Obsidian: a potential natural analogue for nuclear waste glass

Nishi Rani[1], J. P. Shrivastava[1,]* and R. K. Bajpai[2]

[1]Department of Geology, University of Delhi, Delhi 110 007, India
[2]BETDD, Nuclear Recycle Group, Bhabha Atomic Research Centre, Mumbai 400 008, India

For long-term performance assessment of obsidian, we present computation chemistry and experimental data sets on glass dissolution and associated ionic release obtained after treating specimens under near hydrothermal conditions (for 1–64 h time intervals). The EQ3/6 simulated results indicate appearance of quartz (chalcedony) and other mineral species. Besides quartz, SEM-EDX of the precipitate shows presence of smectite having two distinct microstructures which consist of small and large lamellae and their formation is linked with the release of Na, K and other ions accountable for increase in the pH and conductivity of the leachates. The former structure represents paragenesis of an earlier formed alteration product. These observations largely correspond to the simulated results, suggesting its suitability in geological repository.

Keywords: Geochemical codes, hydrothermal alterations, obsidian, microstructures, neo-formed minerals.

THE geological environment in which vitrified waste is possibly stored is complex and most of the natural processes are subjected to variations in the number of parameters including nature of fluids and climatic changes[1]. Basaltic glass is considered as one of the natural analogues for radioactive waste containment[2]. The influence of volcanic glass dissolution by natural processes cannot be overstated[3]. In Indian context, the shocked basaltic glass of Lonar Crater near Bombay (Figure 1 *a*) is believed to be a potential analogue for the nuclear waste glass[4] however, alteration study is yet to be carried out on this glass. More recently, Shrivastava *et al.*[5] reviewed corrosion mechanism in the borosilicate nuclear waste glass for long-term performance assessments in the geological repository, suggesting experiments under induced near hydrothermal conditions in the laboratory and simulation of the data using geochemical codes. The chemical composition of obsidian matches with that of the high silica radioactive waste glasses but its long-term leaching behaviour in the geological repository is yet to be understood.

Experiments alone are insufficient to predict glass alteration because they cannot be performed over the extended time periods of up to tens or thousands of years or over numerous sets of possible conditions of interest. Geochemical models for predicting glass dissolution rates, assuming that the surface reactions control dissolution rate and suggest that only the silica concentration of the solution affects the overall rate[6]. The elemental concentrations of obsidian and possible solid phases were modelled with the software package EQ3/6 (ref. 7), where parameters such as $\log Q/K$ or saturation index were simulated to understand alteration behaviour of obsidian glass. The initial solution composition including all species involved in further reactions was computed. Glass composition, temperature, pressure and pH conditions (such from 7 to 10 at 300°C) were considered in the assessment of experimental and simulated results. The mineral saturation ($\log Q/K$) and product of aqueous species involved in the dissolution reaction of dissolving solid were calculated, where Q is the activity and K is the equilibrium constant for the same solid values against time in years[8]. In Figure 2, reaction progress is plotted against saturation index ($\log Q/K$), indicating saturation with respect to solid phase. Understanding these calculations is required because many factors contribute to the nucleation and growth of secondary phases including kinetic constraints on precipitation[9]. Initially in the experimental results, Na was found to be released preferentially so that this simulation procedure can estimate the saturation indices for solid phases that contain Na. These simulations indicate that chalcedony and Ca–beidellite is formed between 7 and 10 pH at 300°C and 1260 psi.

To substantiate these results, present experiments were performed under accelerated conditions in a laboratory time framework on obsidian glass collected from Osham hill, located 23 km WNW of Junagadh town in Saurashtra, India (Figure 1 *b*). In this area, a circular outcrop is

