MINERALOGICAL MAGAZINE, APRIL 1985, VOL. 49, PP. 195–201

Hydrothermal crystallization of a radioactive waste storage glass

DAVID SAVAGE, JANE E. ROBBINS*, AND RICHARD J. MERRIMAN

British Geological Survey, Nicker Hill, Keyworth, Nottinghamshire NG12 5GG

ABSTRACT. A borosilicate glass, containing 25 wt. % of simulated high-level radioactive waste has been reacted with water at 350 °C and 500 bars for 14 and 48 days using large-volume 'cold-seal' high-pressure equipment. Under these conditions the glass crystallizes a suite of mineral phases including: albite, $NaAlSi_3O_8$; aegirine, $NaFeSi_2O_6$; riebeckite, $Na_2Fe_2(Fe,Mg)_3Si_8O_{22}(OH)_2$; zektzerite, $LiNaZrSi_6O_{15}$; barium–strontium molybdate, $(Ba,Sr)MoO_4$; stillwellite, $(Nd,Ce,La)BSiO_5$; willemite, Zn_2SiO_4; smectite; a lithium–sodium borosilicate hydrate; melilite (åkermanite), $Ca_2MgSi_2O_7$. A description of the morphology of these phases is given, together with a number of chemical analyses. The implications of the incorporation of waste species in these mineral phases to the disposal of high-level radioactive waste is discussed.

KEYWORDS: radioactive waste, borosilicate glass, albite, aegirine, riebeckite, zektzerite, stillwellite, willemite, smectite, melilite.

THE only viable means by which the constituents of high-level radioactive waste (HLRW) may return to the biosphere from disposal in a deep geological repository is by groundwater dissolution of the wasteform coupled with subsequent solute transport (American Physical Society, 1978). Therefore, an essential component of the assessment of the geological disposal of HLRW is an understanding of the reaction of solid wasteforms with aqueous media. The importance of these studies is reflected in the vast volume of researches published in the literature over the last ten years. However, almost all these investigations have dealt with the kinetic breakdown of the solid wasteform and have usually involved the determination of a time-dependent 'leach-rate' function. Only comparatively recently has it been recognized that this type of study is inappropriate for providing data to model radionuclide release from the canister zone on the timescale of 10^3 yrs. (e.g. Neretnieks, 1982).

Instead, attention has now been focused on the determination of waste component 'solubilities', or more correctly, steady-state fluid concentrations, under site specific conditions of temperature, pressure, and groundwater chemistry (Savage and Robbins, 1982, Apted and Myers, 1982). This reorientation has taken place through recognition of the fact that groundwater availability and flow-rate are the dominant factors in governing wasteform dissolution and radionuclide release (Chapman *et al.*, 1980, 1982; Burns *et al.*, 1982). Under low-flow conditions, saturation of waste components in the fluid phase is achieved rapidly (less than 10 days at 100 °C). Steady-state concentrations (solubility may only correctly be applied to systems under true thermodynamic equilibrium, which will not be the case for systems containing metastable solids such as glass) will reflect the 'solubility' of the wasteform if the rate of dissolution of the wasteform is rapid (e.g. glass) compared with nucleation and growth of more stable alteration phases (Dibble and Tiller, 1981*a*, *b*). If the opposite situation is true, then concentrations will mirror alteration phase solubilities (e.g. Grambow, 1982). These metastable steady-states are effectively time-invariant (in the timescale under consideration) and represent the most suitable means by which to predict radionuclide release rates in the long term.

In order to be able to understand and interpret pseudo-equilibrium wasteform studies, it is desirable to carry out a thorough investigation of the fluid phase with respect to speciation and the saturation states of possible alteration phases, along with examination of the solid residues for identification of solid products. At high temperatures (> 250 °C) these alteration products take the form of a suite of exotic mineral phases. This communication describes the results of some simple borosilicate glass–water experiments at 350 °C aimed at synthesizing these mineral phase alteration products, and supersedes previous brief outlines of this work (Savage and Chapman, 1980, 1982; Savage, 1981). These experiments were carried out in order to help elucidate hydrothermal alteration taking place in more complex rock–waste–water systems in the temperature range

---

* British Geological Survey, Geological Museum, Exhibition Road, South Kensington, London SW7 2DE.

100–350 °C, described elsewhere (Savage and Chapman, in prep.).

