

Early Phyllosilicates Formed by Alteration of R7T7 Glass in Water at 250°C.

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ABSTRACT

R7T7 glass samples have been altered during periods of one and seven days at 250°C in distilled water. Ultramicrotomic thin sections were performed in the outermost part of the glass for a study under analytical transmission electron microscope. After one day the alteration layer is about 5 μm thick. It is made up of sheeted silicated particles, tentatively identified as septechlorite (7 Å intervals) mixed with a intercrystalline amorphous matrix of different composition. After seven days the alteration layer is about 11 μm thick. It is made up of sheeted silicated particles of smectite type (10 Å intervals). No 7 Å particles were found in the seven days sample. This study illustrate the capacity of poorly crystalline phyllosilicates to adapt to the chemical changes in solution.

INTRODUCTION

The development of source-term models for predicting the long term durability of nuclear waste-form glasses requires a precise knowledge of the incipient mechanisms of alteration. Numerous studies have been conducted with borosilicate glasses or their natural analogues to establish whether the surficial alteration layers act as diffusion barriers between glass and solution and whether it is possible to model their formation and long-term properties by means of computer codes based on the equilibrium constant approach (Byers et al., 1985; Murakami et al., 1988, Crovisier et al., 1987, 1989a and b, Advocat et al., 1990; Banba et al., 1990, Bourcier, 1991, Bates et al., 1991).

The present work is a complementary study of that of Caurel (1990) and Caurel et al. (1990). These authors performed hydrothermal leach tests at

150 and 250°C in aqueous media during periods of one day to one year. They determined the nature of secondary phases from 30 days to one year (analcite, smectite, zeolites and hydrated calcium silicates), and the reaction kinetics through solution analysis. In the present study we focused our attention on very short periods of time (1 and 7 days) in order to detect the early stages of secondary phases formation using transmission electron microscope.

MATERIAL AND METHODS

The french reference R7T7 borosilicate glass has been used for these hydrothermal experiments made by Caurel (1990). Static leach tests were performed in distilled water at 250°C during periods of 1 and 7 days using polished prisms designed to obtain a surface area to solution volume (SA/V) of 5 cm⁻¹. Experiments were performed in 50 cm³ stainless steel (316L) bombs externally heated. Detailed experimental procedure is given in Caurel (1990) and Caurel et al. (1990).

Ultramicrotomic thin sections 500 Å thick were prepared in the external part of the altered glass for a study under transmission electron microscope (TEM) following the method of Ehret et al. (1986). Textural and structural data were completed by chemical analyses using an energy-dispersive X-ray emission spectrometer.

RESULTS

Structural properties of the alteration layers.

One day altered sample.

The plate I shows a general view of the ultramicrotomic thin section performed in the external part of the altered glass. From the left to the right of the plate we can distinguish an external felt-like alteration layer, about 5 µm thick, and the fresh glass (black fragments).

Crystals are visible in the outermost part of this layer (Plate I, 1A). These crystals have a sheeted structure, evidenced by electron diffraction

patterns (Plate I, 2A) and high resolution images (Plate I, 3A). The mean values obtained from electron diffraction patterns are 7.67 Å while they are 7.63 Å from lattice fringes on high resolution images (Table IA) and B). The values found for the intervals between the sheets vary significantly in a same crystal (Table IB, column 1) and also from one crystal to the next (Table IB, column 3).

Crystals also developed into the porous and amorphous product constituting the central part of the layer (Plate I, 1B). The intervals measured from electron diffraction data (Plate I, 2B and table IA) are 7.22 Å while they are 7.80 Å from high resolution images (Plate I, 3B and table IB). The porous and amorphous matrix is shown on Plate I, 1C.

Electron diffraction reveals the presence of very fine crystalline material giving diffraction rings. The measured values are reported in table IA, columns 5-7 (external zone) and 10 (internal zone).

Seven days altered sample.

A general view of the ultramicrotomic thin section is shown on Plate II. The alteration layer exhibit the same felt-like aspect than previously observed for the one day altered sample. Its thickness is about 11 μm. External crystals are observed in the upper left corner of Plate II, 1 (A) and fragments of glass in the lower right corner. A close view of the external part of the profile is given on Plate II, 2.

Electron diffraction and high resolution images obtained from external crystals (Plate II, 3A and 4A) indicate a sheeted structure with a d spacing superior to 10 Å (Table IIA, columns 1 and 2). A mean value of 10.46 Å was obtained from high resolution images (Table IIB).

Sheeted crystals with a similar d spacing were also found into the layer (Plate II, 2C and 4C). The mean value obtained from high resolution images is 10.49 Å (Table IB, column 2).

