

The ubiquitous presence of silica-rich glass inclusions in mafic minerals: Examples from Earth, Mars, Moon and the aubrite parent body

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Abstract—Highly silicic glass inclusions are commonly present in mafic minerals of xenolithic terrestrial upper mantle rocks (Schiano and Clocchiatti, 1994). They are believed to be the products of volatile-rich silicic melts for which several sources have been proposed (Francis, 1976; Frey and Green, 1974; Schiano *et al.*, 1995), but their origin(s) and, consequently, that of the glasses, remains unknown. However, *in situ* formation by very low-degree partial melting seems to be possible as has been shown by experiments (*e.g.*, Baker *et al.*, 1995; Draper and Green, 1997).

Glass inclusions of silicic chemical composition are also present in some mafic minerals of achondritic meteorites (*e.g.*, Fuchs, 1974; Okada *et al.*, 1988; Johnson *et al.*, 1991). The enstatite achondrites (aubrites) Aubres and Norton County, which record early planetesimal and planet formation in the solar nebula, and the olivine achondrite (chassignite) Chassigny, a rock believed to originate from Mars, contain abundant glass inclusions in their main minerals enstatite and olivine, respectively. Glasses of glass-bearing inclusions have a highly silicic and volatile-rich chemical composition similar, but not identical, to that of glass inclusions in terrestrial upper mantle peridotite minerals. Furthermore, glass inclusions in olivines from the Moon (*e.g.*, Roedder and Weiblen, 1977) are also silica-rich.

Because different physicochemical conditions prevail in the source regions of these rocks, the process of melting is, perhaps, not generally applicable for the generation of silica-rich glasses. Alternatively, the glasses could have been formed *via* precipitation from silicate-loaded fluids (Schneider and Egglar, 1986) or vapors. Another possible mechanism, not previously identified, could be dehydrogenation of nominally nonhydroxous mafic minerals by heating or depressurization that should be accompanied by expulsion of excess silica and incompatible elements. This process will mimic low-temperature, very low-degree partial melting. It could account also for the highly variable glass/bubble ratios observed in glass inclusions in aubrite enstatites. We suggest that such a process could have been operating in the solar nebula, the Moon and Mars, and could be operating still on Earth.

INTRODUCTION

The origin of SiO₂-rich glass inclusions in Mg-rich phases of the Earth's upper mantle is an important and still unresolved matter of debate. This also holds for the high-silica glass inclusions in the olivine of the Chassigny achondrite, a member of the Shergotty–Nakhla–Chassigny (SNC) group of meteorites that is widely believed to originate from Mars (*e.g.*, McSween, 1985), and those in enstatites of the Aubres and Norton County enstatite achondrites (aubrites). It is surprising that minerals (olivine and enstatite) that formed under contrasting conditions, highly oxidizing (in the case of Chassigny) and strongly reducing (in the case of aubrites), and also different from those prevailing in the Earth's upper mantle, contain SiO₂-rich glass inclusions of similar composition. The high content of volatiles in most of these glasses suggests that volatiles probably played an important role in their formation. In the course of our studies of glass inclusions in a variety of meteorites, we recognized the similarity of the chemical compositions of glasses from different meteorite classes and the Earth's mantle. Here we investigate this fact and try to find a mechanism for the formation of these high-silica, aluminous, alkali-rich glasses that could operate under such highly different physicochemical conditions as represented by these rocks.

ANALYTICAL TECHNIQUES

Glasses were analyzed with a Camebax electron microprobe (Centre d'Analyses Comparis, Paris VI) operated at an acceleration voltage of 15 kV, a sample current of 10 nA and a beam diameter varying from 4 to 20 μm. The precision for major element, Cl and S determinations was evaluated by replicate analyses of glass standards (Metrich and Clocchiatti, 1989) and found to be: SiO₂, 61.6 wt% (±0.7); Al₂O₃, 18.5 wt% (±0.5); Na₂O, 5.4 wt% (±0.5); K₂O, 7.9 wt% (±0.4); FeO, 2.7 wt% (±0.2); CaO, 1.8 wt% (±0.1); TiO₂, 0.4 wt% (±0.03); MgO, 0.42 wt% (±0.02); Cl, 4900 ppm (±300); S, 1200 ppm (±200). In order to evaluate the possible Na loss in high-silica glasses, SiO₂ = >70 wt%, measurements with different beam diameters (4 to 12 μm) were made of the KE12 and KN18 pantelleritic glass standards (Mosbah *et al.*, 1991) that have high SiO₂ contents (69–74 wt%). For the KE12 glass and for an initial content of 7.28 wt% Na₂O, the measured values for a beam diameter of 4, 8 and 12 μm were 6.68, 6.88 and 7.17 wt%, respectively. For the KN18 standard glass that contains 5.68 wt% Na₂O, the measured values for the same beam variation were 5.39, 5.6 and 5.6 wt%, respectively. These values are the mean of five analyses performed under the same operating conditions. However, for obtaining the

best Na₂O values, this element was analyzed with a beam diameter of 4 μm and a counting time of 1 s. For K12 and KN18, the Na₂O contents found this way are 7.20 ± 0.23 and 5.60 ± 0.24 wt%, respectively. For analysis of glass of glass inclusions, Na and SiO₂ were measured first with a counting time of 5 s and 10 s, respectively, and the maximum possible beam diameter.

The error for Cl and S analyses is estimated to be <20% as counting times were 20 s. Experiments with different beam diameter were also performed in the KN18 standard glass that contains 3700 ppm Cl. The measured mean value of five analyses each are 3300 ± 500, 3700 ± 600 and 3400 ± 200 for beam diameters of 4, 8 and 12 μm, respectively.

Heating experiments were performed on a Pt₉₀Rh₁₀ high-temperature optical stage in a He atmosphere purified with heated Zr as an O getter (Zapunny *et al.*, 1989). The final temperatures were 900, 1000 and 1200 °C and the quenching times were <1 s.

PETROGRAPHY AND MINERAL CHEMISTRY

The Norton County and Aubres enstatite achondrites (aubrites) are essentially monomineralic breccias consisting of very low-Fe enstatite (En₉₉Wo₁) up to 5 cm in size (Okada *et al.*, 1988; Reid and Cohen, 1967). The Norton County aubrite consists mainly of large angular enstatite crystals. Some Norton County enstatites have irregularly shaped diopside exsolution lamellae (40 to 3000 μm). Metallic Fe,Ni and sulfides are disseminated throughout the fine-grained enstatite matrix (Okada *et al.*, 1988).

Major and minor phases present in Aubres are enstatite, plagioclase, forsterite, troilite and diopside. Metallic Fe,Ni and related sulfides are present as inclusions in enstatite (Watters and Prinz, 1979). Large enstatites in Aubres display undulatory extinction and curved cleavage planes.