Experimental

Starting materials used in the experiments were a UK reference simulated borosilicate waste glass (209/M22) and de-ionized water. The chemical composition of the glass is given in Table I. The glass contains approximately 25 wt. % simulated fission product oxides and 0.06 wt. % U_3O_8. Silica content is approximately 50 wt. % and the molecular SiO_2/B_2O_3 ratio is roughly 5 : 1. Although the glass is theoretically Ca-free, in practice this is not the case since the reagent grade chemicals used to synthesize the glass contain Ca (and also K) as a trace impurity.

TABLE I. Chemical composition (wt.percent) of glass 209/M22

SiO_2	50.9	Pr_6O_{11}	0.4
B_2O_3	11.1	Nd_2O_3	1.8
Al_2O_3	5.1	CeO_2	1.0
Li_2O	4.0	ZrO_2	1.4
Na_2O	8.3	PO_4	0.2
Rb_2O	0.1	Cr_2O_3	0.6
Cs_2O	0.8	MoO_3	1.8
MgO	6.3	Fe_2O_3	2.7
SrO	0.3	RuO_2	0.7
BaO	0.4	NiO	0.4
Y_2O_3	0.2	PdO	0.4
La_2O_3	0.4	ZnO	0.4
U_3O_8	0.1	SO_4	0.1

The glass in monolithic form (cubes of side length 3 mm) was sealed in noble metal capsules together with de-ionized water in a 1 : 1 mass ratio such that water entirely covered the glass. Capsules were placed in externally heated, argon pressurised vessels and heated at 350 °C with a total confining pressure of 50 MPa for 14 and 48 days. Experiments were terminated with a compressed air quench, the capsules cut open, and the solids air-dried at 105 °C.

Analytical

The extracted solids were examined using conventional light microscopy, X-ray diffraction and scanning electron microscopy. Chemical analyses were performed on polished mineral grains mounted in 'Araldite' resin using a Cambridge Instruments Stereoscan S250 scanning electron microscope fitted with a Link Systems Si(Li) energy-dispersive detector and multi-channel analyser. An accelerating voltage of 20 kV and a specimen current of 2.4×10^{-8} A (on cobalt) were used, together with a selection of mineral and pure element standards. Count times were 100 'live' seconds.

Results

The waste glass breaks down and crystallizes a suite of more than ten distinct mineral phases very rapidly. Previous experiments (Savage and Chapman, 1980) have shown this to take place after only two days reaction. No recognizable glass remained after run durations of this length. Characteristically, the original translucent dark green–black glass is transformed into a granular, grey–blue, clay-like material, while the upper portions of the noble metal capsules are usually lined with a fine white or pale green precipitate, which is interpreted as quench material. Mineral phases commonly form complex intergrowths and appear to be dispersed randomly throughout the solid residue. Positively identified mineral phases are listed in Table II. No significant changes in mineral assemblages occurred between 14 and 48 day treatments. Most of the fluid phase was consumed during the experiments and, therefore, chemical analysis of this phase was impractical. However, a series of experiments in the temperature range 100–350 °C involving granite, glass, and water have been carried out to investigate specifically the chemical composition of the fluid phase and the results of these experiments will be reported elsewhere (Savage and Chapman, in prep.).

Table II. Mineral phases synthesised from glass 209/M22 - water experiments at 350°C, 500 bars

Mineral	Identification	
	XRD	SEM
Albite, $NaAlSi_3O_8$	x	x
Aegirine, $NaFeSi_2O_6$	x	x
Riebeckite, $Na_2Fe_2(Fe,Mg)_3Si_8O_{22}(OH)_2$	x	x
Akermanite, $Ca_2MgSi_2O_7$	x	x
Zektzerite, $LiNaZrSi_6O_{15}$	x	x
Ba-Sr Molybdate, $(Ba,Sr)MoO_4$	x	x
Stillwellite, $(Nd,Ce,La)BSiO_5$	x	x
Willemite, Zn_2SiO_4		x
Smectite	x	x
Silica		x
Lithium-sodium borosilicate hydrate	x	x

Albite. This predominantly occurs as quench material, and typically forms intergrowths with aegirine. Crystals are euhedral and tabular, being of the order of 10–50 μm in size (fig. 1*a*). The chemical composition is almost pure albite (Table III), since both Ca and K are below detection limits. Because of the relatively low Al content of the glass (5 wt. %)

