite found as small (30-100 micron) grains in the Jimberlana mafic complex in Western Australia, which is about 2500 m.y. old (Turck, 1966; Lovering, personal communication). Wark (personal communication) has studied several samples and carried out careful electronprobe analyses for U, Th and Pb. The grains range from Th 2.01, U 0.592 to Th 2.191, U 2.172. Wark has shown that the lead abundances in these grains are closely consistent with those expected to result from radioactive decay of the contained U and Th in 2500 m.y. Since it is unlikely that these grains contain any significant amount of common lead, this implies closed system behaviour for U, Th and Pb over a period of 2500 m.y. More recently, Lovering (personal communication) has dated two Jimberlana zirconolite grains by ion microprobe. He obtained lead 206/207 ages of 2500 m.y., thus establishing the closed system behaviour. This is remarkable in view of the enormous amount of radiation damage (sometimes exceeding 3×10^{20} alphas/gram) received by these small grains and the demonstrated fact that water obtained access to the intrusion as shown by partial serpentinization of olivines (Campbell, 1977).

Isotopic Studies

The suitability of SYNROC as a host for high level waste immobilization depends on its ability to retain actinide elements and their decay products in zirconolite and perovskite. We have analysed a number of naturally occurring zirconolites and perovskites for U and Pb by isotope dilution, and for Pb isotopic composition. Work on Th is in progress. The samples are described and chemical analyses are given in an earlier section.

Samples chosen for isotopic work were handpicked to eliminate any traces of carbonate material or inclusions of foreign minerals. A weight of sample sufficient to give 1 to 2 micrograms of Pb was processed using the method of Krogh (1973). Total process blanks were 1 ng for Pb and 0.1 ng for U. Lead samples were run using silica gel plus H_3PO_4 on rhenium filaments. Uranium was run on single rhenium filaments with tantalum oxide plus H_3PO_4 . A mixed ^{208}Pb - ^{215}Po spike was used. The sample weights in some cases were 1 mg or less, so the absolute concentrations of U and Pb have an uncertainty of several percent. However, the use of a mixed spike ensures that the U/Pb ratio will be precisely measured.

Data for Pb and U concentrations and Pb isotopic compositions are given in Table 3. The Th concentrations were calculated using the radiogenic ^{208}Pb concentration and the age calculated from U/Pb systematics. In general, the calculated Th concentration is within 10% of the electron microprobe determinations. The agreement is improved if microprobe data for Th/U are normalized to the U concentration measured by isotope dilution. This shows that there has been no significant loss of ^{208}Pb or Th from these samples. Further work on accurate measurement of Th by mass spectrometry is in progress.

The U and Th concentrations and Th/U ratio in zirconolite are very variable. The samples from Norway have been described as polynignite; however, their chemistry and X-ray diffraction characteristics (Sinclair and Rindwood, in preparation) are close to zirconolite and we will consider them as zirconolites. They have Th/U similar to that normally found in terrestrial igneous rocks. In contrast, the Jacupiranga samples have Th/U greater than 11. Microprobe analyses of single grains have given Th/U as high as 20.

Zirconolite was first described from Sri Lanka by Blake and Smith (1913); the mineral was called zirkelite by them. Three of our samples are similar to the thorium-rich variety described by Blake and Smith (1913). The Th/U ratio of these samples is 11 to 12. The sample S13-12 is high in U and low in Th, although the Th/U ratio is not as low as that of Blake and Smith's sample VI. Zirconolite is found as a residual mineral in the gem gravels in Sri Lanka. The source rock has not been identified. The variability of Th/U in our zirconolite samples suggests that there are at least two original source rocks for Sri Lanka zirconolite which is now found in the gravels.

Lead in the analysed zirconolite and perovskite samples is partly due to that produced by in situ decay of U and Th in the minerals, and partly due to Pb incorporated into the mineral at the time of crystallization. The latter component is usually referred to as common lead. The content of ^{204}Pb in each sample is used as the measure of common lead. All samples except the leucite have low amounts of common lead. Where common lead is small relative to radiogenic lead, it is possible to correct for its presence and to calculate three ages for the samples using the U/Pb systematics (corrections were made using Stacey and Kramers

(1975) model Pb appropriate to the age of the samples). If the three ages agree, the mineral is said to be concordant; if they disagree the mineral is discordant. A concordant mineral has remained a closed system with respect to U and Pb since crystallization. If the mineral is discordant, it is possible to calculate the degree to which it has been an open system.