The Chassigny meteorite is a moderately shocked olivine cumulate rock (chassignite, Johnson *et al.*, 1991; Floran *et al.*, 1978) and belongs to the SNC meteorite group, a specific class of achondrites which, based on their chemical characteristics and their young ages, are thought to originate from Mars (Wasson and Wetherill, 1979; Nyquist *et al.*, 1979; Walker *et al.*, 1979; McSween and Stolper, 1980; Wood and Ashwal, 1981; McSween, 1985). Euhedral olivine (Fo₆₈) has undulatory extinction and irregular fractures. Subordinate grains of augite (En₄₅Wo₄₃) and orthopyroxene (En₇₁Wo₂) contain exsolution lamellae of each other (Le Maitre, 1976). Notwithstanding textural similarities with terrestrial olivine-rich rocks (peridotites), chassignites have a higher Fe/Mg ratio and essentially no ferric iron (Le Maitre, 1976; Floran *et al.*, 1978).

PETROGRAPHY OF GLASS INCLUSIONS

Most of the enstatites in Aubres (sections M 5620 and LS; NM, Vienna) are free of inclusions, but a few contain numerous glass inclusions. A detailed search for glass inclusions revealed the presence of three enstatite grains containing glass inclusions in one section (M 5620) and only one enstatite grain in the other (LS) (Fig. 1a–d).

In contrast, glass inclusions in Norton County (section M 5628; NM, Vienna) are distributed evenly among all enstatite grains (Fig. 2a–d). However, in a second sample (section M5628 LS1; NM, Vienna), very few enstatite grains show glass inclusions.

Inclusions in aubrite enstatites are randomly scattered throughout the host or are located in between and oriented subparallel to the cleavage planes (Fig. 3a,b). The shape of the inclusions is commonly controlled by the host's crystal symmetry ("negative crystals"), and

their size range is generally from 5 to 20 μm. One crystal in Norton County has elongated inclusions that are >100 μm long and only 8–4 μm wide (Fig. 2e,f). In Aubres, enstatites rich in glass inclusions are surrounded by inclusion-free enstatite grains. Examples are shown in Fig. 1c–f. Also, no inclusion decorating healed fractures was observed. As is evident in Fig. 2e,f, fractures crosscut pre-existing glass inclusions. The inclusions are mostly composed of glass only but some contain also a gas bubble. In Norton County, the glass/bubble ratio is highly varied even in inclusions within a single enstatite (Fig. 3b). Some enstatites show a predominance of gas-rich inclusions in certain parts (Fig. 2d). One enstatite in Norton County has a high abundance of very small subrounded inclusions mostly oriented parallel to each other. Locally, well-defined areas have linearly arranged inclusions (Fig. 1e,f). Many of these inclusions are exposed at the polished grain surface. A close inspection under reflected light revealed the presence of small, round, empty holes with no trace of glass, suggesting trapping of gas only.

No other grain with such inclusions was found. All glass inclusions in aubrites are present in enstatites that emitted an intense blue luminescence under electron bombardment.

Chassigny olivine (sections L6101, ChNN1 and ChNN2; NM, Vienna) contains round, elongated, and in some cases euhedral inclusions (<10 to 150 μm). A recent study of Chassigny glass inclusions (Varela *et al.*, unpubl. data) had the following results. Three types of glass-bearing inclusions are present in the Chassigny samples: pure glass, monocrystal and multiphase glass inclusions. Pure glass inclusions up to 20 μm in size have a subrounded shape and generally occur in clusters (Fig. 3c) or outline fractures that do not crosscut grain boundaries with only few of them being isolated. Monocrystal inclusions (glass plus one mineral grain) have a varied size (>20 to 60 μm), a subrounded shape and consist of a single euhedral low-Ca pyroxene plus glass or a chromite plus glass. Multiphase (glass plus minerals) inclusions (>20 to 150 μm) contain micrometer-sized crystals of low-Ca and high-Ca pyroxenes, troilite, chlorapatite, pentlandite, and kaersutite. The multiphase inclusions are generally isolated and only few of them form clusters. Both pure glass and multiphase inclusions can be present in a single olivine grain. Also, multiphase and monocrystal inclusions can occur together in the center of a given olivine. Round, glass-rich inclusions are also present in the center of chromite crystals. The host olivine has radial cracks surrounding all types of inclusions; however, cracks are generally spectacularly well developed around multiphase inclusions.

Glass inclusions have been extensively studied in upper mantle and in Moon rocks (*e.g.*, Roedder and Weiblen, 1970a,b; Weiblen and Roedder 1973, 1976; Schiano and Clocchiatti, 1994; Schiano *et al.*, 1992, 1994, 1995; Szabo *et al.*, 1996; Varela *et al.*, 1998). In upper mantle xenoliths, glass inclusions occur as secondary inclusions in olivine and pyroxene porphyroclasts or as primary inclusions in olivine neoblasts. They consist of glass plus a shrinkage bubble. Sometimes a CO₂ bubble is also present. Common daughter minerals are kaersutite, clinopyroxene and orthopyroxene. On the Moon, silicate-melt inclusions are present in basalts as primary inclusions in plagioclase, in the rim of pyroxene single crystals, and in olivine. They consist of colorless isotropic glass, a shrinkage bubble and some contain also an immiscible sulfide globule.

CHEMISTRY OF GLASS INCLUSIONS

The sizes of the inclusions limited the number of analyses made in a single inclusion. Only one analysis was made in each glass

