EXPERIMENTAL ALTERATION OF A METEORITIC MODEL-GLASS IN DIFFERENT MEDIA

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Abstract: A meteoritic model-glass has been altered under oxidizing conditions in different media (water and sulfuric acid) at 80°C and 0°C. The reactions were followed by analysis of solutions and solids (XRD, FTIR, SEM, TEM). After reaction, all the elements were detected in solution, at different levels of concentration related to the medium. The most aggressive media were sulfuric acid at pH 1 for 80°C and 0°C runs. In such alteration conditions, the surface of the solid evolved rapidly according to the temperature. At 80°C, one noticed the development of a Si-rich layer containing calcium and sulfate ions which combined to form gypsum. At 0°C, only smooth surface with etch pits and scarce gypsum crystals were observed. In contact with glass, ultramicrotomed thin-sections studied by TEM revealed the presence of two kinds of products: Fe-Al silicate phases (in deionized water and H_2SO_4 solution with pH4) and a high-silica content layer (H_2SO_4 solution with pH1, at 80°C).

1. Introduction

The alteration of early anorthositic-like material is an important phenomenon which has to be more investigated for a better understanding of the earliest process evolution of the Earth. One of the most similar materials for this approach is lunar meteorites recovered from Antarctica. But the study of these materials can be hampered by terrestrial weathering and it is important to recognize if alteration products are related either to terrestrial weathering after fall of the meteorite on the Earth or to the evolution of the primitive material.

Among the weathering products identified on Antarctic meteorites, ferruginous oxidation products are the widest ones (Gooding, 1986). However, some other alteration products as white powders (gypsum, nesquehonite, hydromagnesite) are also known (Velbel, 1988; Miyamoto, 1991; Velbel *et al.*, 1991). General weathering hypothesis currently involve the reaction between the meteorite material and the solution resulting from the formation of either a weak carbonic acid solution or a sulfuric acid solution (Mittlefehldt and Lindstrom, 1991). For this last hypothesis, it is interesting to notice some historical descriptions of meteorite fall. For example, for Bérczi and Lukacs (1994), a sulfuric acid rain has been described during the fall event of meteorite (*e.g.* Zsadany meteorite). This fact suggests that

during the fall of the meteorite in the atmosphere, a reaction between sulfides of the meteorite and water of the atmosphere could be possible. An other question related to the evolution of the material in ice must be asked. GOODING (1986) suggested that an "hydrocryogenic" diagenesis could occurred during a period between 10^4 and 10^6 years.

Due to the rarity of the meteoritic samples, an other way for this investigation is possible by comparing the alteration products of natural samples and the alteration products of experimental evolutions under conditions simulating those which may occurred during the cooling of the Earth's atmosphere or during and after the fall of meteorite. The preliminary results presented in this paper concern an experimental investigation in order to simulate the evolution of such a material under different oxidizing alteration conditions. Experiments have been performed in water, and in order to explain the presence of sulfate minerals in the alteration products, in sulfuric acid solutions (pH 4 and pH 1). These last series of runs were performed for simulating the solutions resulting of the reaction between water and sulfides present in meteorites (MITTLEFEHLDT and LINDSTROM, 1991).

2.   Experiments and Analytical Methods

Experiments were performed on a model-glass whose composition (Table 1) is close to the average composition of the matrix analyzed from Yamato-86032 lunar meteorite. We preferred to use an homogeneous glass without primary crystals (plagioclase, olivine, pyroxene). The synthetic glass was obtained by melting oxides (SiO_2, Fe_2O_3), hydroxides ($Al(OH)_3$), carbonates ($CaCO_3$, $CaMg(CO_3)_2$, Na_2CO_3) and phosphates (apatite) at 1500°C in a platinum (20% rhodium) crucible, in a graphite furnace under reducing atmosphere during 3 hours. After melting, the glass was poured into a preheated mould and the temperature was maintained at 550°C during 1 hour in order to avoid internal stresses. This glass is optically isotropic and no crystalline phases were detected by X-ray diffraction.

For each run, 3 or 4 initially fresh chips of glass were used. Samples were disposed on the bottom of a PTFE reactor. The duration of experiments varied from 1 day to 6 months at 80°C (water and H_2SO_4 solution with pH 4) and between 1 day and 2 months at 80°C and 0°C (H_2SO_4 solution with pH 1). For each experiment, the average surface area was equal to 2 cm^2 and the volume of the solution equal to 20 cm^3. So, the ratio solid surface area/volume of solution (S/V ratio) was equal to 0.1. Referring to other experimental conditions, the experiments were performed under rock-dominated ratio. The medium was not stirred and not replenished. After reaction, the samples were thoroughly rinsed with deionized water in order to remove any contamination.