Table 4 summarizes the U/Pb and Pb/Pb ages for our samples. The perovskite samples from Lake Baikal contain approximately 10 ppm of common Pb. Since the samples are relatively young, the common lead correction applied to the abundance of ^{207}Pb is rather large. This causes a large uncertainty in the $^{207}\text{Pb}/^{235}\text{U}$ age for these samples. (The uncertainty has been taken as 50% of the ^{207}Pb correction). The $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages are concordant within the uncertainty of the analyses. If the slight apparent difference in ages is interpreted as recent loss of Pb from the samples, the maximum amount of Pb loss would be 7.8%, and the true age of the perovskites would be 501 m.y.

The carbonatite and jacupirangite at Jacupiranga were dated earlier by Amaral et al. (1967). Their results, when adjusted for a revision in the ^{40}K decay constant subsequent to their report, gave a preferred age for the locality of 136 m.y. The lead analyses on two single crystals of zirconolite extracted from fresh rock material give $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages which are in good agreement with each other and with the K/A age. The samples are too young to allow calculation of a meaningful $^{207}\text{Pb}/^{206}\text{Pb}$ age.

The sample of Jacupiranga zirconolite extracted from weathered rock gives significantly younger U/Pb ages than those obtained on fresh material. The three data points are plotted on a concordia diagram in Figure 3. All three samples plot on the concordia

curve; however, because of the young age of the samples, recent loss of Pb from the samples will not displace the data point from the curve. It is most reasonable to assume that all three zirconolites are the same age, and that the weathered sample has lost a small amount of Pb. In this case, zirconolite 13-19 would have lost 1% of its original lead. This is not unreasonable, considering the extremely altered condition of the rock from which the zirconolite was extracted.

The isotopic data suggest that another reason may exist for part of the discordance in 13-19. The measured $^{207}\text{Pb}/^{206}\text{Pb}$ for the sample is low compared to the fresh zirconolites from Jacupiranga (see above). This implies a common Pb component which is quite different from the usual. It is highly unlikely that a zirconolite crystal could increase its ^{204}Pb content by as much as 1% to only 10% of its radiogenic Pb. It seems more likely that a minor phase which is associated with the zirconolite has lost its radiogenic Pb and at the same time picked up common Pb. This phase could be tavorite ($\text{Ca}_2\text{Zr}_2\text{O}_7$) or zirconite ($\text{CaZr}_2\text{Si}_2\text{O}_9$), both of which occur as intergrowths with zirconolite at Jacupiranga (Sinclair, personal communication).

The Norwegian polyignite (zirconolite) samples give 1 Pb and 11/Pb ages which are concordant and show that the two samples are the same age. The Kola Peninsula and Russian A zirconolites are also completely concordant. These four samples have remained closed systems with respect to U and Pb since their crystallization.

Ages for samples from Sri Lanka show excellent agreement between U/Pb and Pb/Pb ages for four of the samples. The three thorium-rich zirconolites give a pooled age of 556 ± 1 m.y. The uranium-rich sample SL3/12 has slightly younger concordant ages. Sample SL5/14 is a fine grained intergrowth of zirconolite, ilmenite

and baddeleyite (ZrO_2). The U content as measured by isotope dilution is less than half that obtained by electron microprobe analysis of a pure ZrO₂ zirconolite grain. This suggests that somewhat less than 50% of the material dissolved for isotopic analysis was zirconolite proper.

The data for all five Sri Lanka zirconolites are plotted in Figure 4. In Figure 5, the data are shown on a highly expanded scale. Four of the five samples are completely concordant, showing that these minerals have been closed systems to U and Pb since their formation. A tie-line drawn between SL3-12 and SL4-14 passes exactly through the origin. This suggests that both high U zirconolites are 55% m.y. old, but that SL4-14 has recently lost a small fraction of its Pb. On this model, the amount of Pb lost could be 9%. As was the case for the slightly U-enriched Sri Lankan sample, SL4-14 shows an abnormally low $^{206}\text{Pb}/^{238}\text{U}$ ratio. The sample contains 4 times as much common Pb as SL3-12. The relatively high common Pb, combined with the polyphase nature of the sample suggests that some of the discordance may be due to an undetected phase associated with the zirconolite.