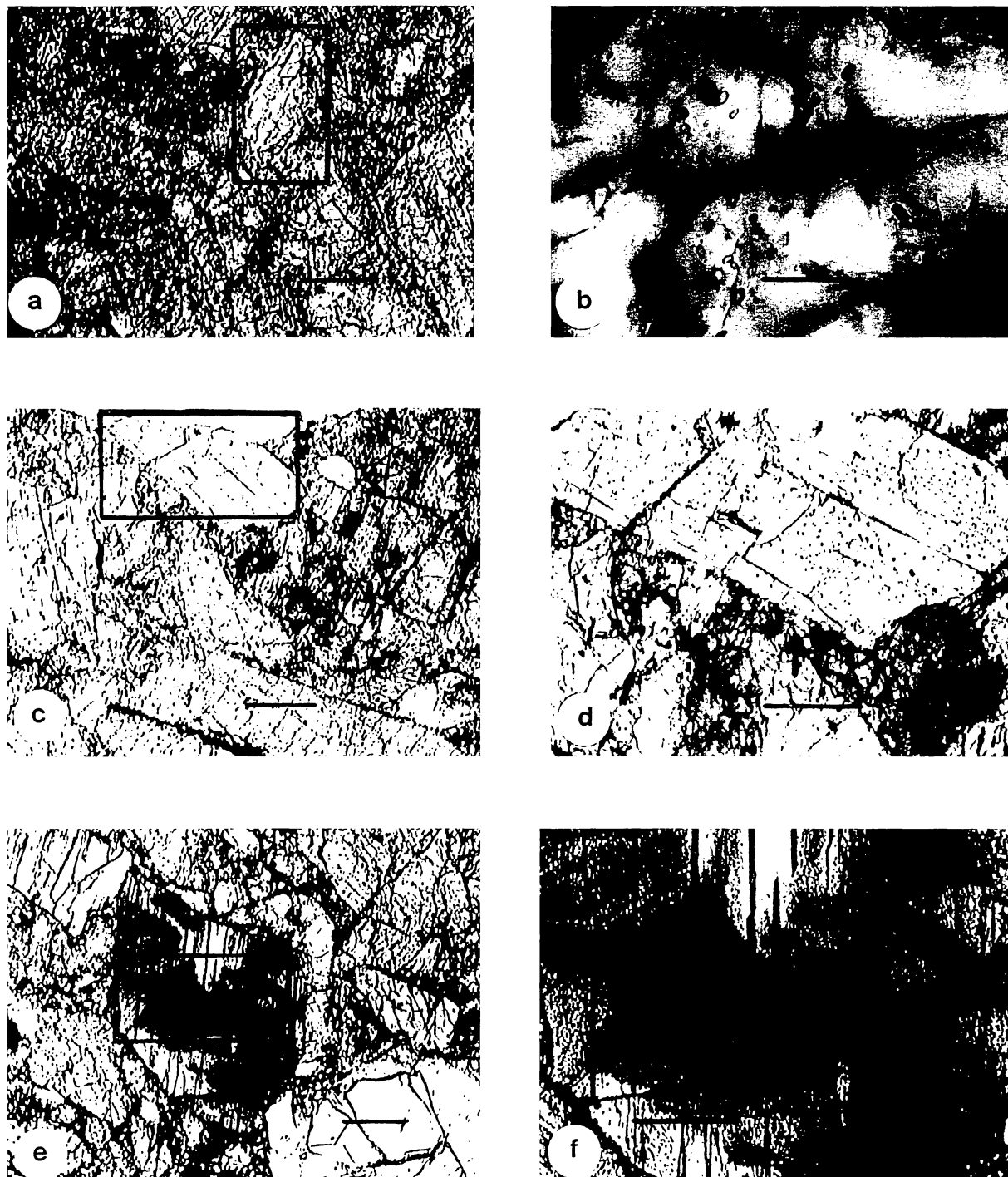


FIG. 1. Silicate glass and gas-rich inclusions in enstatite from the Aubres (section M 5620) (a and b; c and d) and Norton County (section M 5628) (e and f) meteorites in transmitted light. (a, c and e) Low-magnification photomicrographs show the occurrence of the inclusion-bearing grains in the sample. Scale bars = 200 μm . Enlargements of the marked areas on the left are shown in (b), (d) and (f). Scale bars for (b), (d) and (f) = 50 μm .

inclusion from Aubres and Norton County, with a beam diameter varying between 4 and 8 μm . Exceptions are the glass inclusions NC5 and NC6 in Norton County section M5628 LS1 (Fig. 2f) where four and three analyses were made, respectively (Table 1). In a few cases (e.g., NC2c, A1a, A1b, A4a, A4c), some excitation of the inclusion's walls by generated x-rays during analysis (fluorescence) was unavoidable.

The major element compositions of glass inclusions from all three meteorites are characterized by high contents of SiO_2 (64–80.3 wt%), Al_2O_3 (12–19.8 wt%), and Cl (100–4000 ppm); and low contents of CaO (≤ 1.3 wt%), MgO (≤ 3.5 wt%) and FeO (≤ 3.6 wt%) (Table 1). The glass in the inclusions in Aubres and Norton County has varied Na_2O (1–4 wt%), K_2O (1.5–5.5 wt%) and SO_3 (0.4–1.1 wt%) contents.

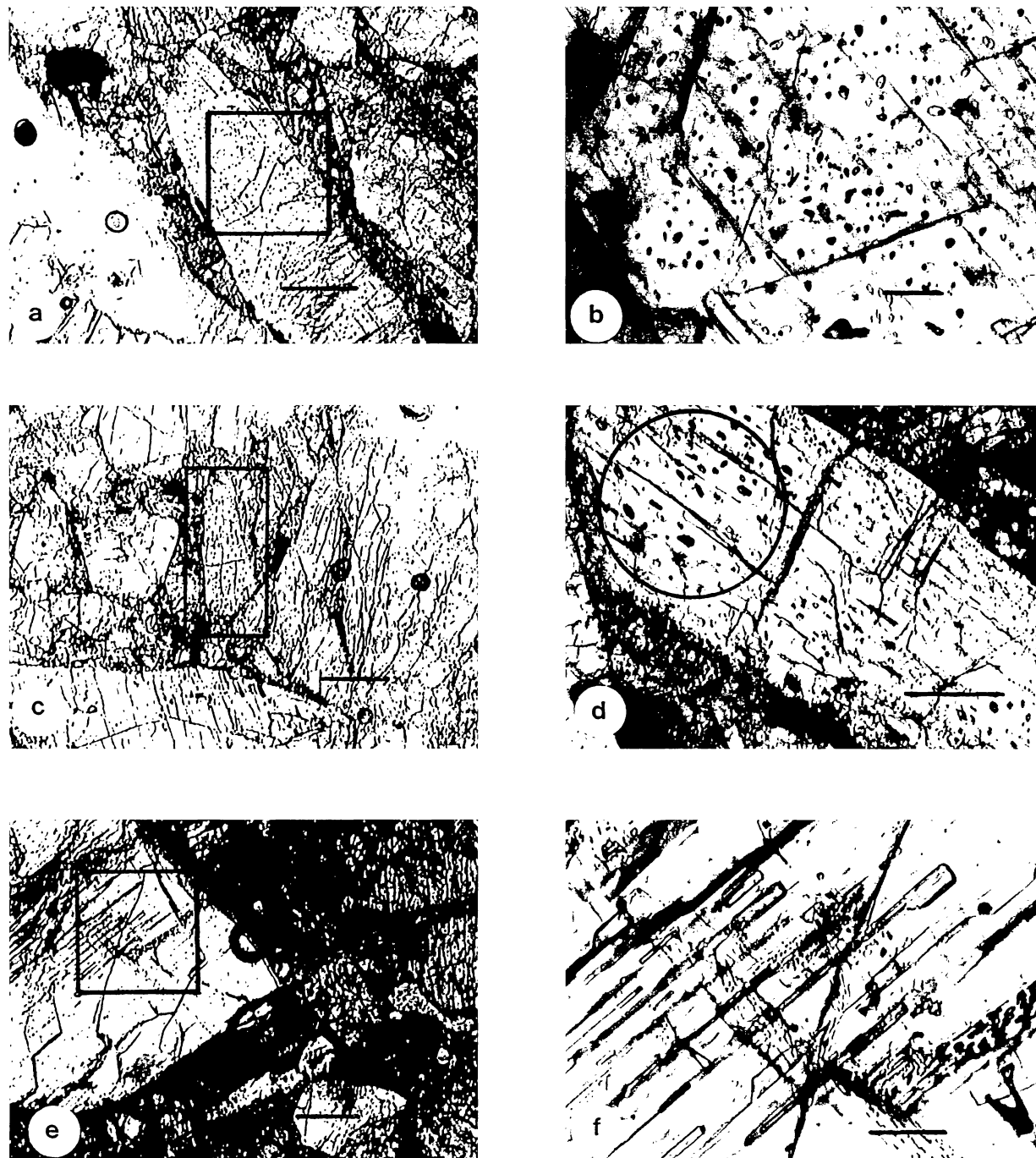


FIG. 2. Transmitted light photomicrographs of silicate glass inclusions in Norton County (sections M 5628, a–d; section M 5628 LS1, e–f). (a, c and e) Low-magnification photomicrograph showing the position of the crystal in the meteorite. Scale bars for (a), (c) and (e) = 200 μm . Photomicrographs (b), (d) and (f) are enlargements of the marked areas shown in (a), (c) and (e), respectively. Glass inclusions can have a totally random distribution (b) or are controlled by the host symmetry (d–f). The encircled area (in d) shows a part of the enstatite crystal with predominance of pure gas inclusions. Note (in f) the fractures that crosscut the preexisting glass inclusions. Scale bars for (b), (d) and (f) = 50 μm .