Table 1.   Chemical composition of the model-glass (wt%).

SiO_2	Al_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	Fe_2O_3
46.43	26.74	0.016	5.35	15.45	0.53	0.1	0.24	5.67

The reacting solutions were characterized by measurement of pH and analysis of elements (Si, Al, Fe, Mg, Ca by absorption flame spectroscopy, K, Na by emission flame spectroscopy and S by titration). The solid phases were studied by X-ray diffraction (Philips PW 1730), Infrared diffuse reflectance spectroscopy (Nicolet 510 FT-IR), scanning electron microscopy (secondary electron images obtained with a JEOL JSM 6400 equipped with a Kevex EDS system) and transmission electron microscopy TEM (Philips CM 12, acceleration voltage 120 keV, EDAX Si-Li detector, nanoprobe mode with diameter beam less than 50 nm). The k factors used are those from the EDAX software PVSUPQ, version 2.18. They were determined by ZALUZEC (1979). The semi-quantitative results obtained by X-EDS analysis performed on large sections of the ultramicrotomed sections were compared with those obtained by chemical analysis. The standard error deviation was so small that the k factor was not changed. By TEM, we have studied ultramicrotomed thin-sections of materials which provide samples on which it is possible to analyse the relationship between alteration products and glassy matrix (CROVISIER et al., 1983; THOMASSIN, 1984; BRADLEY and BROWNLEE, 1986; BRADLEY, 1988). Then, using these sample characterization techniques, many information can be acquired on morphology, texture and microanalysis of the sample.

3. Results

3.1. Solution data

At 80°C, for each medium, pH was found increasing with time (Fig. 1). In deionized water and H_2SO_4 solution with pH4, the values of pH increased up to slight
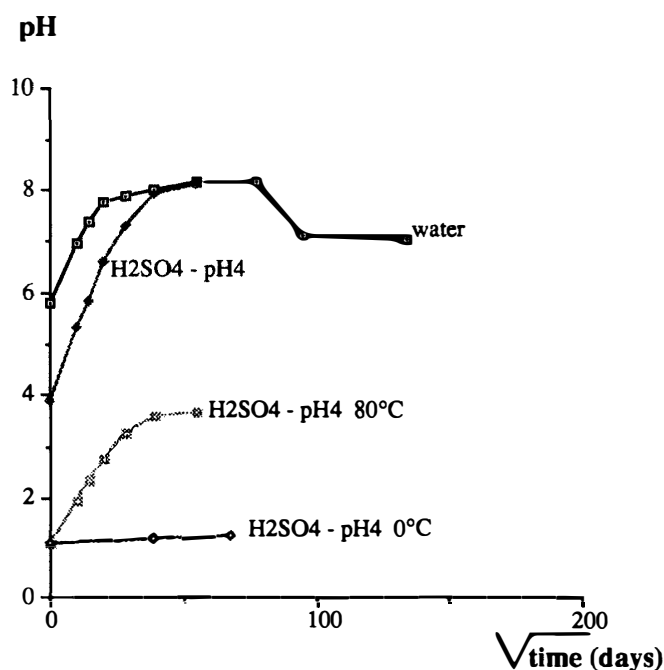

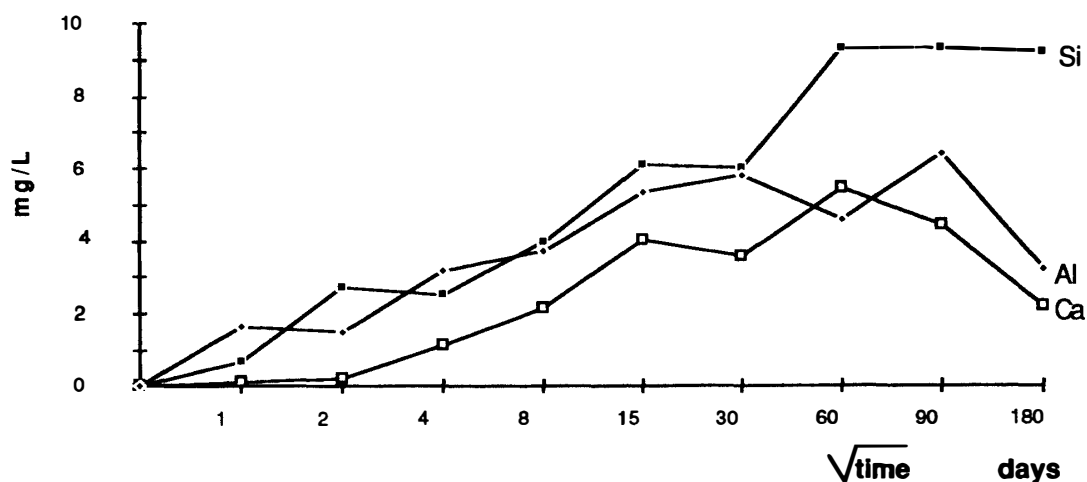Fig. 1.   Change of pH values in each solution with time.