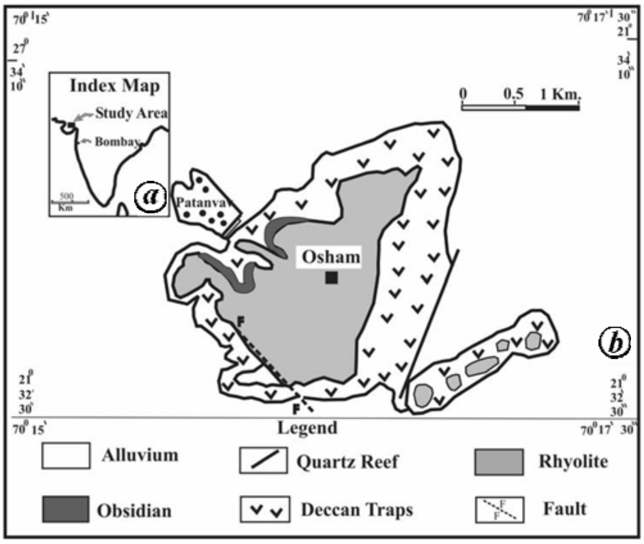

Figure 1. ***a***, Location map of the area; ***b***, Detailed geological map of the area around Osham hills, Saurashtra, Gujarat (modified after Maithani *et al.*[10]).

---

*For correspondence. (e-mail: jpshrivastava.du@gmail.com) exposed, covering approximately an area of 6 km^2, comprising rhyolite and obsidian lava flows (at the base of the hill), near the contact of the Deccan basaltic lava flows. The acid volcanic rocks occur in the central and southeastern parts of the hill, having 2–5 m thick obsidian lenses and consist of glass, spherulites and feldspars[10]. Fresh obsidian lenses were chipped out from the working quarry and considered for the present work. Obsidian glass is optically translucent, pitch black to dark brown in colour, shows vitreous lustre. It is often banded having conchoidal fractures (Figure 3 *a*). Unaltered glass chips were picked up for experiments. Major elemental compositions of obsidian test samples were determined by X-ray fluorescence (XRF) technique (Table 1). Present major-oxide data for obsidian have been compared with the published data[11,12] indicating a tight chemical closeness. These data sets when plotted over total alkali–silica diagram, lie close to each other and are confined to the rhyolite field.

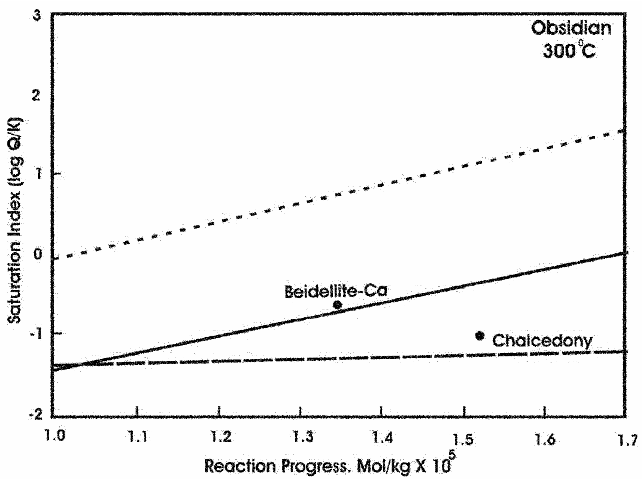

Figure 2. Sequence of saturation indices for mineral phases formed in the obsidian sample.

Table 1. Chemical composition of untreated glass

Oxides (wt %)	AVS	Natural analogues		
		Rhyolite	Impact glass	Present glass
SiO_2	44.25	74.53	50.86	71.18
TiO_2	12.95	00.36	02.85	00.36
Al_2O_3	0.56	12.55	13.51	09.71
Fe_2O_3	10.08	02.47	01.52	05.26
FeO	–	–	13.60	–
MnO	5.01	00.03	–	00.11
MgO	0.22	00.19	05.32	00.11
CaO	0.61	00.97	09.56	01.96
Na_2O	25.59	03.45	02.17	05.51
K_2O	0.56	05.30	00.59	00.03
P_2O_5	0.17	00.06	–	05.76
Total	100	100	100	100