Glasses in the pure glass, monocrystal and multiphase inclusions in Chassigny have varied contents of Na_2O (1.5–8.2 wt%) and CaO (0.4–1.3 wt%), and consistently high contents of Cl (2500–4000 ppm). Glasses of pure glass inclusions in Chassigny form two compositional groups (Fig. 4a) with low (0.5–2 wt%) and high (4–9.5 wt%) Na_2O contents (Table 1). The Na_2O content of the glass is independent of the inclusion's size. Heating experiments were performed in glass-bearing inclusions in Chassigny. These experiments allow us to

reverse the phenomena that occurred inside the inclusion during natural cooling and, thus, allow reconstruction of the composition of the melt as it was trapped. However, the glass in the Chassigny inclusions that was heated to final temperatures of 900, 1000 and 1200 $^\circ\text{C}$, respectively, is also rich in SiO_2 (68–72 wt%), Al_2O_3 (16–18 wt%), Na_2O (3–3.7 wt%), K_2O (3–5 wt%), and FeO (2–3 wt%); and poor in MgO (0.5–2.8 wt%), CaO (1.2–1.7 wt%), and TiO_2 (0.17–0.6 wt%) (Table 1).



FIG. 3. Photomicrographs of silicate glass inclusions in achondritic meteorites. (a) Glass inclusions in enstatite from Aubres (enstatite achondrite). Their shape is controlled by the host crystal. Their occurrence between enstatite cleavage planes suggests a primary origin. (b) Glass inclusions in enstatite from Norton County (enstatite achondrite) with variable glass/bubble ratios. (c) Glass inclusions in olivine from Chassigny. Scale bars = 15 μm .

For comparison, selected glass compositions of glass inclusions in olivine of terrestrial peridotites and lunar basalt are given in Table 2. Glass inclusions in terrestrial peridotites are characterized by high contents of silica (≥ 60 wt% SiO_2), alkalis, and alumina; and low contents of MgO, FeO and CaO. Silicate-melt inclusions from lunar basalts are also rich in silica (~ 76 to 94 wt% SiO_2); have varied contents of K_2O (0.1–6.5 wt %) and Al_2O_3 (1.5–11.5 wt%); and low contents of FeO, MgO and CaO (Roedder and Weiblen, 1971, 1977)

DISCUSSION

Several processes have been invoked for the formation of silica-rich glasses in mafic minerals. In the following section, we discuss some of these processes, present evidence for and against considering them as possible mechanisms for generating the glasses described here and, finally, propose a new mechanism for silicic glass formation.

Mechanisms for Producing Silica-rich Glasses

Partial Melting—A very likely process to produce highly silicic and alkali-rich glasses in the Earth's upper mantle could be very low-degree partial melting (Schiano *et al.*, 1995; Schiano *et al.*, 1997). The high SiO_2 contents of such melts reflect a decrease of the activity coefficient of silica by the high alkali content (Kushiro, 1975; Ryerson, 1985); a hypothesis supported by near-solidus high-pressure experiments on peridotites (Baker *et al.*, 1995). Recently, Draper and Green (1997) showed that the most silica-rich glasses (>63 wt% SiO_2) in the upper mantle are difficult to explain by processes like melting of mantle peridotite under hydrous or anhydrous conditions (*e.g.*, Maaloe and Printzlau, 1979; Griffin *et al.*, 1984); melting of amphibole or phlogopite-bearing peridotites (*e.g.*, Amundsen, 1987; Francis, 1991); or by amphibole breakdown and reaction of that melt with peridotite minerals or fractional crystallization (Chazot *et al.*, 1996; Yaxley *et al.*, 1997). Under hydrous and anhydrous conditions, and for upper mantle pressures and temperatures, high-silica, aluminous, alkaline melts could reach near equilibrium with harzburgites. A low-degree partial melting of peridotites that were metasomatically enriched in alkalis and volatiles is proposed (Draper and Green, 1997) as a mechanism to form acid glasses. However, the anticorrelation of Na_2O and SiO_2 of glasses in glass inclusions described here contradicts the partial melting model.

Precipitation from Silicate-loaded Fluids—A possible alternative could be glass formation by precipitation from a silicate-loaded (\pm other species) fluid. Experimental data on the compositions of solutes from fluids (H_2O and/or CO_2) in equilibrium with mantle peridotite minerals have shown that they are characterized by a silica- and alkali-rich composition (Schneider and Eggler, 1986). The high volatile-element contents present in all the analyzed inclusions suggest that volatiles probably played an important role in the generation of high-silica glasses. Glass formation by this method appears to be viable and could account for primary and secondary glass inclusions in upper mantle minerals.

The occurrence of secondary glass inclusions in upper mantle phases, outlining healed fractures in a single crystal, or crosscutting grain boundaries, or decorating deformation lamellae in olivines, suggest migration of fluids during or after the deformation processes. Thus, they can represent only samples of silicate-loaded fluids that have already been displaced from their sources which, however, remain unknown. Also, the so-called "primary" glass inclusions in

TABLE 1. Representative analyses in glass inclusions from the Aubres, Norton County and Chassigny meteorites.

	NC1a	NC1b	NC1c	En	NC2a	NC2b	NC2c	En	NC3a	NC3b	NC3c	En	NC4a	NC4b	NC4c	En
SiO ₂	75.8	76.8	77.4	60.4	75.5	74.4	74.4	59.7	75.4	76.7	76.9	59.8	78.3	77.1	80	59.9
TiO ₂	0.00	0.15	0.00	0.00	0.00	0.02	0.17	0.18	0.03	0.00	0.01	0.03	0.00	0.00	0.02	0.07
Al ₂ O ₃	16.3	15.5	16.6	0.02	16.1	15.4	15.1	0.02	14.4	14.4	16.6	0.08	14.2	14.5	13.9	0.01
FeO	0.00	0.03	0.00	0.00	0.02	0.00	0.02	0.00	0.16	0.00	0.02	0.09	0.00	0.03	0.00	0.00
MnO	0.00	0.00	0.03	0.03	0.08	0.00	0.08	0.02	0.00	0.03	0.08	0.00	0.08	0.00	0.02	0.06
MgO	0.09	0.11	0.12	38.6	0.58	0.58	1.63	38.9	0.69	0.75	0.07	38.7	0.37	0.82	0.03	39.4
CaO	0.00	0.06	0.00	0.69	0.04	0.04	0.09	0.74	0.00	0.08	0.00	0.75	0.04	0.02	0.02	0.72
Na ₂ O	1.64	1.55	1.28	0.04	2.38	4.36	3.10	0.03	2.94	3.19	1.60	0.03	2.32	1.57	1.11	0.00
K ₂ O	3.03	2.71	2.98	0.00	2.43	2.81	2.49	0.00	2.08	2.49	2.29	0.01	2.16	2.34	2.17	0.00
SO ₃ ppm	0.43	0.51	0.37		0.36	0.40	0.40		0.74	1.15	0.50		0.87	0.69	0.71	
Total	97.29	97.42	98.78	99.78	97.49	98.01	97.48	99.59	96.44	98.79	98.07	99.49	98.34	97.07	97.98	100.2
Cl ppm	2100	2260	1700		2070	2520	1760		320	340	370		1370	2340	1240	