Fig. 2. *Relation among the concentration of elements in solution and time, for experiments in deionized water at 80°C.*
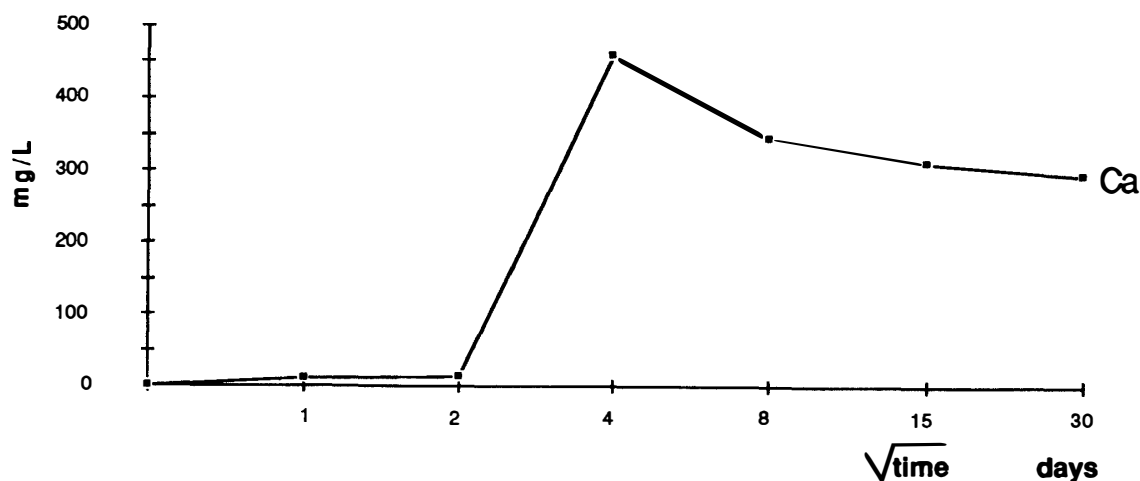

Fig. 3. *Calcium content evolution in solution versus time, for H_2SO_4 solution with pH4 at 80°C.*

basic value (~8.2) whereas in the H_2SO_4 solution with pH1 the pH increased to 3.6. At 0°C, in the H_2SO_4 solution with pH1, pH values do not change significantly (from 1.00 to 1.26).