Chemical properties of the crystals, tentative identification.

One day altered sample

The chemical compositions obtained from X-microanalysis under the transmission electron microscope are summarized in table III.

The external crystals are mainly made up of silica, iron and zinc. The structural informations indicate that the crystals could be classified among the septechlorite, as already suggested by Nagues (1984) and Murakami et al. (1989) for comparable crystals formed on nuclear glasses. However, the unusually high Zn and Fe contents of these crystals on one hand, and the irregularity of the d spacing (Table IA) on the other hand, could indicate that they are actually made up of silicated sheets but also of octahedral $Zn(OH)_2$ sheets. As a matter of fact, the measured intervals: 4.41, 2.57, 2.44 and 1.50 Å (Table IB) are compatible with a wulfingite structure.

The composition of the internal crystals is more difficult to appreciate insofar as they are mixed with an amorphous matrix of different composition. The results obtained for crystalline aggregates into the layer are given in table IIIB, and for the intercrystalline matrix in table IIIC. Another series of analyses has been made in the innermost part of the layer, in direct contact with the glass, where no crystals are observable (Table IIID). It can be seen that the composition found is very similar to that of the intercrystalline matrix (column C) indicating a chemical homogeneity of this amorphous matrix along the profile. A calculation has been made to compare the composition of internal crystals (analyzed together with some matrix, table IIIB) with the external ones (column A). The calculation requires the knowledge of the respective proportion of crystals and matrix: it can be observed that iron, nickel and zinc contents are higher in the external crystals than they are in the matrix. The concentration of other elements like calcium, neodymium or

zirconium are depleted in external crystals, relative to the matrix. It can be noticed that the concentrations of the majority of elements in the internal aggregates (column B) are intermediary between external crystals (column A) and amorphous matrix (columns C and D) as could be expected in the case of a simple mixing. The Nd_2O_3 content of the external crystals is very low (1.2%), compared to the concentration in the amorphous matrix (13%, columns C and D). Calculation shows that the concentration of 9.1% for Nd_2O_3 found in the crystalline aggregates (column B) would correspond to a mixing of 67% matrix (13% Nd_2O_3) with 33% of crystals which composition would be the same as the external ones (1.2% Nd_2O_3). The results of the same calculation for the other elements are reported in the column E of the table III. It can be observed that the resulting composition is very similar to the composition of column B, except a slight difference for nickel and cesium.

In other words, this calculation strongly suggests that the internal crystals are identical to the external ones.

Seven days altered samples.

The chemical composition of the different components of the layer are given in table IV.

The external crystals (Table IVA) are mainly made up of silica, zinc, iron and cesium. These data, together with the informations obtained from high resolution images and diffraction patterns suggest a smectite-like mineral (expandable 10 Å) already observed by Thomassin et al. (1983) and Murakami et al. (1989) on altered nuclear glasses. The high zinc content would suggest a sauconite, but the unusual iron and cesium contents lead to consider a mixing with poorly crystalline hydroxides. Some analyses reveal the presence of silica-poor areas, rich in cesium, iron and zinc (Table IV, column A'). The cesium could also be adsorbed on the surface of the crystals which can not be evidenced under the electron microscope. Few

calcium silicate crystals were also evidenced (Table IVA''). Calcium silicates (tobermorite and/or okénite) were observed by Caurel (1990) for longer duration of the same series of experiments.

A layer made up of porous and amorphous product is observed in the external part of the layer (Plate II, 1B and 2B). Its composition is given in table IV, column B. The cesium is absent of this product which contains about 11% neodymium and calcium and 48% silica.

The compositions of internal crystalline aggregates and associate amorphous matrix (Plate II, 1C 1D and 2C) is given in table IV C and D. Cesium is also absent of these products.

An internal amorphous matrix, in direct contact with the glass, was also distinguished (Plate II, 1E and 2E) and analyzed (Table IVE). Contrarily to the observation made on the one day altered sample, the composition of the amorphous matrix varies significantly from one zone to the other (Table IVB, D and E). Hence the calculation made for the previous sample to estimate the composition of internal crystals is not possible.

DISCUSSION, CONCLUSIONS

1) After an interaction of one day at 250°C in distilled water, the external part of R7T7 glass consists in an alteration layer, about 5 μm thick. This layer can be divided into three different zones:

- external crystals that are mainly phyllosilicates with 7 Å intervals, (septechlorites ?). They are probably mixed with zinc and iron hydroxides.

- a central zone made up of crystalline aggregates and an amorphous matrix. From structural and chemical points of view, the crystalline aggregates are similar to the external crystals.

- an internal amorphous zone, in contact with the glass, similar to the central amorphous matrix.