	A1a	A1b	A1c	En	A2a	A2b	A2c	En	A3a	A3b	A3c	En	A4a	A4b	A4c	En
SiO ₂	74.3	74.6	73.9	59.9	75.2	76.2	75.1	59.2	78.8	80.3	79.1	59.9	76.4	75.3	76.7	58.5
TiO ₂	0.04	0.00	0.00	0.00	0.09	0.08	0.00	0.00	0.04	0.1	0.04	0.00	0.01	0.00	0.02	0.07
Al ₂ O ₃	12.2	13.1	14.7	0.05	15.5	15.7	15.2	0.11	14.0	14.3	13.5	0.08	13.2	13.3	13.2	0.09
FeO	0.00	0.00	0.02	0.08	0.00	0.06	0.04	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.10	0.00
MnO	0.00	0.08	0.00	0.00	0.05	0.03	0.04	0.04	0.00	0.07	0.00	0.03	0.07	0.02	0.03	0.09
MgO	3.38	1.00	0.28	38.6	0.56	0.44	0.83	38.9	0.51	0.52	0.14	39.2	1.07	0.73	2.92	40.6
CaO	0.05	0.06	0.05	1.29	0.02	0.01	0.03	0.67	0.04	0.02	0.00	0.65	0.95	2.04	0.09	0.72
Na ₂ O	2.68	3.23	4.03	0.00	2.97	2.98	2.98	0.02	2.18	1.07	2.02	0.00	2.95	2.55	2.84	0.00
K ₂ O	5.08	5.00	5.49	0.00	2.30	1.49	2.23	0.02	1.99	1.57	1.63	0.01	2.16	2.67	1.51	0.03
SO ₃	0.41	0.41	0.47		0.63	0.72	0.62		0.56	0.56	0.79		0.55	0.56	0.48	
Total	98.14	97.48	98.94	99.92	97.32	97.71	97.07	98.98	98.12	98.51	97.24	99.87	97.36	97.17	97.89	100.1
Cl ppm	1150	1220	1290		1330	1470	1260		260	110	170		240	480	180	

	NC5*	STD	NC6*	STD	En	Ch1	Ch2	Ch3	Ch4	Ch5	Ch6	Ch7	Ch8	OI	OI
SiO ₂	73.7	0.35	75.9	0.21	60.0	64.1	67.2	75.8	75.8	68.8	69.9	71.1	70.0	37.2	36.7
TiO ₂	0.05	0.03	0.05	0.04	0.00	0.04	0.12	0.02	0.21	0.24	0.15	0.12	0.20	0.00	0.02
Al ₂ O ₃	14.4	0.03	12.8	0.08	0.04	17.4	18.9	19.8	19.3	18.2	17.5	16.4	16.8	0.03	0.02
FeO	0.06	0.05	0.02	0.02	0.02	3.62	1.44	0.58	0.72	0.85	1.19	2.08	3.28	28.3	28.4
MnO	0.01	0.02	0.02	0.03	0.24	0.00	0.00	0.05	0.06	0.04	0.06	0.04	0.11	0.63	0.51
MgO	0.04	0.01	0.06	0.02	39.1	2.59	0.49	0.04	0.04	0.03	0.83	0.52	1.16	34.3	34.3
CaO	—	—	—	—	0.71	1.27	1.22	0.78	0.33	0.49	0.81	1.24	1.31	0.09	0.16
Na ₂ O	3.62	0.09	3.03	0.09	0.00	7.36	7.69	1.62	1.57	8.15	3.67	3.78	3.62	0.00	0.00
K ₂ O	6.44	0.07	6.11	0.04	0.01	2.46	2.52	0.66	0.78	2.90	4.53	4.11	3.19	0.00	0.00
SO ₃	0.78	0.04	0.69	0.03	0.00	—	—	—	—	—	—	—	—	—	—
Total	99.10		98.68		100.1	98.84	99.58	99.35	98.81	99.70	98.72	99.43	99.74	100.6	100.1
Cl ppm	75	45	60	50		3260	4040	2660	4070	2295	—	—	—		

Groups of three glass inclusions (*e.g.*, NC1 a–c) that occur in the same host are given for Aubres (section M 5620) and Norton County (section M 5628). NC5* and NC6* are the mean value of three and four analyses, respectively (section M5628 LS1). Ch = glass-bearing inclusions in Chassigny (section L6101, ChNN1, ChNN2); Ch1–Ch5 = unheated inclusions; Ch6–Ch8 = heated inclusions.

olivine are of secondary origin because upper mantle rocks are the product of an unknown number of recrystallization events. However, glass inclusions in most extraterrestrial rocks are truly primary, as discussed below.

Fractional Crystallization and Liquid Immiscibility—Another possible process to create silica-rich glasses is fractional crystallization and liquid immiscibility. This phenomenon has been shown to be responsible for the generation of silica-rich glasses in lunar environments (Roedder and Weiblen, 1971). Some of these (*e.g.*, high-FeO melts) are difficult to detect as the melt can contain up to 80% normative pyroxene (Roedder and Weiblen, 1971). The pyroxene component can crystallize onto the walls of the host pyroxene and, thus, can go undetected (Roedder, 1984). However in our case, considering the low FeO contents of both the glass in the inclusions and that of the host pyroxene, the existence of high-FeO

melts would be rapidly detected. On careful inspection, we could not find any evidence pointing to such a silicate-silicate immiscibility in any of our samples from upper mantle and extraterrestrial sources.

Residual Glass from a Parent Magma—Glass inclusions representing residual glasses from a parent magma are known not only from the Moon but also from terrestrial rocks (*e.g.*, melt inclusions in basalt minerals that evolved by fractional crystallization). The liquid trapped in an inclusion can be clearly representative of the parent magma (Clocchiatti and Bizouard, 1979) allowing us to elucidate the processes that have affected the rocks. Experimental results (*e.g.*, heating experiments) have demonstrated that glass inclusions can be used as experimental crystallization environments (Clocchiatti and Massare, 1985). However, the silica-rich glass inclusions in upper mantle xenoliths are incompatible with such a genesis, as are also the glass inclusions in the studied meteorites.