Table III. Microprobe analyses of albite, aegirine and riebeckite

	Albite (6)	Aegirine (7)	Riebeckite (6)
SiO_2	69.58	53.01	54.01
ZrO_2	n.d.	0.75	0.64
Al_2O_3	16.87	0.79	0.84
Fe_2O_3*	0.97	29.14	22.25
Cr_2O_3	0.28	0.30	0.94
MgO	-	1.62	4.76
ZnO	n.d.	0.57	1.07
CaO	-	0.66	0.23
Na_2O	12.02	11.83	9.96
Total	99.72	98.67	94.70
Numbers of ions on the basis of:-			
	32 O	6 O	23 O
Si	12.188	1.984	7.166
Zr	-	0.014	0.041
Al	3.482	0.035	0.132
Fe	0.128	0.821	2.222
Cr	0.038	0.009	0.099
Mg	-	0.090	0.941
Zn	-	0.016	0.104
Ca	-	0.027	0.033
Na	4.081	0.856	2.562
Total	19.917	3.852	13.300

*Total iron calculated as Fe_2O_3.

- not detected.

n.d. not determined.

Numbers in parentheses after each mineral indicate the number of spots included in each analysis.

small amounts of Fe_2O_3 and Cr_2O_3 are present in tetrahedral sites. Albite is a common hydrothermal mineral in both natural and synthetic systems, but its recorded occurrence as an alteration product of hydrothermal dissolution of radioactive waste glasses is rare. Sasaki *et al.* (1982) have reported the presence of oligoclase after the hydrothermal degradation of a borosilicate waste glass containing 3.5 wt. % Al_2O_3 at 300 °C. Although such feldspars have the potential of incorporating radiologically significant nuclides, such as ^{90}Sr and ^{226}Ra, the alkaline-earth elements are preferentially incorporated into other phases (see below).

Aegirine. This mainly occurs as quench material, where it forms fine laths and blades (fig. 1*a*). The typical greenish colouration of the quench material is believed to be due to the presence of finely intergrown aegirine. The chemical composition of the synthesized aegirine (Table III) shows it to contain trace amounts of Zr, Cr, and Zn but incorporation of Ca and Mg is minimal. Aegirine (together with riebeckite) is a common constituent of alkaline igneous rocks and also occurs in regionally metamorphosed schists, hydrothermal veins, and in diagenetic environments. Kempe and Deer (1970) analysed aegirines from the Kangerdlugssuaq alkaline intrusion in E. Greenland which contained up to 0.65 wt. % ZrO_2. Aegirine has been synthesized hydrothermally as a by-product of quartz-growing at temperatures of 250° to 350 °C at pressures between 400 and 1000 bars in silica saturated Na-CO_2-H_2O solutions (Nosyrev *et al.*, 1969). Aegirine is stable at room temperature under the approporiate environmental conditions as evidenced by its occurrence, together with riebeckite, as an authigenic mineral in the Green River Formation sediments of Colorado, Wyoming, and Utah (Milton and Eugster, 1959). Aegirine has been reported as an alteration product during the dissolution of simulated borosilicate waste glass at 300 °C and 300 bars by McCarthy *et al.* (1978) and by Sasaki *et al.* (1982), although neither of these authors presented compositional data on the pyroxenes.

Riebeckite. This phase occurs as a product of glass dissolution only when run lengths exceed 5–10 days and is then present as aggregates of green stubby prisms (fig. 1*b*) or as yellowish asbestiform growths up to 1–2 mm across. It is commonly intergrown with acicular laths of aegirine. A chemical analysis of the synthesised riebeckite (Table III) shows incorporation of trace amounts of Zr, Cr, and Zn. The Mg/(Mg+Fe) atomic ratio is less than 0.5, which is compatible with riebeckite, using the nomenclature of Leake (1978). Ca, Al, and K contents of the amphibole are minor, which reflect the composition of the original glass. Like aegirine, riebeckite is a common constituent of alkaline igneous rocks, hydrothermal mineral veins particularly those associated with fenitized rocks, low-grade schists, and diagenetic sedimentary environments. Riebeckite has not previously been identified as a product of the interaction of radioactive waste glass and water by other workers in this field.