The concentrations of elements in solutions evolved differently according to the alteration conditions. In water (Fig. 2), only Si, Ca and Al were detected at low concentrations. This fact is related to the low solubility of such a glass in this medium. In the later stage of experiment, the pH decrease and the Al and Ca contents decrease are related to the precipitation of phases on the sample surface. In H_2SO_4 solution with pH 4, the Ca content of the solution strongly increased after 4 days alteration (Fig. 3). The later stage, characterized by a slow decrease of Ca content, corresponds to the incorporation of this element in the superficial layer. In H_2SO_4 solution with pH1 at 80°C, all the elements were well detected in the solution (Fig. 4). There is a good correlation between the decrease of Ca and S after 2 days which corresponds to the precipitation of calcium sulfate on the surface of the sample (see solids data), and
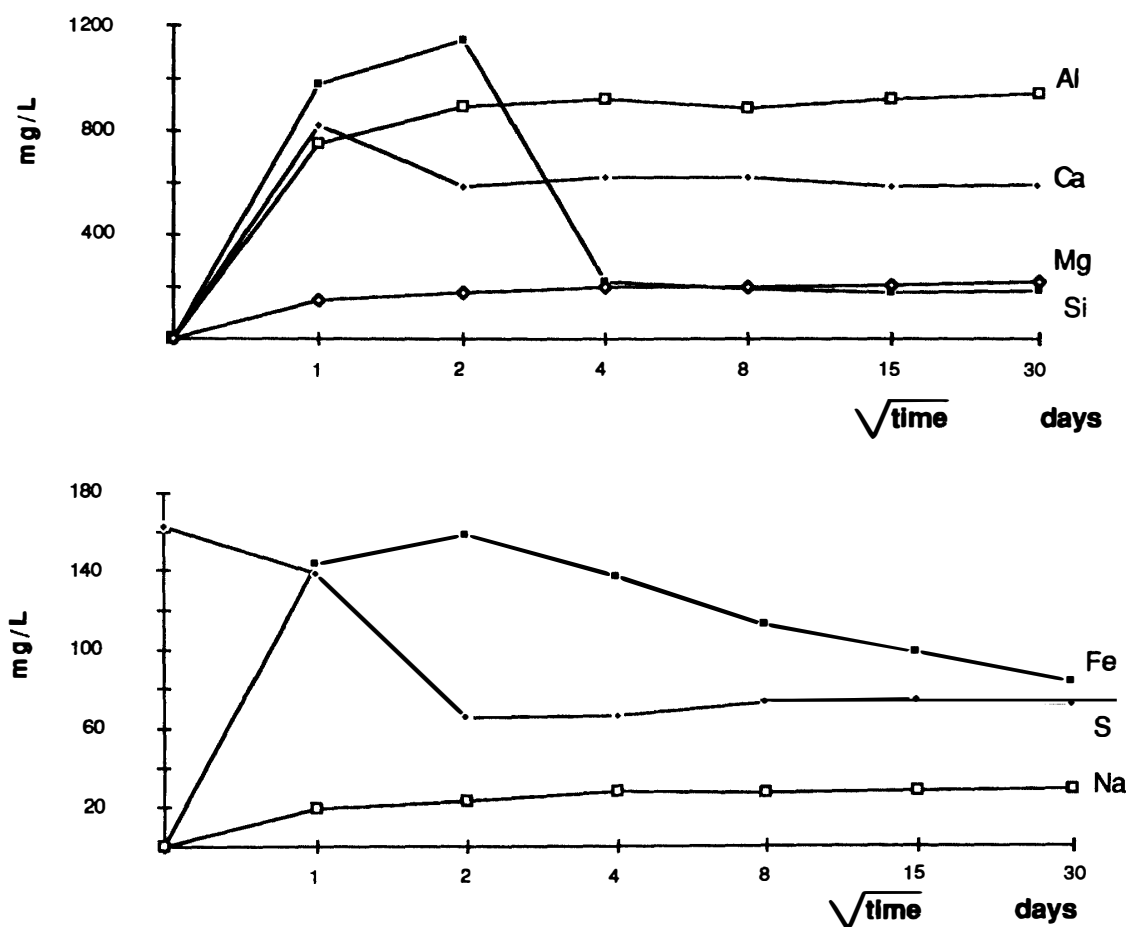
Fig. 4. Evolution of the elements concentration in solution through time, for H_2SO_4 solution with pH1 at 80°C.

the decrease of silica after 4 days which corresponds to the precipitation of a silica-rich layer. In H_2SO_4 solution with pH1 at 0°C, all the elements were well detected in the solution (Fig. 5). For us, this observation is very important, because that acidic medium simulates the alteration of meteorite in ice. We can then deduce that a certain mobility of elements occurs during the storage of meteorite in ice.

3.2. Solids data

No phases were detected by X-ray diffraction except for H_2SO_4 solution with pH1 conditions at 80°C. In that case, the presence of gypsum is revealed after 8 days alteration (Fig. 6).