To achieve optimum *S*/*V* (surface area/volume) ratio for the test glass, obsidian chips were pulverized and sieved to obtain particle size of 100–120 μm. Glass specimens were prepared after the glass powder was ultrasonically cleaned in deionized water and allowed to dry at 90°C for 24 h. The specific area and density of each specimen was determined by Brunauer, Emmett and Teller (BET) (Krypton) measurements[13]. The values so obtained are in the order of 663 cm^2/g and 2.405 g/cm^3 respectively. The alteration experiments were conducted in corrosion-resistant Parr Reactor^{TM} (model: 4568). Glass specimens composed of 1.0 g of granules were wrapped in a stainless steel mesh (100) and treated with 80 ml of deionized water for 1, 2, 4, 8, 16, 32 and 64 h at 300°C at corresponding pressure (1260 psi). The residue (representing the newly formed minerals) and leachates were collected after each experiment. The electrical conductivity and pH of the leachates were determined and the surface morphology of the newly formed crystalline mineral phases was studied using scanning electron microscopy (SEM) technique. Generally, boron is considered as reaction tracer for the evaluation of glass alteration mechanism but it is very low in concentration in obsidian, hence its aqueous dissolution has not been taken into account[14]. Na is the element which participates easily in the ion exchange reaction with water therefore, its concentration along with K as an additional check has been taken into account for the present calculations. Mass loss and release rates for Na and K have been calculated to evaluate glass alteration mechanism. To quantify mass loss, mass of each glass specimen was measured before and after each experiment.

$$\mathrm{ML} = (m_o - m_1)/(\mathrm{SA}), \tag{1}$$

where ML is the total mass loss (g/m^2); m_o the total unaltered glass specimen in g; m_1 the total altered glass specimen in g; SA the sample surface area.

The normalized mass loss is linked with the rate of release of sodium concentration in solution. It corresponds to the mass of the glass altered in the unit surface area (NL_i), using the following equation, normalized mass loss for each specimen is calculated after each experiment[15].

$$[(\text{Na leached}/\text{Na present in the sample}) \times \text{wt of sample}]/ \\ \text{surface area (cm}^2) \times \text{time (days)}. \tag{2}$$

The glass–water interaction includes chemical reactions and mass transport processes. It has been established that the ion-exchange, network hydrolysis and precipitation are important mechanisms of glass leaching. Out of these, precipitation reactions usually play an important role under saturated conditions and for long-term performance, whereas, ion exchange and network hydrolysis are the dominant processes under short term or weak alteration