Zektzerite. This is an abundant phase, forming white orbicular aggregates up to 1–2 mm in diameter (fig. 1*c*). A partial chemical analysis of this phase has been presented elsewhere (Savage, 1981; Savage and Chapman, 1982), which revealed the zektzerite to contain up to 20 wt. % ZrO_2 (as compared with 1.4 wt. % in the original glass) and 0.7 wt. % U_3O_8 (0.1 wt. % in the original glass). Zektzerite was first identified in miarolitic cavities of the Golden Horn granitic batholith of Washington, USA, where it is associated with quartz, microcline, riebeckite, zircon, astrophyllite, elpidite, and acmite (aegirine) (Dunn *et al.*, 1977). Its structure has been investigated by Ghose and Wan (1978) and Marr and Glasser (1979), whose studies revealed that zektzerite contains a six-repeat unit double chain silicate anion ('sechserdoppelkette') and that a wide variety of cation substitutions is

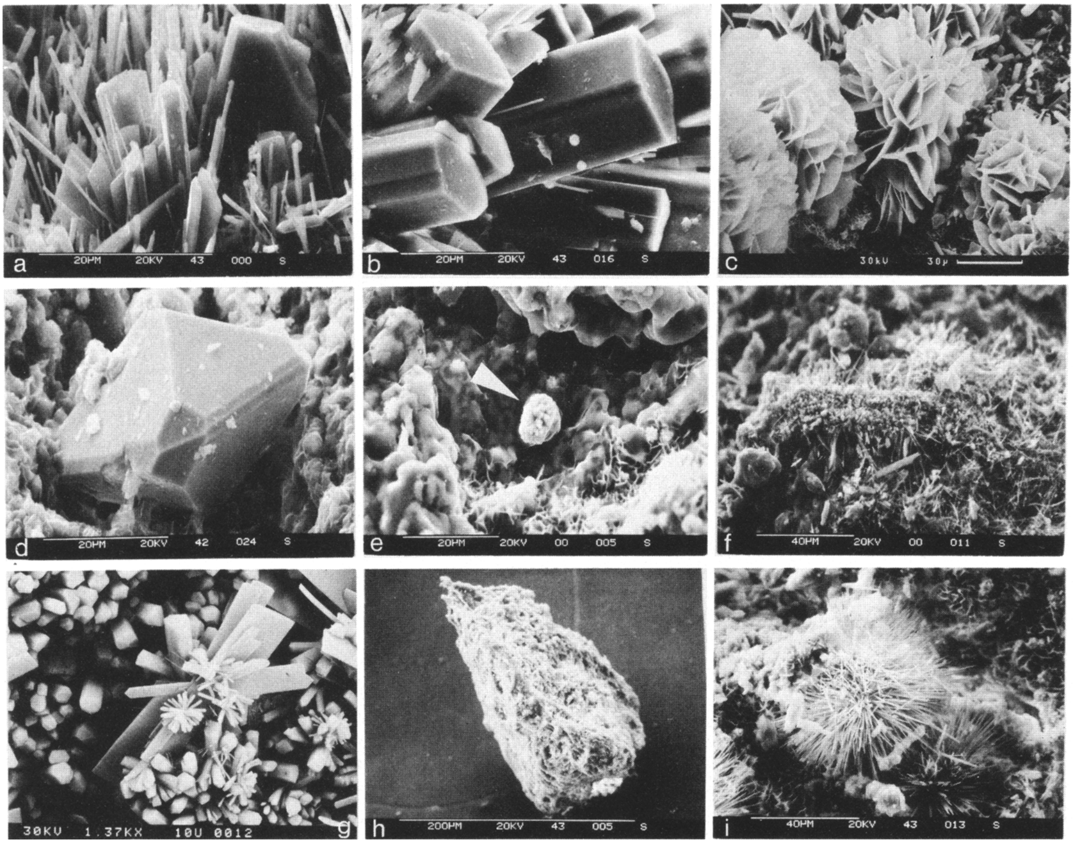

FIG. 1, *a–i*. Scanning electron photomicrographs of mineral phases synthesized at 350 °C, 500 bars. (*a*) Tabular prisms of albite (centre, right) and laths of aegirine. (*b*) Riebeckite prisms. (*c*) Orbicular aggregates of zektzerite. (*d*) Ba–Sr molybdate. (*e*) Stillwellite (arrowed). (*f*) Swathe of willemite laths. (*g*) Blades and flowery aggregates of sodium–lithium borosilicate hydrate (centre) and riebeckite prisms (left). (*h*) Melilite. (*i*) Silica needles on a smectite substrate.