The lead isotopic data clearly show that most natural zirconolite samples remain closed systems with respect to U and its decay products despite in situ radiation damage to the crystal lattice. Only two samples show slight loss of Pb, and in both cases the high common Pb component suggests the possibility of the presence of a second mineral phase in the sample analysed. The zirconolites are remarkably good at retaining U, Th and Pb when compared to zircons or other minerals which are generally used in isotopic dating. Other evidence on the tight nature of the zirconolite lattice was given by Blake and Smith (1979) in their work on Sri

Linka zirconolites. They measured the helium content of Th-rich zirconolite and found 1.0 cc of He (0°C , 760 mm) per gm of zirconolite. This corresponds to 36% of the total He produced over the life of the zirconolite sample. This retention of helium is remarkable in view of the ease with which helium diffuses through most minerals and glasses.

It has been expressed in several quarters that the incorporation of U, Th and Pu into waste forms might be compromised by the effects of radiation damage on its constituent minerals. The radiation damage caused is effectively dissipated through the diffusion of fission products out of the crystal lattice. The retention of fission products in crystal lattices is shown experimentally to be related to the structure present in zirconolite and perovskite phases.

These studies have shown that zirconolite contains sites to accommodate a remarkable capacity to immobilize U, Th and their decay products even when the mineral is completely retained. The zirconolites from Sri Lanka are completely retained, yet they have retained a residual system to U, Th and Pb for 5×10^5 yr. The radiation dose received by these zirconolites is 6 to 8 times higher than that which zirconolites in SINCOR containing high level waste will receive. Our data on perovskite are limited and more work remains to be done. However, the limited data available indicates that perovskite will be sufficiently stable under radiation to be a satisfactory host for high level waste elements. Strong arguments can be made that a storage period of 10^5 yr will be sufficient for the decay of radwaste to safe levels. The perovskites from Lake Baikal have SYNGR ages of 1 to 2×10^5 yr. The total radiation dose to achieve a HLW storage age of 10^5 yr is only double that found in the Baikal perovskites.

The natural zirconolites and perovskites studied here have experienced complex geological histories, including elevated temperatures and pressures, contact with groundwaters, weathering, and erosion over periods hundreds or even thousands of times longer than are needed for decay of high level waste to safe levels. They have been subjected to a range of geochronological stresses, far more intense than are likely to be found in any geological waste repository. Despite this they have retained their waste elements (alpha emitters) quantitatively. These observations provide the strongest grounds for confidence that the integrity and safety of SYNROC as a waste-form will not be adversely affected by radiation damage before the high level wastes have decayed to safe levels. The kind of evidence which we have described is important in another context. It provides a means of demonstrating to the general public in a readily understandable way that safe immobilization of radioactive waste elements over periods which are enormously long in comparison with human experience can indeed be achieved. This factor is likely to exert a strong influence on public acceptability of the feasibility of waste disposal. It should be noted that borosilicate glass waste forms, preferred by the nuclear power establishment, are intrinsically incapable of providing this kind of reassurance.

Acknowledgements

We wish to record our appreciation of the persons and institutions who made it possible to obtain the samples of rare minerals used in this investigation. In this respect, we are particularly indebted to Jörg Keller, Gene Kaula, Carl Francis, Brian Mason, Arne Röhlein, Andrew Graham, Andrew Clark, Geraldo

Melcher, Salvador Tarabay, Monica Cassola, T.R. Cuttillan, H.D.N. Pathirana, and to the British Museum (Natural History), the Smithsonian Institution, Harvard University, Mineralogische und Geologisches Museum (Oslo), University of Freiburg, Serrana S/A de Mineralos, Sri Lanka Geological Survey, and the USSR Academy of Sciences. We are also indebted to Professor J.F. Lovering and Mr. D. Wark of the Department of Geology, Melbourne University, for permission to quote from unpublished results. The researches described in this paper were supported by grants provided by the National Energy Research Development and Demonstration Program of the Commonwealth Department of National Development and by the Australian Atomic Energy Commission. This support is gratefully acknowledged.