Infrared diffuse reflectance spectroscopy gives some informations on the evolution of the sample surface according to the alteration conditions In deionized water and H_2SO_4 solution with pH4 at 80°C, only OH absorption band labels the evolution of the surface. In H_2SO_4 solution with pH1 conditions at 80°C, the spectra indicate major evolutions with the presence of bands corresponding to calcium sulfate compound and a broad absorption band near 3000 cm^{-1}. In H_2SO_4 solution with pH1 at 0°C, only the presence of OH group band near 3500 cm^{-1} was detected.
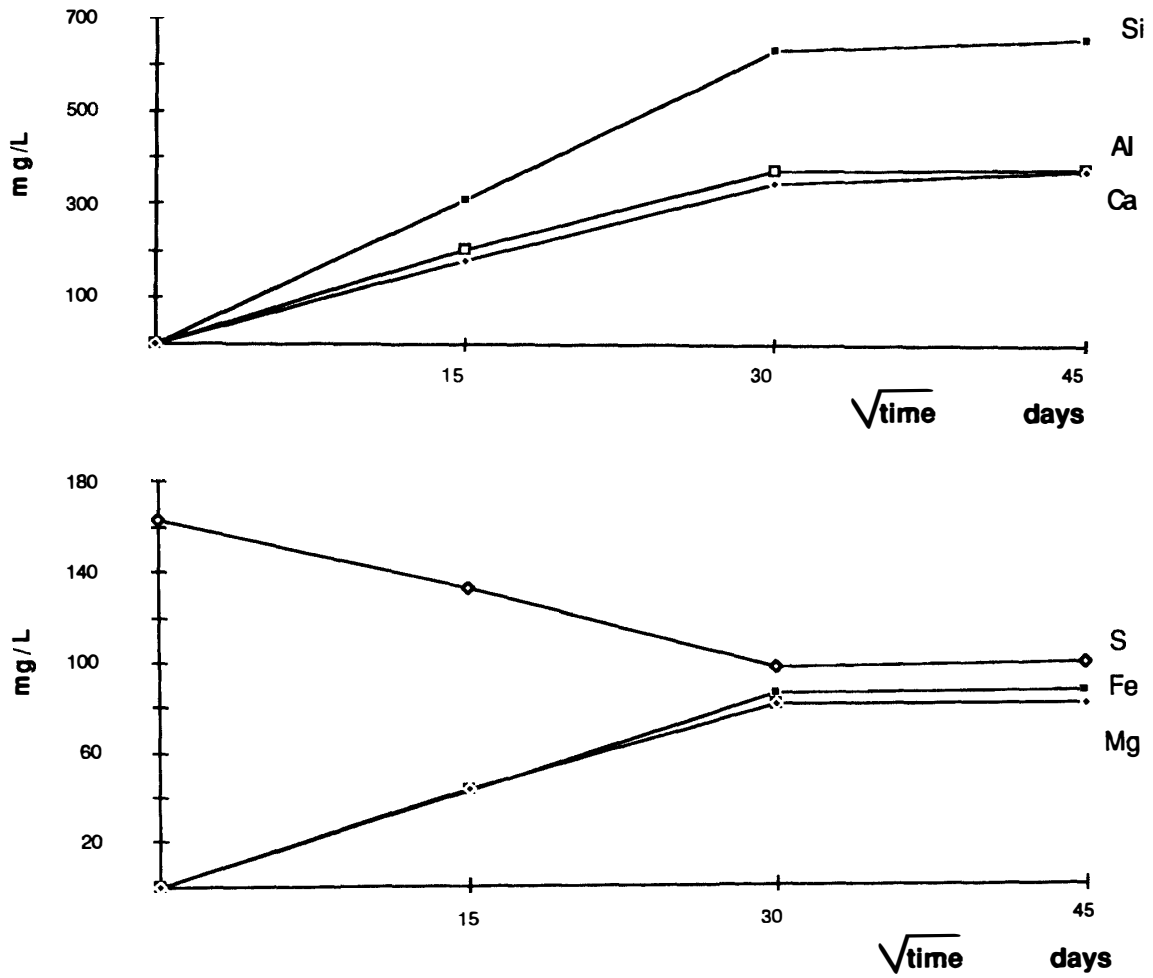
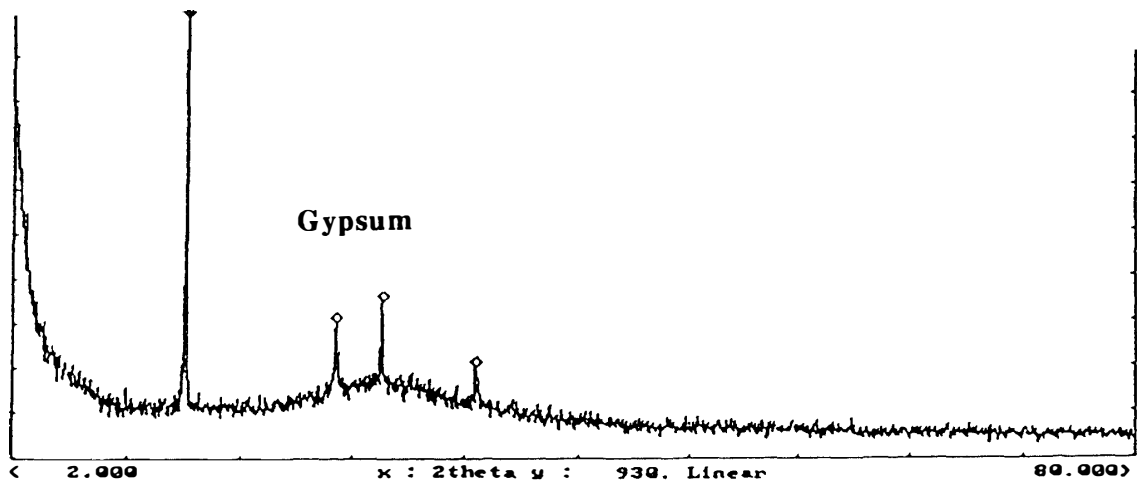Fig. 5. *Evolution of the elements concentration in solution through time, for H_2SO_4 solution with pH1 at 0°C.*

Fig. 6. *X-ray diffraction diagram of the run product developed on the surface of the sample altered in H_2SO_4 solution with pH1 at 80°C ($\lambda Cuk\alpha$-$\Diamond$gypsum).*