possible. Thus zektzerite, $LiNaZrSi_6O_{15}$ is isostructrual with tuhualite, $(Na,K)_2Fe_4Si_{12}O_{30}$ (Merlino, 1969), emeleusite, $Na_2LiFeSi_6O_{15}$ (Upton *et al.*, 1978), $Li_2ZrSi_6O_{15}$ (Quintana and West, 1981), and a series of phases of the general formula $LiNa_2M^{3+}Si_6O_{15}$, where M^{3+} = Fe,Cr, Sc,In,Y,(Yb + Lu),Er,Ho,Dy,Gd,Sm (Marr and Glasser, 1979). Therefore, there is considerable scope for the incorporation of a number of cations of radiological significance in the zektzerite structure, although the mineral synthesized in these experiments only included trace amounts of Zn, Mo, and U (Savage, 1981; Savage and Chapman, 1982). Zektzerite has not been identified by other workers investigating waste-glass–water interactions, although emeleusite $(Li_2Na_4Fe_2Si_{12}O_{30})$ has been tentatively identified as a product of waste-glass–granodiorite–water interactions at 350 °C (Savage and Chapman, in prep.)

Ba–Sr molybdate. This is an abundant phase, forming bright yellow, euhedral tetragonal crystals up to 100 μm in size (fig. 1*d*). The chemical composition is presented in Table IV. The molybdate showed a preferential incorporation of Ba relative to Sr, consisting of roughly 90 mol. % of $BaMoO_4$, 10 mol. % of $SrMoO_4$ and the $CaMoO_4$ (powellite) component being below detection limits under the analytical conditions employed. This contrasts sharply with the starting glass composition which has approximately equimolar contents of SrO and BaO, suggesting preferential incorporation of Sr into another phase (solid or fluid). The molybdate also shows a pronounced concentration of Ba and Sr compared with the original glass. Thus the mineral contains approximately 46 and 3.5 wt. % of BaO and SrO respectively, as compared with 0.4 and 0.3 wt. % of these components in the glass. Ba–Sr molybdates are isostructural with scheelite

Table IV. Electron microprobe analysis of Ba-Sr molybdate (average of 6 spots)

BaO	46.25
SrO	3.54
CaO	-
MoO_3	49.54
Total	99.73
Numbers of ions on the basis of 4 oxygens	
Ba	0.869
Sr	0.098
Ca	-
Mo	0.999
Total	1.966

($CaWO_4$) and powellite, which have structures derived from the tetragonal-I zircon structure (Haaker and Ewing, 1981). Ba-Sr molybdate has not been found in the geological environment, although scheelite and powellite occur in contact-metasomatic rocks, hydrothermal veins, and pegmatites, together with quartz, calcite, beryl, and fluorite (Hsu and Galli, 1973). Depositional temperatures of these rocks are in the range 100-500 °C (Haaker and Ewing, 1981). A Ca-Ba-Sr molybdate solid solution is one of nine crystalline phases constituting 'supercalcine ceramic', which is a proposed encapsulating medium for high-level radioactive waste. The phase relations of this solid solution have been investigated by Scheetz *et al.* (1982). Powellite has been observed as a solid product of hydrothermal interactions of a simulated borosilicate high-level waste glass, shale, and water at 400 °C by Freeborn *et al.* (1980). Chapman *et al.* (1981) noted the potential incorporation of ^{226}Ra in this solid solution.