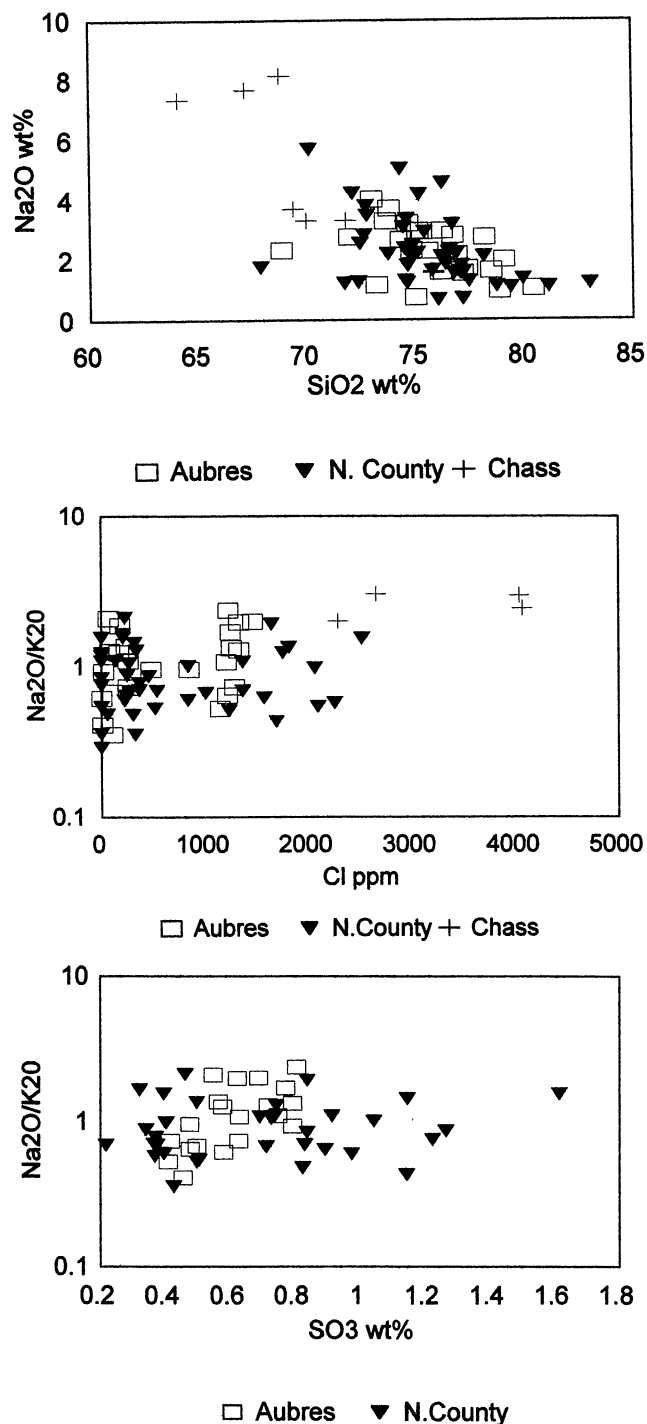


FIG. 4. Compositional variation of glasses from achondritic meteorites: (a) Na₂O vs. SiO₂, (b) Na₂O + K₂O vs. Cl and (c) Na₂O + K₂O vs. SO₃.

Silica-rich glasses in multiphase glass inclusions in the Chassigny meteorite have been interpreted as residual phases after closed system cooling (Johnson *et al.*, 1991), producing a quenched glass and an assemblage of daughter crystals. A recent report including heating experiments, detailed phase analyses, and some trace elements data on all three types of glass-bearing glass inclusions of the Chassigny meteorite (Varela, *et al.*, unpubl. data), suggested that the glass cannot be a residual melt. The glass very likely

TABLE 2. Representative glass analysis of glass-bearing inclusions from lunar basalts (M1–M3) and terrestrial upper mantle rocks (UM1–UM3) in wt%.

	M1	M2	M3	UM1	UM2	UM3
SiO ₂	93.8	75.8	76.3	61.9	65.2	67.8
TiO ₂	–	0.53	0.68	0.84	0.11	0.5
Al ₂ O ₃	1.51	11.4	11.5	17.2	19.0	16.5
FeO	2.32	2.5	3.0	1.35	0.97	0.65
MnO	–	–	0.05	0.02	–	0.00
MgO	1.61	0.25	0.07	1.70	0.60	0.20
CaO	0.06	1.80	1.60	2.47	2.02	0.60
Na ₂ O	<0.05	0.35	0.14	3.60	5.38	6.00
K ₂ O	0.11	6.4	6.7	4.04	4.89	7.10
S ppm				790	<100	<100
Total	99.4	99.0	100.8	93.4	99.3	99.4
Cl ppm				3460	7970	1160

M1 = Luna-24 drillcore material (Roedder and Weiblen, 1977); M2–M3 = Immiscible-silicate-melt inclusions (Roedder and Weiblen, 1971). Secondary glass inclusions from olivine porphyroclasts = UM1: Batan island (Schiano *et al.*, 1995); UM2: Comores Island, La Grille (Schiano and Clocchiatti, 1994); UM3: Northern Patagonia (Varela *et al.*, 1998).

represents an independent component that was trapped with or without mineral phases that could have been formed as precipitants from a fluid that existed during crystallization of Chassigny constituents.

In summary, several processes can be responsible for the formation of glass-bearing inclusions in the minerals of a variety of rocks. Low-degree partial melting appears to be a possible mechanism for the formation of acidic glasses in upper mantle rocks and has received experimental support. However, fluid precipitation in highly alkaline and CO₂-rich environments can be considered also as a likely process operating in the Earth's upper mantle. Fractional crystallization of a parent magma can give rise also to acidic glasses and is a feasible process for many magmatic rocks on any planetary body. Finally, a vapor/fluid precipitation can be considered also and could have been a likely process operating in the solar nebula.

It is surprising that this variety of processes produces glasses of similar silicic chemical composition. The glass compositions are independent of the host phase that can be silica-undersaturated olivine or silica-saturated pyroxene. The genesis of most of glass-bearing inclusions in terrestrial and extraterrestrial rocks seems to be the result of one of the above mentioned processes. However, some observations are incompatible with any of these processes suggesting that an alternative process and/or additional processing is needed.

Chemical Similarity of Glasses

It is remarkable that different minerals (olivine and pyroxene) of very different achondritic meteorites, the strongly reduced aubrites (including also Bishopville, Cumberland Falls and Shallowater; see also, Fuchs, 1974, Olsen *et al.*, 1977, Keil *et al.*, 1989), and the highly oxidized Chassigny, contain high-SiO₂ glass inclusions of similar chemical composition. They are not only rich in SiO₂ but are also rich in Na₂O, K₂O and Cl. Glass inclusions with similar chemical compositions are also present in terrestrial upper mantle peridotites and lunar basaltic rocks (Fig. 5).