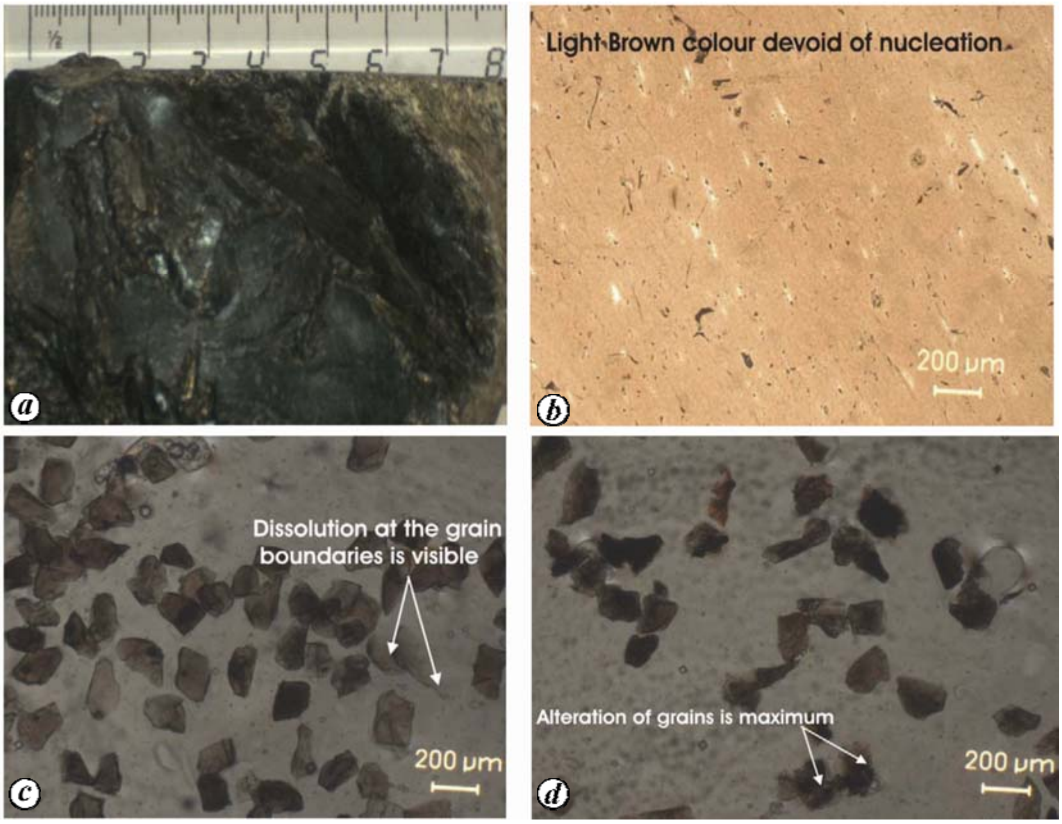

Figure 3. Obsidian sample (***a***) showing banding and conchoidal fractures, (***b***) photomicrograph showing light brown coloured unaltered amorphous phase devoid of nucleation, (***c***) altered sample after treatment at 300°C for 1 h and (***d***) altered samples after treatment at 300°C for 62 h, showing maximum dissolution of grains.

condition[16,17]. Glass is unstable at low temperatures and reacts with water to partially dissolve and form crystalline and non-crystalline secondary solids[18]. When glass comes in contact with water, the first step is the adsorption of H_2O (H^+, H_3O^+) on the glass surface, then H_2O diffuses into glass. At high pH (approximately at 10), deprotonation reaction of monosilicic acid takes place leading sharply to the release of Si ions and it further causes increase in the solubility of glass. Dissolution rates of silicate minerals and glass, measured in the laboratory indicate that weathering is typically controlled by the pH-dependent detachment of framework elements from the solid surfaces[19,20].

Glass specimens were coated with gold and microstructures as well as surface layers in case of the altered glass specimen with or without crystalline domains were studied using SEM (ZEISS Model: EVO 50). Weathering and alteration of volcanic glass is one of the main sources of smectites[21]. Glass altered experimentally under low temperature hydrothermal conditions[22–24]. The experimental study on alteration of a rhyolitic obsidian showed that the clay minerals may grow to form micrometric packets of layers[28]. In the present study, the grain surface of obsidian is altered and shows presence of a few curved laminae, very small in size (Figure 4 *a* and *c*) and whose number increases with increasing time. The chemical composition of glass and curved laminae is slightly different (Figure 5 *a*). One type is a curved clay-like material occurring on the glass surface, developing a mosaic texture and it completely covers the grains (Figure 4 *a* and *c*). The second morphology is typical of smectite and consists of clay-like flakes forming rosette-like particles. They are present as isolated particles on the glass surface or forming large aggregates (Figure 4 *b*).

Temperature plays an important role in the glass dissolution mechanism. At 300°C, average dissolution rate is highly elevated and glass alteration increases with rising temperature. The precipitation of analcime after several weeks of reaction correlates with an abrupt increase in glass dissolution rate[25]. The formation of secondary phases does have an important effect on glass dissolution rates in that they control the concentrations of dissolved elements such as aluminum and silicon (Figure 5 *a*–*c*). This is the reason for the observed abrupt increase in the dissolution. The elevated participation of ion exchange process, particularly when high *S*/*V* ratio of the test sample is available, causes overall release of elements which perhaps is responsible for the increase in the pH values of leachates. The release of sodium ions from the glass matrix is primarily responsible for the elevation of alkalinity