Stillwellite. This is a relatively rare phase amongst the mineral products, and forms small (< 10 microns) crystals showing poor development of crystal faces (fig. 1*e*). Only qualitative X-ray analytical data are available for the phase, which showed concentrations of La, Nd, and Ce, in roughly the proportions contained within the initial glass. Stillwellite was first identified by McAndrew and Scott (1955) from the uranium deposit at Mary Kathleen, Queensland, Australia where it occurs with allanite, garnet, and uraninite as a metasomatic replacement of metamorphosed calcareous sediments. It has since been reported as occurring in nepheline syenite pegmatite dykes with feldspar, nepheline, zircon, fluorite, aegirine, pyrophanite, and pyrochlore (Neumann *et al.*, 1966); in a magnetite ore (Klemic and Loferski, 1979); and has also been synthesized hydrothermally in the temperature range 150-500 °C by Nekrasov and Nekrasova (1972). Stillwellite has not previously been reported as a product of waste-glass dissolution experiments. Similar experiments at lower temperatures (100-200 °C) on glass 209/M22 carried out by the authors have failed to synthesize stillwellite crystals. However, because stillwellite contains approximately 60 wt. % of rare-earth element oxides (Gay, 1957) and also because of the many similarities in lanthanide and actinide element chemical behaviour, this phase could potentially be very important in limiting the solubility of such radiologically significant nuclides as ^{237}Np, ^{239}Pu, and ^{241}Am.

Willemite. This phase is relatively rare and has only been identified by scanning electron microscopy. It occurs in the solid residues as fine, fibrous crystals, up to 20 μm in length (fig. 1*f*). Qualitative X-ray spectra revealed Si and Zn peaks, without appreciable concentrations of other elements. The stoichiometric content of ZnO in willemite is approximately 60 wt. %, which compares with approximately 0.4 wt. % in the original glass. Willemite has been synthesized in previous waste-glass dissolution experiments, by amongst others, Shade (1982) at a temperature of 250 °C, and by Sasaki *et al.* (1982) at 300 °C. Natural occurrences of willemite include its presence as a pneumatolytic mineral in hydrothermal veins around pegmatitic intrusions at Franklin Furnace, New Jersey and as an alteration product of sphalerite in an albitite from the Ilimaussaq alkaline intrusion, S. Greenland (Metcalf-Johansen, 1977). In this latter occurrence, willemite is associated with (amongst others) albite, aegirine, arfvedsonite, and analcime and the intrusion is believed to have crystallized in the temperature range 400-600 °C at a pressure of approximately 500 bars. Willemite has also been synthesized hydrothermally from ZnO, quartz and HCl solution starting materials at temperatures of 400-500 °C at pressures of 400-1000 bars (Kodaira *et al.*, 1975).

Lithium-sodium borosilicate hydrate. This is the most abundant phase after smectite in the run products and forms glassy, transparent tabular crystals or broad, bladed crystals (fig. 1*g*). The X-ray powder diffraction data for this phase cannot be matched with those of any published mineral data, which suggests it is a new phase. A detailed chemical analysis of the borosilicate is presented in Savage (1981) and Savage and Chapman (1982), which shows it to consist of Li, Na, Si, B with a trace of Al, but with no significant contents of waste species. More detailed crystallographic and chemical studies of this phase are in progress.

Melilite. This forms anhedral, orange-brown crystals up to 200–300 microns in size (fig. 1*h*). Qualitative X-ray spectra and XRD data suggest this phase to be towards the åkermanite end of the melilite series. Åkermanitic melilites generally occur in contact metamorphosed limestones (e.g. Tilley and Harwood, 1931), meteorites (e.g. Fuchs, 1978) and occasionally, in regionally metamorphosed calc-silicate rocks (Valley and Essene, 1980). P–T conditions of åkermanite stability are approximately 700–1200 °C and $P < 9$ kbar (Yoder, 1973). The occurrence of åkermanite in the run products at a temperature of 350 °C is therefore problematical. In the CO_2-bearing system (dissolved CO_2 would inevitably have been present in the fluid phase during the course of these experiments) the pertinent reaction for åkermanite stability is:

$$\underset{\text{akermanite}}{Ca_2MgSi_2O_7} + CO_2 = \underset{\text{diopside}}{CaMg(SiO_3)_2} + \underset{\text{calcite}}{CaCO_3}.$$

From the available experimental work at 500 bars (Walter, 1963), the åkermanite stability field lies above 900 °C, diopside + calcite being stable at temperatures lower than this. However, there is no evidence of these latter phases in the run products. Helgeson *et al.* (1978) have questioned the reliability of Walter's data on the grounds of probable metastability of run products which may explain the unexpected occurrence of åkermanite in these experiments. Clearly, more experimental work is necessary in this area to clear up this discrepancy.