The similarity between internal and external crystals indicate a

chemical equilibrium through the layer, which has important implications for modelling.

2) For the sample altered 7 days, the alteration layer is about 11 μm thick. The structure of this layer is more complex than those of the previous sample. We can distinguish between:

- external crystals of smectite-like nature (expandable 10 Å), calcium silicates and probably iron and zinc hydroxides.

- an external amorphous zone, under the crystals, rich in neodymium and zirconium.

- a central zone with numerous crystalline aggregates, which structure is the same as the one of external crystals.

- an internal and amorphous zone, poor in neodymium and zirconium, rich in nickel and zinc.

It is not possible to compare the chemical composition of the internal and external crystals after 7 days, due to the complexity of the layer. The increasing complexity of the layer is probably due to the selective repartition of some elements (like cesium) by adsorption on preferential sites. However, high resolution images have shown an structural identity.

3) An important fact is that the crystals formed after 7 days are totally different of those formed after one day which illustrates the capacity of such crystals to adapt to chemical variations of the environment (composition variation of the aqueous phase). It is very interesting to note that all crystals (external and internal) are structurally different of those formed after one day. This indicate that the alteration layers do not keep *memory* of previous events. This observation was already made for the alteration products of basaltic glasses from Iceland (Crovisier, et al. ,1989a and b)

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TABLE I

Sample altered 1 day. High resolution and electron diffraction data obtained for the crystalline particles constituting the alteration layer.

A ELECTRON DIFFRACTION									
External crystals							Internal crystals		
1	2	3	4	5	6	7	8	9	10
7.67	7.67	7.67	7.67				7.22	7.22	
						6.96			
					4.41			4.91	4.41
3.58	3.56	3.72	3.56			3.46	3.66	3.66	3.61
				2.71					2.76
					2.57				2.56
2.47	2.48	2.48	2.45	2.37	2.44		2.43		2.37
				2.01					2.12
							1.83		1.96
				1.49	1.50				1.49
Mean 7.67 Å					1.48		Mean 7.22		

B HIGH RESOLUTION			
Measured values for a same crystal		Measured values for different crystals	
1	2	3	4
Ext. crystal	Int. crystal	Ext. crystals	Int. crystals
8.21	8.21	8.05	8.75
6.47	7.41	7.01	8.78
7.82	9.12	7.53	7.19
6.09	8.35	7.26	7.03
8.26	5.76	7.40	8.17
7.35	5.71	8.50	7.52
8.41	9.41		7.19
6.38	7.03		
7.76	6.71		
6.94			
7.94			
6.56			
8.00			
Mean: 7.40 Å	Mean: 7.52 Å	Mean: 7.63 Å	Mean: 7.80 Å

TABLE II

Sample altered 7 days. High resolution and electron diffraction data obtained for the crystalline particles constituting the alteration layer.

A ELECTRON DIFFRACTION					B HIGH RESOLUTION	
External crystals			Internal crystals		External crystals	Internal crystals
1	2	3	5	6	1	2
11.16	10.23				10.78	10.67
7.92					10.22	10.67
5.45					10.45	10.60
5.22	5.22				10.21	10.06
		4.55	4.48		11.48	10.47
3.72					10.59	
3.56	3.51				10.75	
3.46						
3.15						
2.85						
2.64	2.64					
		2.59	2.56	2.56		
2.34		2.26		2.43		
2.12	2.10			2.05		
		1.71				
		1.51	1.48			
		1.30			Mean: 10.46 Å	Mean: 10.49 Å

TABLE III
Sample altered 1 day. at 250°C. Chemical composition of the different zones .of the alteration layer

From outside to inside of the layer

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	A		B		C		D		E
	External crystals		Internal crystalline aggregate		Amorphous Inter-crystalline matrix		Internal amorphous matrix		
	±		±		±		±		
Na ₂ O	0.3	0.6	0.0						
Al ₂ O ₃	5.5	3.7	3.6	3.0	3.4	2.3	3.2	1.8	4.1
SiO ₂	21.5	13.4	25.1	16.6	25.7	16.9	25.8	12.3	24.3
CaO	3.9	1.0	13.3	3.0	18.5	4.3	21.3	3.4	13.7
Cs ₂ O	2.7	2.6	0.6	0.6	0.9	0.9	1.2	0.7	1.5
Nd ₂ O ₃	1.2	1.6	9.1	2.8	13.0	4.6	13.1	2.7	9.1
Fe ₂ O ₃ *	21.7	5.7	13.2	4.2	9.6	3.7	8.3	2.1	13.6
NiO	6.7	1.9	7.4	2.6	2.7	2.5	1.0	1.0	4.0
ZnO	33.1	11.6	15.6	4.8	9.7	5.0	7.1	2.2	17.4
UO ₂	1.1	0.8	1.8	0.6	2.7	1.5	3.2	1.5	2.2
ZrO ₂	1.6	1.5	9.1	2.8	12.0	4.2	13.1	3.3	8.6
MoO ₃	0.6	0.6	1.2	0.9	1.6	0.7	2.6	1.1	1.3
N.A.	9		9		10		10		

Fe₂O₃* Total iron expressed as Fe₂O₃, N.A. Number of analysis.