Fig. 7.   SEM photograph of the surface of the glass altered in deionized water at 80°C after 1 month (scale bar=10 μm).
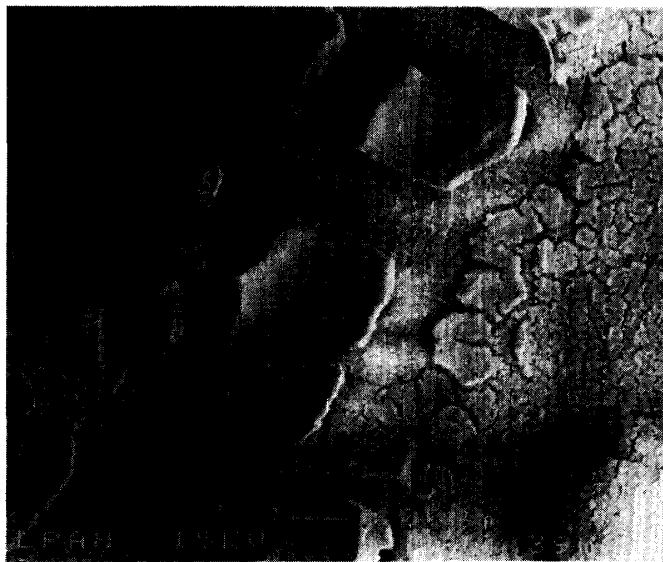
Fig. 8.   SEM photograph of the surface of the alteration products layer developed on the glass after 8 days alteration in H_2SO_4 solution with pH1 at 80°C (scale bar=100 μm).
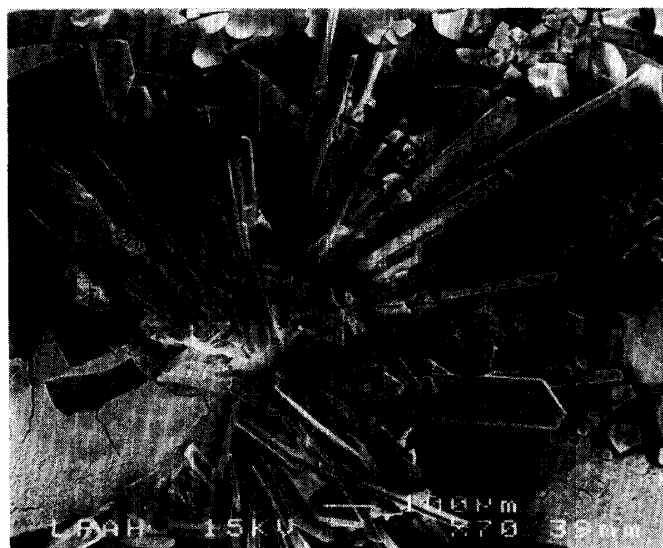
Fig. 9.   Growth of calcium sulfates during experiment 8 days alteration in H_2SO_4 solution with pH1 at 80°C (scale bar=100 μm).
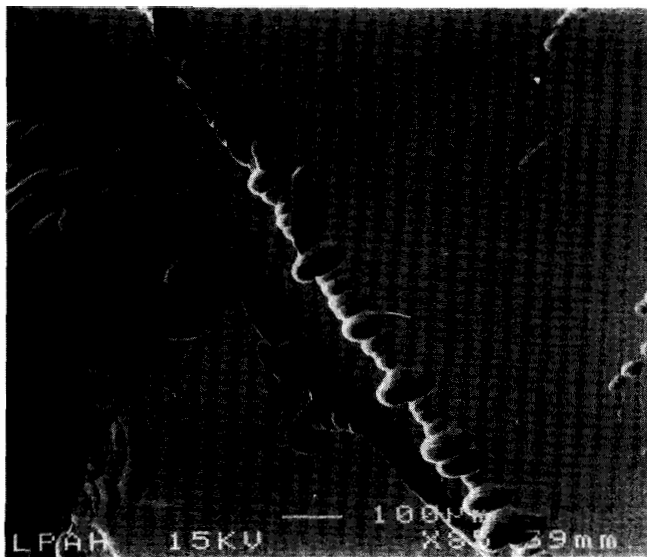
Fig. 10. Smooth surface and etch pits observed by SEM on the sample altered after 2 months in H_2SO_4 solution with pH1 at 0°C (scale bar=100 μm).
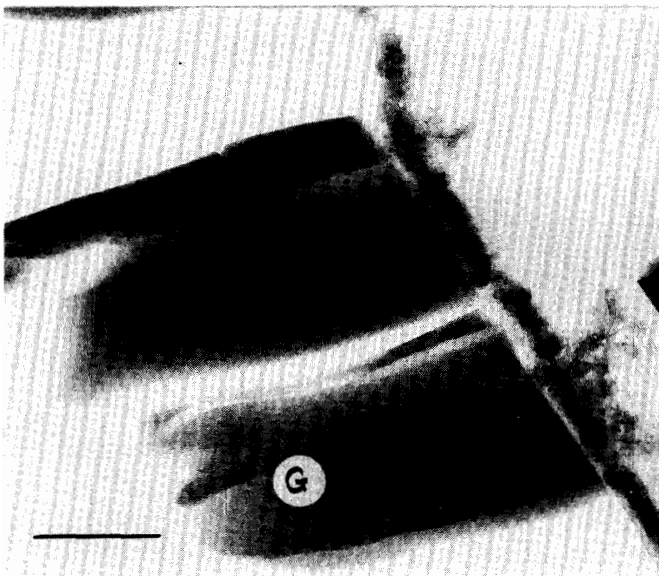
Fig. 11. Texture of the ultramicrotomed thin-section of the sample altered in water after 1 month at 80°C (G=glass; scale bar=250 nm).