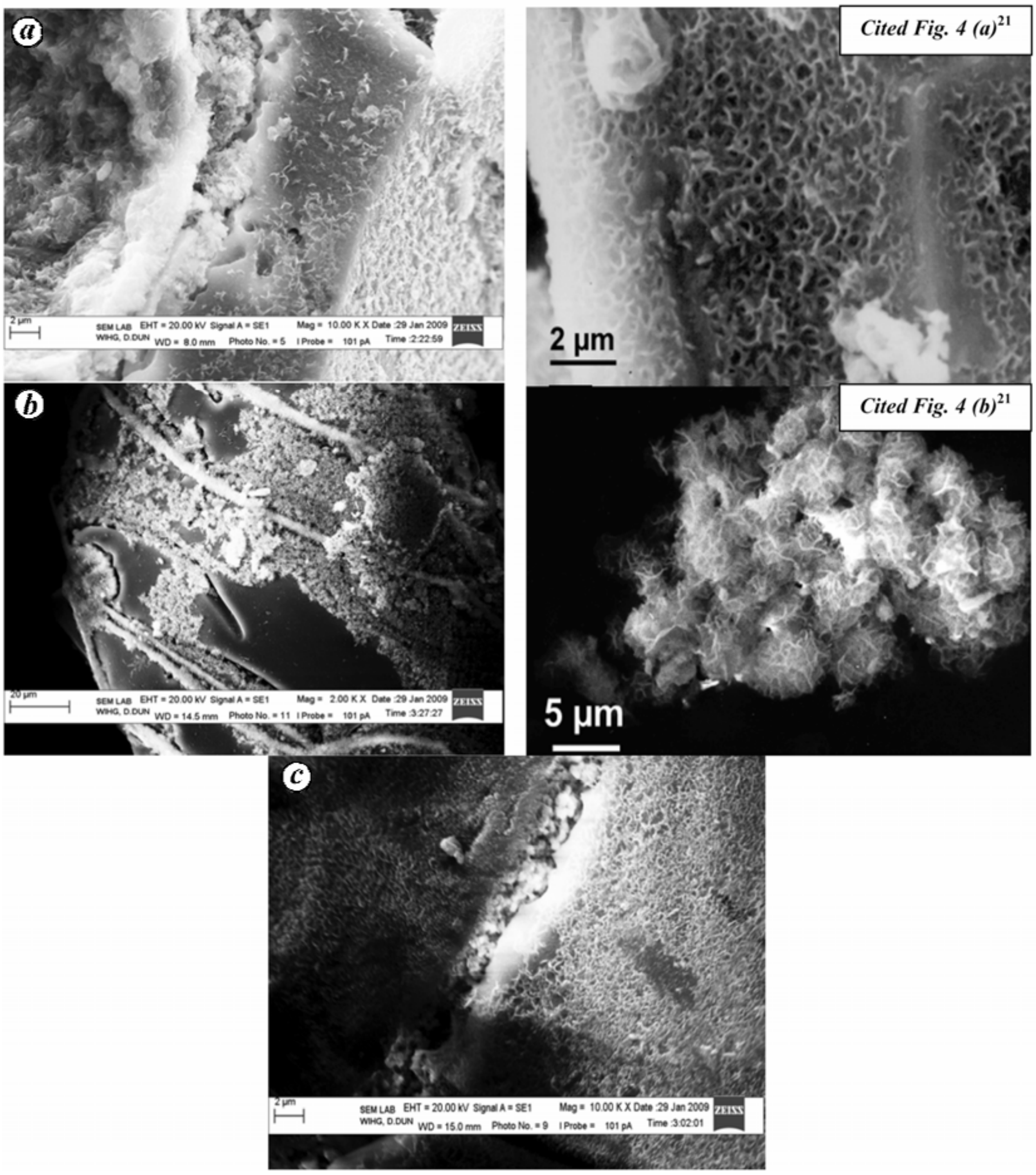

Figure 4. SEM-back scattered images of obsidian specimens treated (***a***) 300°C for 1 h shows curved clay-like material occurring on the glass surface and develop a mosaic texture and it completely covers the grains very much similar to the published[21] morphology, (***b***) altered sample after treatment at 300°C for 64 h is typical of smectite and consists of clay-like flakes forming rosette-like particles. They are present as isolated particles on the glass surface or forming large aggregates and (***c***) 300°C for 2 h in which the grain is completely enveloped by neo-crystallized flakes exhibiting honeycomb texture.

in the leachates (Figure 5 *b* and *c*), hence pH value increases. The present study revealed that the release of potassium ions was less than that of the sodium ions. X-ray diffractograms indicate that the mineral phases were formed when alteration rate is high. These minerals appear when pH and conductivity values are 8.03 and 140.9 mhos/cm respectively.