Smectite. This is by far the most abundant phase produced in the experiments, but is also probably the least well characterized because of its fine-grained nature. It typically occurs as a cellular honeycomb network and forms a substrate upon which other minerals crystallize (fig. 1*i*). Qualitative X-ray spectra indicated the presence of Na and Mg, and Na is the dominant interlayer cation which, together with its di-octahedral XRD powder pattern, suggest a composition towards the montmorillonite (s.s.) end of the montmorillonite-beidellite series. Smectite has been identified as an alteration product of glass 209/M22 at temperatures of 100–200 °C (Savage, 1981; Savage and Chapman, 1982) and in nature is an extremely common alteration product of volcanic glasses from room temperature through to 400 °C.

Silica. The aqueous solutions coexisting with the glass alteration assemblage at 350 °C are supersaturated with respect to quartz and amorphous silica (Savage and Chapman, in prep.). A considerable amount of silica precipitates from the fluid phase during the quenching of the pressure vessels from 350 °C to room temperature which manifests itself in the run products as aggregates of fine needles (fig. 1*i*). This material is X-ray amorphous, despite its crystalline appearance. The presence of this silica emphasizes the need for autoclave leach tests to be sampled at run temperature and pressure, rather than after a quench period, in order to monitor accurately the concentration of silica (and hence, glass breakdown) in the aqueous fluid phase.

Conclusions

The results of these experiments demonstrate that a borosilicate waste glass breaks down rapidly in the presence of an aqueous fluid phase at high temperature to produce a mineral assemblage characteristic of late-stage hydrothermal veins and pegmatites in granitic (s.l.) and alkaline igneous rocks. This mineral assemblage effectively acts as a 'secondary waste form', since most waste species are incorporated into mineral lattices. The effect of precipitation of these mineral phases is to limit the concentrations of various waste species in the co-existing fluid phase and also buffer fluid composition in the near-field. Indeed, many waste species exhibit *lower* steady-state fluid phase concentrations in glass dissolution experiments at 350 °C than at 100 °C as a direct result of mineral precipitation (Savage and Chapman, in prep.).

Although temperatures of 350 °C are now considered unlikely in most countries' disposal scenarios, maximum temperatures of 150–200° may be reached in deep geological repositories in the first few hundred years after disposal. It is highly likely that a large proportion of the minerals synthesized in these experiments at 350 °C in a few days would also crystallize at these lower temperatures over a longer timescale, and thus buffer waste component solubilities. The results presented in this communication have served to identify and characterize the mineral forms likely to be produced during waste glass breakdown. Further work is now necessary to help define stability fields and solubilities of these phases.

Acknowledgements. The authors would like to thank Chris Wheatley for preparing the polished mineral separates. This paper is published by permission of the Director, British Geological Survey (NERC).

REFERENCES

American Physical Society (1978) *Rev. Mod. Phys.* **50,** S1–186.

Apted, M. J., and Myers, J. (1982) *Comparison of the hydrothermal stability of simulated spent fuel and borosilicate glass in a basaltic environment.* Rockwell Hanford Operations Report RHO-BW-ST-38 P, 101 pp.

Burns, W. G., Hughes, A. E., Marples, J. A. C., Nelson, R. S., and Stoneham, A. M. (1982) *Nature,* **295,** 130–2.

Chapman, N. A., McKinley, I. G., and Savage, D. (1980) *Proc. NEA Workshop on Radionuclide Release Scenarios for Geologic Repositories*, Nucl. Energy Agency-Org. Econ. Coop. Dev., Paris, 91-103.

—————(1981) *Proc. NEA Workshop on Near-field Processes in Geologic Repositories for Radwaste*, Nucl. Energy Agency-Org. Econ. Coop. Dev., Paris, 83-90.

—————and West, J. M. (1982) In *Scientific Basis for Nuclear Waste Management*, **4** (S. V. Topp, ed.), North Holland, 347-54.

Dibble, W. E., and Tiller, W. A. (1981*a*) *Clays Clay Mineral.* **29**, 323-30.

———(1981*b*) *Geochim. Cosmochim. Acta*, **45**, 79-92.

Dunn, P. J., Rouse, R. C., Cannon, B., and Nelen, J. A. (1977) *Am. Mineral.* **62**, 416-20.

Freeborn, W. P., Zolensky, M., Scheetz, B. E., Komarneni, S., McCarthy, G. J., and White, W. B. (1980) *Hydrothermal interactions between calcine, glass, spent fuel and ceramic waste forms with representative shale repository rocks.* Topical Report No. 3, ONW1/SUB/78/E-512-005.