Fig. 12. Relationship among glass and alteration layer observed by TEM from ultramicrotomed thin-section-experiment 1 month in H_2SO_4 solution with pH1 conditions at 80°C (G=glass; scale bar=400 nm).

Table 2.   Representative compositions of alteration products in contact with the glassy matrix (wt%).

Runs		MgO	Al₂O₃	SiO₂	Fe₂O₃	CaO	SO₃	K₂O
Water 8 days	alteration	1.3	38.2	19.3	35.2	4.2	0	0
	alteration	1.2	38.5	20	36.1	4.2	0	0
	glass	4	39.6	47.8	4.4	4.2	0	0
	glass	4.9	32	54.4	3	5.7	0	0
	glass	4.5	30.5	52	3.1	10	0	0
Water 1 month	alteration	1	25	21.6	49.6	2.8	0	0
	alteration	1.4	28.3	20.9	44.9	4	0	0
	alteration	3.3	33.3	22.8	37	3.1	0	0
	glass	5.4	30.2	54.4	2.7	7.2	0	0
	glass	6.9	31.9	47.3	7	8	0	0
	glass	4.5	30.5	52	3.1	10	0	0
H₂SO₄ pH4 8 days	alteration	0.8	34.1	26.1	33.6	1.2	3.2	0
	alteration	1.2	34.3	21.7	36.9	1.3	2.5	0
	alteration	0	38.5	23.2	33.8	1.3	2.1	0
	alteration	0	40.5	22.7	33.3	1.4	1.2	0
	glass	4.3	35.5	52	2.5	5.7	0	0
	glass	6.4	35.9	49.1	2.3	6.3	0	0
	glass	8.2	33.8	45	2.9	9.9	0	0
H₂SO₄ pH4 1 month	alteration	0.9	36.9	23.1	35.1	2.5	0	0
	alteration	0.8	37.3	21.4	36.6	2.8	0.6	0
	alteration	1.3	37.9	23.9	34.1	2.7	0	0
	glass	3.8	25.6	63.6	1.9	5	0	0
	glass	2.8	30	58.7	2.3	6.2	0	0
	glass	5.6	35	48	2.7	8.3	0	0
H₂SO₄ pH1 8 days	alteration	0	18.6	78.8	1.8	0.1	0.4	0.3
	alteration	0	18.7	78.3	1.8	0.5	0.1	0.6
	alteration	0	19.1	77.8	1.6	0.6	0.3	0.6
	alteration	0	21.5	74.4	1.3	1.3	0.7	0.9
	glass	6.5	32.5	51.2	2.3	7.5	0	0
	glass	8.2	35.8	43	2.9	9.9	0	0
	glass	7.2	36	43	3.1	10.6	0	0

The SEM observations underline the difference between the alteration media. In deionized water and H₂SO₄ solution with pH4 at 80°C, only few products precipitate on the sample surface. A typical representative view is given in Fig. 7 on which a very thin layer of iron-rich products is observed. This layer is not sticking to the surface sample. In H₂SO₄ solution with pH1 at 80°C, the evolution of the morphology of the surface is more significative. After 8 days a multilayered skin overlapped the surface of the glass (Fig. 8) and some radially grown euhedral of calcium sulfate crystals can be observed (Fig. 9). In H₂SO₄ solution with pH1 at 0°C, the surface of the glass was apparently smooth, with typical etch pits (Fig. 10) and sometimes crystallizations of

calcium sulfate can be observed.