Table 1. Chemical analyses ZIRCONOLITES

	Stavern	Larvik	Jacupiranga	Kamsian A	Yola	Falun (3)	Sri Lanka (S10-5)	Sri Lanka (S1-99)	Sri Lanka (S2-90)	Sri Lanka (S14-170)	Sri Lanka (S14-15)
Nb_2O_5	15.10	8.05	11.3	7.6	21.5	7.7	3.7	7.6	7.5	29.7	0.8
Ta_2O_5	1.15	0.69	0.2	<0.1	<0.1	7.2	—	—	—	<0.1	<0.1
TiO_2	18.44	27.00	24.3	35.4	18.0	27.9	28.0	23.3	27.0	35.5	32.6
ZrO_2	29.52	31.40	35.2	36.5	31.7	31.5	29.4	30.9	29.3	35.6	36.1
ThO_2	3.98	4.11	7.4	1.2	3.6	5.0	7.5	7.15	21.8	0.9	2.2
UO_2	1.04	1.27	0.5	0.5	4.8	1.8	2.3	2.1	1.7	4.6	10.5
FeO	7.99	6.88	7.2	5.0	7.4	7.8	5.0	2.1	3.0	3.4	4.0
NaO	0.70	0.43	0.2	<0.1	0.3	0.4	—	—	0.7	0.2	<0.1
MgO	—	—	0.4	—	0.3	0.3	2.1	2.4	2.5	0.6	0.4
CaO	7.82	9.15	11.5	15.1	10.8	12.1	6.1	7.9	7.7	12.1	10.2
Y + REE	12.95	9.34	2.6	1.9	2.1	0.9	—	—	—	—	n.d.

Data for Stavern and Larvik supplied by A. J. Baker.

Data for other samples are electron microprobe analyses (R. J. Waring, unpubl.).

Table - Chemical Analyses P.M. 73-1158

	Elemental Analysis	Calcd
NO ₂	6.1	6.4
H ₂ O	1.1	0.1
Cl	44.1	44.1
Br	1.1	1.1
S	0.1	0.1
P	0.1	0.1
Na	1.1	1.1
K	1.1	1.1
Ca	1.1	1.1
Mg	1.1	1.1
Fe	1.1	1.1
Al	1.1	1.1
Si	1.1	1.1
T - other	1.1	1.1

Chemical analysis : Not done. (p. 11)

Table 3. Pb, U concentrations and Pb isotopic compositions.

Locality	Mineral	Pb (ppm)	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸	Pb ²⁰⁶ /Pb ²⁰⁷	Pb ²⁰⁶ /Pb ²⁰⁸
Lake Baikal	Perevskite A	116	0.115	0.005	0.0008	0.008817	174
	B	128	0.155	0.005	0.0006	0.007900	650
Levozero	Loparite	189	0.005	0.02	0.0002	0.0097	21.79
Stavern	Polymignite*	778	0.96	2.7	0.0134	0.00375	1691
Larvik	Polymignite*	863	1.04	3.1	0.01717	0.00600	1650
Jacupiranga	ZA-JM2-1	384	0.454	5.1	0.0078	0.0055	1810
	ZB-JM2-2	442	0.548	5.1	0.0041	0.00517	1360
	ZC-J2-19	524	0.496	7.5	0.0018	0.00578	720
Russian A	Zirconolite	872	0.552	1.7	0.00387	0.00620	18,000
Kola	Zirconolite	2829	4.186	3.2	0.0001	0.00505	12,650
Sri Lanka	Z1-BM1905	5992	1.699	12.4	0.0003	0.00029	8870
	Z2-B20-92	5557	1.552	12.3	0.0009	0.00010	11,800
	Z3-B1800	5557	1.431	12.5	0.0008	0.00012	7200
	Z5-SL4-12	3775	4.06	0.36	0.000007	0.00010	3811
	Z5-SL4-14	3007	3.00	0.35	0.000018	0.00010	884

154

*X-ray diffraction studies show that this mineral is structurally similar to, and may be identical with zirconolite.

Table 4. U/Pb and Pb/Pb ages.