The present study demonstrates an agreement between the experimentally observed mineral phases and the mineral phases obtained after the computer simulations of the chemical data. The appearance of quartz is observed experimentally as well as in the simulations. Extrapolation of the experimental data predicted formation of amorphous silica which is least thermodynamically stable, quartz, the most stable and chalcedony having intermediate stability. The appearance of quartz in the residue was inferred from the X-ray diffraction patterns. The simulations aided in predicting the stability of secondary mineral phases if the experiments were to be carried out for longer periods. However, owing to experimental constraints, some inconsistency between experimental and simulated results was also noticed. Thus, obsidian glass network structure shows high order of durability when treated at near hydrothermal conditions and considered as

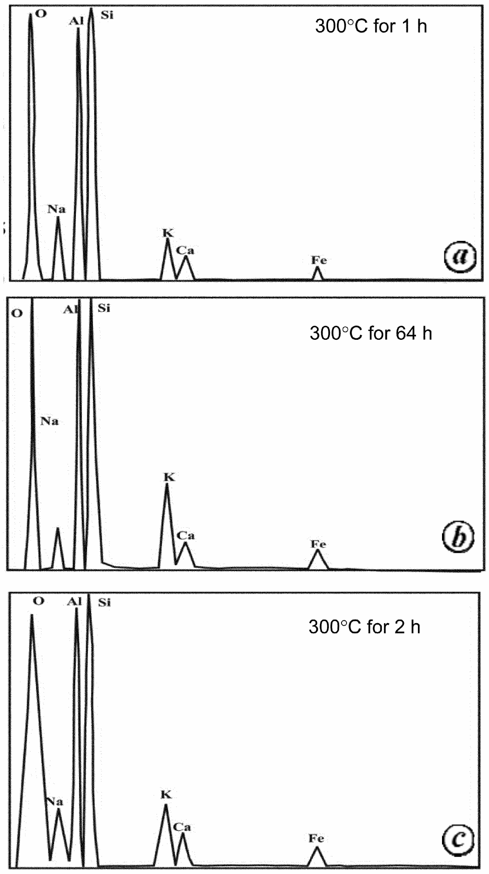

Figure 5. EDX spectra of obsidian specimen treated. ***a***, 300°C for 1 h; ***b***, 300°C for 64 h and ***c***, 300°C for 2 h.

a potential natural analogue for the disposal of nuclear waste in the geological repository.