Fuchs, L. H. (1978) *Meteoritics*, **13**, 73-88.

Gay, P. (1957) *Mineral. Mag.* **31**, 455-68.

Ghose, S., and Wan, C. (1978) *Am. Mineral.* **63**, 304-10.

Grambow, B. (1982) In *Scientific Basis for Nuclear Waste Management*, **5** (W. Lutze, ed.), North Holland, 93-102.

Haaker, R. F., and Ewing, R. C. (1981) Ibid. **3** (J. G. Moore, ed.), Plenum Press, 299-306.

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K. (1978) *Am. J. Sci.* **278**-A, 1-229.

Hsu, L. C., and Galli, P. E. (1973) *Econ. Geol.* **68**, 681-96.

Kempe, D. R. C., and Deer, W. A. (1970) *Meddels. Grønland*, **190**, 3, 1-95.

Klemic, H., and Loferski, P. J. (1979) *U.S. Geol. Surv. Prof. Pap.* 1150, 8 pp.

Kodaira, K., Ito, S., and Matsushita, T. (1975) *J. Cryst. Growth*, **29**, 123-4.

Leake, B. E. (1978) *Am. Mineral.* **63**, 1023-52.

McAndrew, J., and Scott, T. R. (1955) *Nature*, **170**, 509-10.

McCarthy, G. J., White, W. B., Roy, R., Scheetz, B. E., Komarneni, S., Smith, D. K., and Roy, D. M. (1978) Ibid. **273**, 216-17.

Marr, J. M., and Glasser, F. P. (1979) *Mineral. Mag.* **43**, 171-3.

Merlino, S. (1969) *Science*, **166**, 1399-401.

Metcalf-Johansen, J. (1977) *Mineral. Mag.* **41**, 71-5.

Milton, C., and Eugster, H. P. (1959) In *Researches in Geochemistry*, **1**, (P. H. Abelson, ed.), John Wiley, 118-50.

Nekrasov, I. Y., and Nekrasova, R. A. (1972) *Dokl. Earth Sci. Sect.* **201**, 179-82.

Neretnieks, I. (1982) In *Scientific Basis for Nuclear Waste Management*, **5** (W. Lutze, ed.), North Holland, 559-68.

Neumann, H., Bergstol, S., and Nilssen, B. (1966) *Norsk Geol. Tidsskr.* **46**, 327-34.

Nosyrev, L. V., Shaposhnikov, A. A., Smirnov, A. A., Sipavina, L. V., and Khadzi, I. P. (1969) *Dokl. Earth Sci. Sect.* **187**, 109-12.

Quintana, P., and West, A. R. (1981) *Mineral. Mag.* **44**, 361-2.

Sasaki, N., Komarneni, S., and Roy, R. (1982) *Am. Ceram. Soc. Bull.* **62**, 649-55.

Savage, D. (1981) *Rep. Inst. Geol. Sci.* ENPU 81-8, London, 33 pp.

——and Chapman, N. A. (1980) Ibid. ENPU 80-12, 27 pp.

————(1982) In *Geochemistry of Radioactive Waste Disposal* (G. W. Bird and W. S. Fyfe, eds.) *Chem. Geol.* **36**, 59-86.

——and Robbins, J. E. (1982) In *Scientific Basis for Nuclear Waste Management*, **5** (W. Lutze, ed.), North Holland, 145-52.

Scheetz, B. E., Freeborn, W. P., Pepin, J., and White, W. B. (1982) Ibid. **4** (S. V. Topp, ed.), 155-62.

Shade, J. W. (1982) In *Geochemistry of Radioactive Waste Disposal* (G. W. Bird and W. S. Fyfe, eds.) *Chem. Geol.* **36**, 103-22.

Tilley, C. E., and Harwood, H. F. (1931) *Mineral. Mag.* **22**, 439-68.

Upton, B. G. J., Hill, P. G., Johnsen, O., and Petersen, O. V. (1978) Ibid. **42**, 31-4.

Valley, J. W., and Essene, E. J. (1980) *Contrib. Mineral. Petrol.* **74**, 143-52.

Walter, L. S. (1963) *Am. J. Sci.* **261**, 488-500.

Yoder, H. S. (1973) *Fortschr. Mineral.* **50**, 140-73.