Sample	Ages (m.y.)		
	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{207}\text{Pb}/^{206}\text{Pb}$
Barkal A	464 $\pm$ 2	472 $\pm$ 19	539 $\pm$ 69
B	461 $\pm$ 3	469 $\pm$ 19	508 $\pm$ 46
St. Gern.	296 $\pm$ 2	297 $\pm$ 3	299 $\pm$ 20
Larvik	294 $\pm$ 2	292 $\pm$ 3	272 $\pm$ 22
Gasparan A	133.5 $\pm$ 1.5	130 $\pm$ 5	-
B	128.5 $\pm$ 1.5	123 $\pm$ 5	-
C	115 $\pm$ 2	113 $\pm$ 6	-
Kibulau A	646 $\pm$ 2	643 $\pm$ 2	654 $\pm$ 7
Pala	376 $\pm$ 1	377 $\pm$ 1	379 $\pm$ 3
Orl. Links 01	555 $\pm$ 2	555 $\pm$ 2	551 $\pm$ 2
02	559 $\pm$ 2	560 $\pm$ 2	545 $\pm$ 3
03	555 $\pm$ 2	554 $\pm$ 2	552 $\pm$ 7
24	546 $\pm$ 1	546 $\pm$ 1	543 $\pm$ 3
25	494	503	502 $\pm$ 14

Figure Captions

- Figure 1. Total α dose vs. age for SYNROC samples between 10^3 and 10^6 yr. Natural samples with equivalent doses are shown by arrows.
- Figure 2. Total α dose vs. age for SYNROC samples between 10^6 and 10^8 yr. Natural samples with equivalent doses are shown by arrows.
- Figure 3. Pb isotopic data for Jacupiranga, Brazil zirconolites plotted on the concordia diagram.
- Figure 4. Pb isotopic data for Sri Lanka zirconolites plotted on the concordia diagram. Solid points are high Th samples; crosses are high U samples.
- Figure 5. Expanded scale plot of Sri Lanka zirconolite data. The 95% confidence limits are given by the size of the symbols.

References

- Amaral, J., Kusnee, J., Cordani, U.G., Kawashita, K. and Reynolds, J.H. (1967) Potassium-argon ages of alkaline rocks from southern Brazil. *Geochim. Cosmochim. Acta* 31, 117-122.
- Fiske, C.C. and Smith, G.V.H. (1913) On varieties of zirkolite from Ceylon. *Mineral. Mag.* 19, 309-316.
- Lampitt, L.H. (1977) A study of Macro-rhythmic layering and cumulative processes in the Jamberlana intrusion, Western Australia. Part 1: The Upper Layered Series. *J. Petrol.* 18, 217-219.
- Olsen, L.L. (1977) High-level radioactive waste from light water reactors. *Rev. Mod. Phys.* 49, 1-23.
- Leitch, J. and Prior, G.T. (1991) Lewisite and zirkolite, two new Canadian minerals. *Mineral. Mag.* 55, 1-10.
- Kozlov, L.I., Mikhailovskaya, A.B. and Danilevich, S.I. (1966) The age of the alkaline intrusions of the Chibinka and Lavrentyevskaya (Kola Peninsula). *Dokl. Akad. Nauk. SSSR* (Earth Sciences Trans.) 135, 31-33.
- Krogh, T.E. (1973) A low-contamination method for heat-thermal decomposition of zircon and extraction of U and Th for isotopic age determinations. *Geochim. Cosmochim. Acta* 37, 485-494.
- Pudovkina, Z.V. and Pyatenko, Yu.A. (1966) Zirconolite and its crystallographic features. *Tr. Mineral. Mest., Akad. Nauk. SSSR* 17, 124-133 (in Russian).
- Sinclair, W. and Ringwood, A.E. The effect of nuclear radiation on the structure of zirconolite and perovskite, in preparation.

- Stacey, J.S. and Krarers, J.D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* 26, 207-221.
- Turek, A. (1969) Rubidium-strontium isotopic studies in the Palparlie-Norseman area, Western Australia. Aust. Natl. Univ., Ph.D. thesis.
- Von Kobermann, H. (1968) The chemistry and optical properties of some minerals of the Alnö alkaline rocks. *Arkiv Mineral. Geol.* 5, 94-156.
- Williams, J.T. (1970) Uranium-enriched minerals in metastasis areas of the Ihua Layered Pluton, *Contrib. Mineral. Petrol.* 29, 20-39.

FIGURE 1

α Dose vs SYNROC Age
for Zirconolite & Perovskite

FIGURE 2

FIGURE 3

FIGURE 4

Sri Lanka
Zirconolite

FIGURE 5