The TEM investigations on ultramicrotomed thin-sections give more details on the evolution of the surface of the glass depending of the alteration conditions. According to the above examinations, the differences are quite obvious. In deionized water and H_2SO_4 solution with pH4 at 80°C, the morphology is the same and the thickness of the layer of alteration products does not evolve very much with time (Fig. 11). The reaction front between glass and alteration layer is straight. The representative composition of the alteration layer is a Fe-Al-Si compound (Table 2). In H_2SO_4 solution with pH1 at 80°C, the ultramicrotomed thin-section (Fig. 12) does not represent the whole alteration layer, but shows only the relationship among the glassy matrix and the beginning of the alteration layer. The most important fact is the morphoscopic continuity between the two parts and the high-silica composition of the typical alteration products (Table 2) . We already mentioned such a peculiar composition of glassy matrix on the ultramicrotomed thin-section of Y-86032 meteorite (THOMASSIN et al., 1995)

4. Discussion

Two kinds of evolution related to the alteration conditions may be distinguished from our data. We choose to model the alteration under oxidizing conditions: in water in order to approach the weathering of meteorites after the fall on the earth and in sulfuric acid solutions for modelling the contact between meteorite and solutions in contact with sulfides (oxidation of pyrite, development of sulfuric acid solution—MITTLEFEHLDT and LINDSTROM, 1991). The two tested temperatures were selected either for accelerating the reaction between solid and solution (80°C) or to simulate the alteration which could occur in the ice of Antarctica glacier (0°C).

In deionized water and H_2SO_4 solution with pH4 conditions, the precipitation of a Fe-Al-silicate layer occurred. This layer seems to be a protective one and its thickness does not evolve very significantly with time. From a geochemical point of view, it is important to notice that iron was not detected in solution. Therefore, this element immediately precipitates at the earliest stages of reaction among solid and solution and then the iron-rich layer traps elements such as Al and Si. This phenomenon has been already demonstrated, e.g. for the alteration of basaltic model-glass in several conditions (water and seawater: THOMASSIN et al., 1983, 1989; CROVISIER et al., 1983; THOMASSIN, 1984). This geochemical behaviour is characteristic of iron evolution under oxidizing conditions.

In H_2SO_4 solution with pH1, the evolution of the glass can be compared with two natural systems. At 80°C, the crystallization of gypsum and the development of a silica layer underline a quick reaction between solid and solution. The temperature of the reaction is therefore still unknown, but probably relatively higher. At 0°C, the behaviour of elements revealed in our experiments has to be taken in consideration particularly for the evolution of meteoritic material which is stored in ice. Indeed, the dissolution process of the glass is found congruent, all the elements are dissolved and etch pits are observed. This evolution is *a priori* unexpected but similar conclusions were found by CROVISIER (1989) and CROVISIER et al. (1992) who studied the alteration

of volcanic glasses in seawater at 3°C. At the present time, there is no good explanation for this dissolution phenomenon. Regarding the general evolution of the system, the most stricking fact is the silica content of the leaching solution. Two hypothesis have to be invoked to explain this data . First, the leaching of silica is classically well known in basic pH (>9). If so, the hypothesis of a local pH in the thin film of solution in contact with the glass is needed. Secondly, the acidic solution presents a high complexation power in front of modifier ions of the glassy network (Ca, Fe, Na and a part of Al). These elements could be rapidly trapped in the solution, the remaining network is broken down and then silica goes into the solution. In order to choose between the two hypothesis, more data are now requested, may be by SIMS analysis for a better knowledge of the diffusion profiles of the elements near of the solid surface.

5. Summary and Conclusions

Experimental investigations on a model-glass with a meteoritic composition altered in oxidizing conditions at different pH and temperatures give the following conclusions:

1) In each series of experiment, pH of solution increased with time. Some elements (Si, Al, K) were detected in solutions (deionized water and in sulfuric acid). In H_2SO_4 solution with pH4, Ca was also detected. In H_2SO_4 solution with pH1, all the elements were detected in solutions, especially silicon at the beginning of the experiments.

2) The solids characterization indicates the quick development of an alteration layer whose composition and structure are different according to the alteration medium. In deionized water and H_2SO_4 solution with pH4, the layer is enriched in iron. With time, this layer overlaps an other one mainly composed of Si and Al. In pH1 conditions, a silica gel layer grows with time. When hydrated, this gel layer contains also calcium and sulfate ions, which give gypsum crystallization during evaporation after extraction of the sample at the end of the experiments.

3) From the ultrathin sections analysis, one can underline the role of iron for the development of the alteration layer, especially in water and pH4 conditions. With this technique, the study of the relationship among the alteration layer and the transformed glassy matrix gave many informations from a geochemical and mineralogical point of view. The results obtained after alteration in the highest acidic conditions revealed the presence of sulfur in the alteration products.

The results obtained by experimental way, compared with those determined on natural samples, give some informations on the alteration of the meteorites under oxidizing conditions. In order to get a better comparison, other experimental conditions have to be investigated with a special insight on the effect of temperature, pressure and of S/V ratio, and with one more or less crystallized material.

Acknowledgments

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