---

1. Crovisier, J. L., Advocat, T. and Dussossoy, J. L., Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (natural analogs of waste containment glasses). *J. Nucl. Mater.*, 2003, **321**, 91–109.
2. Lutze, W., Malow, G., Ewing, R. C., Jercinovic, M. J. and Keil, K., Alteration of basalt glasses: implications for modeling the long-term stability of nuclear waste glasses. *Nature*, 1985, **314**, 252.
3. Abdelouas, A., Crovisier, J. L., Lutze, W., Fritz, B., Mosser, A. and Muller, R., Formation of hydrotalcite-like compounds during R7T7 nuclear waste glass and basaltic glass alteration. *Clays Clay Miner*., 1994, **42**, 526.
4. Bajpai, R. K. and Narayan, P. K., Shock basaltic glasses from Lonar Lake, Maharashtra: a potential natural analogue of nuclear waste glasses. *J. Geol. Soc. India*, 2005, **65**, 775–777.
5. Shrivastava, J. P., Bajpai, R. K. and Rani, N. A., Review on corrosion mechanism in borosilicate nuclear waste glass for long-term performances assessments in geological repository. *J. Geol. Soc. India*, 2008, **72**, 238–244.
6. Grambow, B., A general rate equation for nuclear waste glass corrosion. *Mater. Res. Soc. Symp. Proc.*, 1985, **44**, 16–27.
7. Wolery, T. J., EQ3/6, a software package or geochemical modeling of aqueous systems, package overview and installation guide (version 7.0), Lawrence Livermore National Laboratory, 1992.
8. Cunnane, J. C. *et al.*, High level nuclear waste borosilicate glass: a compendium of characteristics. Scientific Basis for Nuclear Waste Management Symposium, Boston, MA, 1992.
9. McGrail, B. P., Ebert, W. L., Bakel, A. J. and Peeler, D. K., Measurement of kinetic rate law parameters on a Na–Ca–Al borosilicate glass for low-activity waste. *J. Nucl. Mater*., 1997, **249**, 175–189.
10. Maithani, P. B., Goyal, N., Banerjee, R., Gurjar, R., Ramachandran, S. and Singh, R., Rhyolites of Osham hills, Saurashtra, India. In *Gond. Geol. Mag.* (eds Deshmukh, S. S. and Nair, K. K. K.), 1996, vol. 2, pp. 213–224.
11. Le Maitre, R. W., A proposal by the IUGS subcommission on the systematics of igneous rocks for a chemical classification of volcanic rocks based on the total alkali silica (TAS) diagram. *J. Petrol.*, 1976, **17**, 589–637.
12. Le Maitre, R. W., *Numerical Petrology*, Elsevier, New York, 1982.
13. Munier, I., Crovisier, J. L., Grambow, B., Fritz, B. and Clement, A., Modelling the alteration gel composition of simplified borosilicate glasses by precipitation of an ideal solid solution in equilibrium with the leachant. *J. Nucl. Mater*., 2004, **324**, 97–115.
14. Sheng, J., Shanggeng, L. and Tang, B., The leaching behavior of borate waste glass SL-1. *Waste Manage*., 1999, **19**, 401–407.
15. Kaushik, C. P., Mishra, R. K., Sengupta, P., Kumar, A., Das, D. Kale, G. B. and Raj, K., Barium borosilicate glass – a potential matrix for immobilization of sulfate bearing high-level radioactive liquid waste. *J. Nucl. Mater*., 2006, **358**, 129–138.
16. Hench, L. L., Clark, D. E. and Harker, A. B., Review: nuclear waste solids. *J. Mater. Sci*., 1986, **21**, 1457–1478.
17. Abrajano, T. A., Bates, J. K. and Mazer, J. J., Aqueous corrosion of natural and nuclear waste glasses: II. Mechanisms of vapour hydration of nuclear waste glasses. *J. Non-Cryst. Sol*., 1989, **108**, 269–288.
18. Bourcier, W. L., Affinity Functions for Modeling Glass Dissolution Rates Atomic Energy Commission – Vallee due Rhone Summer Workshop: Glass: Scientific Research for High Performance Containment, Mejannes-le-Clap, France, 1998.
19. Blum, A. and Lasaga, A., Role of surface speciation in the low temperature dissolution of minerals. *Nature*, 1988, **331**, 431–433.
20. Brady, P. V. and Walther, J. V., Controls on silicate dissolution rates in neutral and basic pH solutions at 25°C. *Geochim. Cosmochim. Acta*, 1989, **53**, 2823–2830.
21. Fiore, S., Huertas, F. J., Huertas, F. and Linares, J., Smectite formation in rhyolitic obsidian as inferred by microscopic (SEM–TEM–AEM) investigation. *Clay Miner*., 2001, **36**, 489–500.
22. Kawano, M. and Tomita, K., Formation of allophane and beidellite during hydrothermal alteration of volcanic glass below 200°C. *Clays Clay Miner*., 1992, **40**, 666–674.
23. Tomita, K., Yamane, H. and Kawano, M., Synthesis of smectite from volcanic glass at low temperature. *Clays Clay Miner*., 1993, **41**, 655–661.
24. Fiore, S., Huertas, F. J., Tazaki, K., Huertas, F. and Linares, J., A low temperature experimental alteration of a rhyolitic obsidian. *Eur. J. Mineral*., 1999, **11**, 455–469.
25. Van Iseghem, P. and Grambow, B., The long-term corrosion and modeling of two simulated Belgian high-level reference waste glasses. *Mater. Res. Soc. Symp. Proc.*, 1988, **112**, 631–639.

ACKNOWLEDGEMENTS. We acknowledge the Board of Research in Nuclear Sciences, Bhabha Atomic Research Centre, Department of Atomic Energy for providing financial assistance. For SEM-EDX of the samples, we thank Dr P. P. Khanna, Dr N. K. Saini and Mr N. K. Juyal, WIHG, Dehradun.

Received 15 November 2009; revised accepted 15 March 2010