Glasses of glass-bearing inclusions in aubrites and the Chassigny meteorite have similar major element contents and differ only slightly in their Al₂O₃ and Na₂O contents. However, with respect to volatile element contents, the chassignite and the aubrites clearly differ from each other. Chlorine contents vary in the aubrite glasses between 70 and 2260 ppm and S from 1640 to 3180 ppm. In contrast,

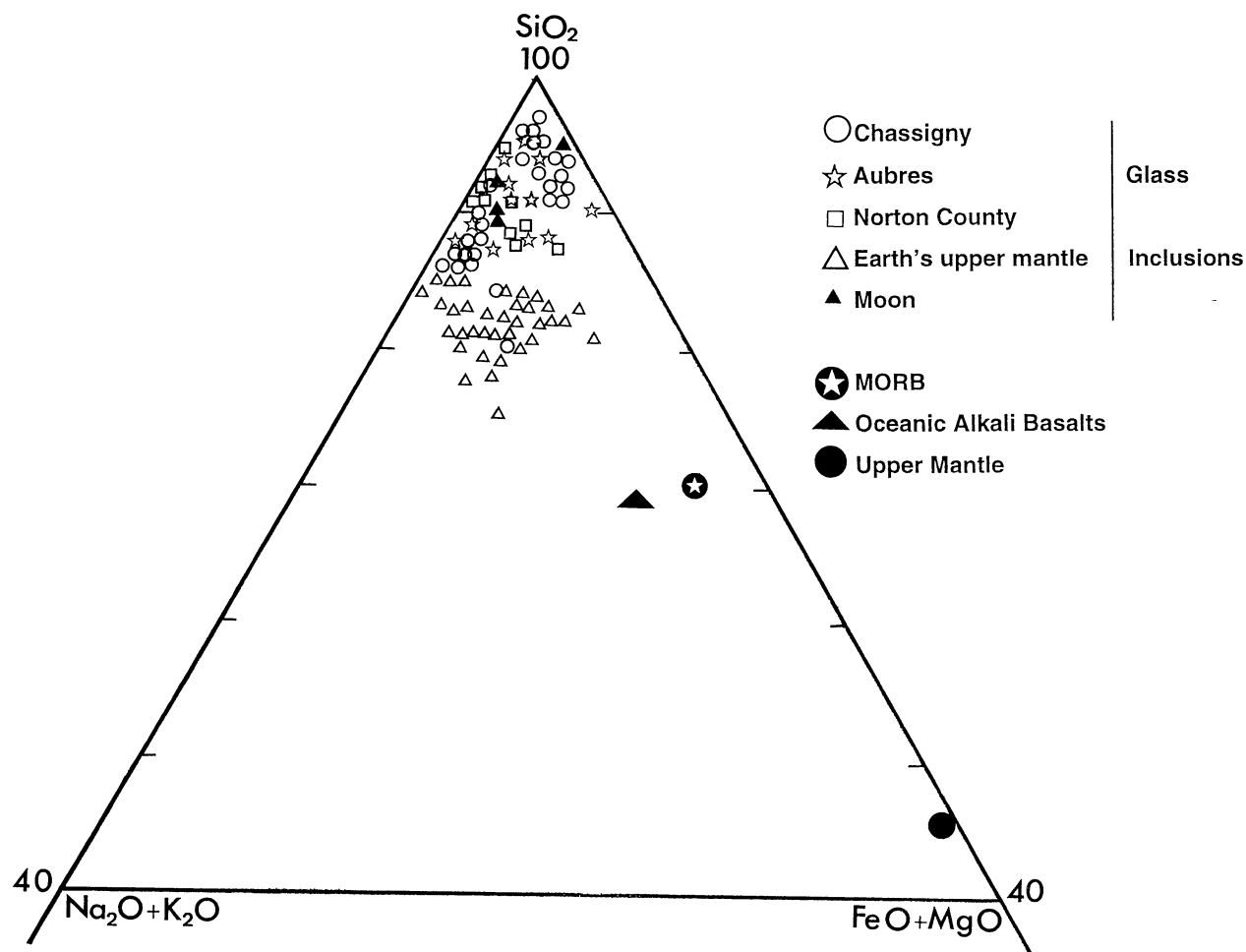


FIG. 5. Projection of the contents (in wt%) of SiO_2 –($\text{Na}_2\text{O} + \text{K}_2\text{O}$)–($\text{FeO} + \text{MgO}$) for glass inclusions in minerals from the Norton County, Aubres, and Chassigny meteorites, and terrestrial upper mantle peridotites (Schiano and Clocchiatti, 1994; Schiano *et al.*, 1995; Varela *et al.*, 1998). Compositions of typical mid-ocean ridge basalt (MORB), oceanic alkali basalt (Condie, 1982) and terrestrial upper mantle (Taylor, 1992) are added for comparison.

the glass in Chassigny is characterized by consistently high contents of Cl (2300 to 4070 ppm) and very low contents of S (<100 ppm) (Table 1). These variations in volatile elements clearly indicate different environments.

One characteristic of the inclusions in Aubres and Norton County is their high S content. Sulfur solubility in silicate melts is dependent on melt composition and decreases with increasing SiO_2 in the melt (Katsura and Nagashima, 1974). The high S concentrations of aubrite glasses very likely reflect a high S fugacity environment, which is in accordance with the sulfide mineralogy of aubrites (with sulfides of lithophile elements). The large heterogeneities in volatile element contents could be the result of an inhomogeneous source or of an incomplete metasomatic exchange between the local nebular vapor and the mineral grain (Kurat, 1988).

Glass inclusions in Aubres have similar chemical compositions in a given enstatite grain. However, compositions vary from grain to grain (Table 1). This compositional diversity is mainly due to variations in the Cl content that defines two compositional groups (Fig. 4b). Norton County has a much less heterogeneous distribution of glass inclusions compared to that of Aubres but the glass has a larger variation in SO_3 and Cl contents (Fig. 4c). The high variability in the Cl contents cannot be attributed to possible Cl migration as

demonstrated by experimental studies of Cl behavior in glasses (Métrich and Rutherford, 1992). The compositional variations could reflect differences in the source. This implies that a given enstatite crystal could not have acquired its glass inclusions in a homogenous environment. Rather it must have seen different places during growth; a condition which is almost impossible to provide by a melt, but which can easily be met by a gaseous environment, in accordance with previous observations that individual mineral grains from a meteorite record individual preaccretionary histories (Kurat, 1988).

In addition, the highly variable glass/bubble ratio of inclusions and the high abundance of pure gas inclusions in Norton County suggest that the inclusions were formed in a gas-rich environment, supporting a vapor/fluid growth origin. However, the highly variable glass/bubble ratios are hard to reconcile with a solar nebula environment as the gas pressure cannot fluctuate to an extent as indicated by the glass/bubble ratios. None of the processes identified so far for the formation of glass-bearing inclusions can account for this observation.

The composition of the glass in Chassigny multiphase inclusions (which contain several minerals in addition to glass) and that of the pure glass inclusions are similar (Table 1). This is in accordance with petrographic observations that indicate heterogeneous trapping

of the glass and preexisting minerals. If the enclosed minerals were formed from a melt by postentrapment crystallization, a chemical variability of the residual melt would be expected, and this is not observed. Moreover, the similarity of the chemical compositions of the glass in heated and unheated inclusions indicates that the glass does not represent a residual melt formed by crystallization of minerals after the inclusion was closed (Varela *et al.*, 1997). This compositional similarity of glasses of heated and unheated inclusions in olivine and pyroxenes, a feature also observed in terrestrial upper mantle rocks (Schiano *et al.*, 1992), indicates possible equilibrium between the silicic melt and the host.