B* The composition for **E** was obtained assuming that the compositions measured for the internal crystalline aggregates (column B) corresponds to a simple mixing of 33% of external crystals (column A) and 66% of amorphous matrix (column D).

TABLE IV
Sample altered 7 days at 250°C. Chemical composition of the different zones

From outside to inside of the layer

	A		A'	A''	B		C		D		E	
	External crystals				External amorphous matrix		Internal crystalline aggregate		Amorphous Inter-crystalline matrix		Internal amorphous matrix	
	±				±		±		±		±	
Na ₂ O												
Al ₂ O ₃	6.4	3.9	1.2	5.3	3.6	0.7	6.0	2.1	4.0	2.6	5.4	0.6
SiO ₂	27.9	12.0	5.3	39.2	47.9	2.2	45.1	7.3	34.7	13.5	52.9	6.0
CaO	1.1	0.7	2.4	35.0	11.6	0.8	8.7	2.1	12.4	4.4	13.4	3.1
Cs ₂ O	13.1	3.0	18.2						1.1	1.3		
Nd ₂ O ₃			0.5	0.8	10.9	1.9	4.7	1.4	9.8	4.8	5.1	0.9
Fe ₂ O ₃ [*]	23.6	6.2	34.3	8.4	7.8	0.7	11.1	2.6	9.4	1.6	6.4	1.5
NiO	1.7	0.8	1.5	0.4			5.3	1.6	2.0	1.1	2.0	1.7
ZnO	23.2	7.3	33.3	5.7	2.7	0.3	8.9	2.3	6.8	1.0	4.6	1.2
UO ₂	0.9	0.6	2.5	4.7	2.8	0.7	1.6	1.5	4.8	2.4	1.9	1.3
ZrO ₂			0.5	0.4	11.3	0.5	6.7	2.1	12.3	5.4	6.1	2.2
MoO ₃	0.9	0.6	0.4		1.1	0.5	1.1	0.8	2.3	1.1	1.8	0.9
N.A.	8		2	1	11		10		6		10	

Fe₂O₃^{*} Total iron expressed as Fe₂O₃, N.A. Number of analysis.

PLATE CAPTIONS.**Plate I**

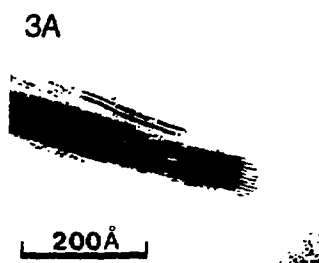
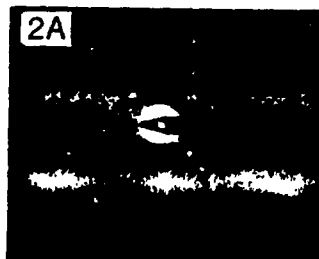
R7T7 glass altered 1 day at 250°C in distilled water

- 1 General view of the ultramicrotomic thin section performed in the outermost part of the altered glass. (A) external 7 Å phyllosilicate crystals, (B) internal 7 Å crystalline aggregates (phyllosilicates), (C) intercrystalline amorphous matrix (D) internal amorphous matrix. The same references are used in table I for chemical compositions.
- 2 Electron diffraction patterns obtained in the external (2A) and internal (2B) crystals.
- 3 High resolution images showing the lattice fringes of the external (3A) and internal (3B) crystals. The mean measured values are 7.63 Å (external crystals) and 7.80 Å (internal crystals).

Plate II

R7T7 glass altered 7 days at 250°C in distilled water.

- 1 General view of the ultramicrotomic thin section performed in the outermost part of the altered glass. (A) external 10 Å phyllosilicate crystals, (B) external amorphous matrix (C) internal 10 Å crystalline aggregates (phyllosilicates), (D) intercrystalline amorphous matrix (E) internal amorphous matrix. The same references are used in table II for chemical compositions.
- 2 Details of the external (A and B) and internal part of the profile.
- 3 Electron diffraction pattern (3A) and high resolution image (4A) of the external and internal (4C) crystals. The measured intervals (table II A and B) indicate an expandable 10 Å phyllosilicate.



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