Several lines of evidence point to a heterogeneous trapping of the constituents of the glass inclusions in the Chassigny meteorite. Hence, a vapor/fluid deposition appears to be a feasible process. However, inhomogeneities in glasses indicate either a secondary metasomatic alteration or a secondary origin of glasses (at least for the pure glass inclusions).

A Possible Mechanism for Glass Inclusion Formation

The similarity in chemical composition and the dissimilarity in the occurrence of glass inclusions in meteorites and the Earth's upper mantle could also be the result of a single process that could operate under a variety of conditions as provided by Earth's upper mantle, interiors and surfaces of planetesimals, and the solar nebula. A possible mechanism could be a dehydration reaction of nominally anhydrous but H-bearing mafic minerals.

Support for water being involved in small-degree partial melting processes is given by several experimental works. Hydrothermal experiments on olivine grains (1573 K and 50–300 Mpa) show that olivine can accommodate 0.0034 wt% of water (Bai and Kohlstedt, 1993). The presence of water will affect both the melting point of silicate phases (Sweeney, 1997) and the physical properties of olivine. Only trace amounts of H (0.001 wt% H₂O) are needed to weaken this silicate phase (Mackwell *et al.*, 1985).

Also substantial amounts of OH can be incorporated into the α and β phases of (Mg,Fe)₂SiO₄ at mantle pressures (Young *et al.*, 1993). Hydrothermal annealing of single olivine crystals show that the OH content in the β field is $\sim 400\,000\text{ H}/10^6\text{ Si}$ (24 000 wt ppm H₂O) at 14–15 GPa and 1100 °C (Kohlstedt *et al.*, 1996). However, diffusion of hydrogen in olivine (Mackwell and Kohlstedt, 1990) and experimental results on annealed olivines in the presence of H₂O (Miller *et al.*, 1987) suggest that the abundance of OH in olivines in the mantle could be quite different to that measured in samples derived from the mantle.

Hence, practically all phases in the Earth's upper mantle contain some H (*e.g.*, Bell and Rossman, 1992), and phases immersed in the H₂(H⁺)-rich solar nebula should also contain some H. Charge compensation in hydrogenated phases causes a nonstoichiometric ratio of octahedral (Mg²⁺, Fe²⁺) to tetrahedral (Si⁴⁺) cations according to the formula (Mg,Fe)_{2-0.5x}[SiO_{4-x}(OH)_x] for hydrogenated olivine. Changing conditions, like pressure release (in the case of upper mantle rocks) or heating (in the upper mantle and in the solar nebula), will lead to dehydrogenation of the phases that will result in a nonstoichiometric composition of the phase involved. As a consequence, the phase (*e.g.*, olivine) will expel the surplus SiO₂ resulting from the Mg deficit of the hydrogenated phase. Acid glasses were experimentally produced on olivine surfaces by laboratory-induced nonstoichiometry (Jaoul *et al.*, 1987), based on the nonstoichiometric model of Nakamura and Schmalzried (1983). Beside SiO₂, the phase will also try to expel the incompatible

elements (B, F, Na, Cl, Al, rare earth elements) that it had dissolved in the hydrogenated state (in part, as a charge compensation, *e.g.*, Al for Si and Na for Mg). In this way, silicic glasses could be formed with varying composition and in a variety of textural settings. The stress-free environment of the solar nebula could lead to pseudo-primary, exsolution-like glass inclusions; whereas, in the tectonically active terrestrial upper mantle, glass will segregate into trails and into intergranular space. This model can explain the presence of all elements in the glasses as observed in meteoritic and terrestrial settings except, perhaps, for K, an ion that appears to be too large to be accommodated by the densely packed lattices of both olivine and pyroxene. However, under very high-pressure conditions, pyroxenes accept K into their lattice (*e.g.*, Harlow, 1997) from which it will be released in case of pressure release. Thus, variable K contents of glasses in upper mantle xenoliths could be the result of variable supplies from near or far pyroxene sources and fluids. However, this mechanism does not work in the case of glass inclusions in meteoritic minerals, all of which were formed under low-pressure conditions. In this case, the varying K contents (and also the halogen contents) could be the result of metasomatic reactions with vapors of varying composition at different places; a process evident from most meteoritic components (*e.g.*, Kurat, 1988). In particular, Na/K ratios as well as halogen contents of, for example, chondrules and rock fragments in meteorites have similarly chaotic variations as those seen in the glass inclusions described here (*e.g.*, Kurat, 1984, Wasson, 1985).

This mechanism also offers a solution to the problem of highly diverse glass/bubble ratios present in aubrite enstatites. During growth from the vapor phase, variable amounts of gases will be dissolved in the mineral. The gas solubility could have been governed by the amount of stacking faults that will depend on the growth rate and the growth mechanism that could fluctuate on a small scale. As a result, the freshly grown crystal will be poorly crystallized and stuffed with incompatible elements and gases. A subsequent heating event will lead to recrystallization and expulsion of the incompatible elements, the excess silica and the gases. Expulsion will take place like exsolution normally takes place: the expelled phases will fill a space that is oriented with respect to the host's crystal structure. In this way, negative crystals could have formed, as observed. The variable glass/bubble ratios will reflect then the local amounts of stacking disorder that governs the trapping of gases.

CONCLUSIONS

Glass inclusions in olivine and orthopyroxene from achondritic meteorites (Norton County, Aubres and Chassigny) give additional evidence for the coexistence of primary high-silica glasses with ultramafic minerals. Notwithstanding the different conditions prevailing in the early solar nebula, on the Moon, on Mars, and in the Earth's upper mantle, high-silica, aluminous, alkali-rich glasses in glass-bearing inclusions are present in analogous minerals. Probably many processes are involved in their formation. Silicic glass-bearing inclusions in terrestrial and lunar igneous rocks are commonly related to fractional crystallization of trapped parental melt. Inclusions in olivine and pyroxene of upper mantle peridotites more likely are related to a very low degree of partial melting; whereas, those in achondritic meteorites more likely are precipitations from fluids and/or vapor. In addition, a new process has been identified in this study that could have been active in the solar nebula: dehydrogenation of nominally nonhydrous minerals such as olivine

and pyroxene. Such dehydrogenated phases have nonstoichiometric compositions and tend to recover stoichiometry by expulsion of SiO₂, Al₂O₃, alkalis and other incompatible elements. These compounds could precipitate as glass inside the dehydrated and recrystallized mineral and mimic primary inclusions as found in a variety of rocks. This process also offers an explanation for the highly variable glass/bubble ratios observed in glass-bearing inclusions of aubrite enstatites, as highly different amounts of gases could have been trapped by different portions of crystals growing from the vapor. These gases will be expelled together with the compounds listed above and will enter the glass-bearing inclusions, forming bubbles of sizes according to the amount of gas locally available.

Because hydrogenated, nominally nonhydrous, minerals are ubiquitously present in the Earth's upper mantle, such a mechanism could also operate on Earth and be responsible for at least some of the silicic glasses commonly found in olivines and pyroxenes of upper mantle peridotites. Consequently, it should also work on other planets as well.

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