# Highly-silicic glass inclusions in eucrites and diogenites

Kouhei Kitazato<sup>1,2\*</sup> and Masanori Kurosawa<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033

<sup>2</sup>Department of Planetary Science, Institute of Space and Astronautical Science,

Japan Aerospace Exploration Agency, Yoshinodai, Sagamihara 229-8510

<sup>3</sup>Institute of Geoscience, University of Tsukuba, Tennodai, Tsukuba 305-8571 \*Corresponding author. E-mail: kitazato@planeta.sci.isas.ac.jp

(Received December 22, 2003; Accepted August 11, 2004)

*Abstract:* Textural and chemical descriptions are reported for glass inclusions from the Dhofar 007 cumulate eucrite and the Johnstown and Tatahouine diogenites. Although previous studies described inclusions of tridymite or cristobalite, the glass inclusions found in the present samples are distributed in planar arrays transecting mineral grains, indicating a secondary origin. These glass inclusions often contain precipitated daughter minerals, such as negative crystals of chromite and troilite. Assuming each of these inclusions originally was a single phase having a homogeneous composition, EPMA and LAM-ICP-MS data suggest that the parent melts were highly silicic and sulphur-rich, and had low abundances of incompatible elements. These glass inclusions in cumulate eucrites and diogenites may be derived from silica-rich melts generated from the incongruent melting of orthopyroxene.

key words: glass inclusion, eucrite, diogenite, incongruent melting

### 1. Introduction

The eucrites are pyroxene-plagioclase achondrites with basaltic, gabbroic, or cumulus textures; diogenites are hypersthene achondrites predominantly composed of coarse orthopyroxene grains. Based on remote sensing data, both are currently believed to have originated on a single parent body, the asteroid 4 Vesta (Binzel and Xu, 1993; Gaffey, 1997). Asteroids similar in size to Vesta with only 500 km diameter could be considered not to have completely evolved magmatic processes, and these materials may contain important information about the early stages of asteroidal and planetary formation in the solar system. Although these rocks experienced significant postcrystallization shock and thermal metamorphism (Metzler *et al.*, 1995; Yamaguchi *et al.*, 1996), information about early igneous processes may remain in the microaccessory regions of the minerals.

Glass inclusions, which represent tiny droplets of melt trapped within mineral grains or mesostatis, commonly occur in both terrestrial and extraterrestrial materials. These glass inclusions are considered to preserve information about (1) magmatic processes and fluid circulation and (2) degassing and shock melting resulting from

impact. Although these inclusions have been reported in eucrites and diogenites since the early days of petrography, relatively few detailed studies have been conducted on them. Most of these previous studies have described them as silica polymorphs, tridymite or cristobalite (e.g., Gooley and Moore, 1976; Papike *et al.*, 2000; Benzerara *et al.*, 2002). In the present study, we investigated the textures and the chemical characteristics of glass inclusions in one cumulate eucrites and two diogenites in order to gain insights into formation mechanisms.

## 2. Experimental

Polished thin and thick sections were prepared from hand specimens of the Dhofar 007 cumulate eucrite and the Johnstown and Tatahouine diogenites. The polished thin sections were examined by optical microscopy, and then were carbon-coated using a high-vacuum coating system. A scanning electron microscope (SEM) was used to obtain backscattered electron images. For glass inclsuions and their host minerals, abundances of the major elements SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, FeO, MnO, NiO, MgO, CaO, Na<sub>2</sub>O, and  $K_2O$  were measured with an electron probe microanalyzer (EPMA), JEOL JXA-8621, at the University of Tsukuba, Japan. The microprobe was operated at an accelerating voltage of 20 kV, a beam current of 10 nA, a beam diameter of 12 microns and a counting time of 20 s. Approximate compositions of individual phases in multiphase inclusions were determined with a beam defocused to a diameter of ~8 microns. Corrections were made using the oxide ZAF program. Abundances of trace elements Na, Si, Ca, Sc, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Yb, Hf, Pb, Th, and U were measured for glass inclusions in thick sections with a Laser Ablation Microprobe Inductively Coupled Plasma Mass Spectrometry (LAM-ICP-MS), a PerkinElmer Sciex ELAN6000, at the Venture Business Laboratory of the University of Tsukuba, Japan. Details of the analytical technique are described in Kurosawa et al. (2002). The data acquisition was performed in time-resolved signal mode, as signal intensity versus time plot with progressing analysis. For each analysis, data were acquired for 2 min: 60 s prior to ablation (gas blank) to establish instrumental background and 60s after initiation of ablation. The laser ablation pit was  $\sim$ 20 microns in diameter. When the pit size was larger than the inclusion size, a correction method similar to that employed by Halter et al. (2002) was used for determination of the trace element abundances of inclusions to avoid contamination by their matrices. In the correction method, trace element concentrations in the inclusions are quantified based on a relative difference of ablation signals and trace element contents in the host mineral.

## 3. Results

#### 3.1. Textures of inclusions

The Dhofar 007 cumulate eucrite is a monomict breccia derived from a magmatic rock having a gabbroic texture consisting of subhedral grains (0.2-0.8 mm) of pyroxene and plagioclase. Accessory minerals include metal, troilite, and chromite. Floran *et al.* (1981) described the Johnstown diogenite as a brecciated orthopyroxenite that is predominantly composed angular to subrounded clasts of orthopyroxene in a variably

comminuted matrix of the same material. Minor phases include plagioclase, troilite, chromite, ilmenite, and Fe-Ni metal. The Tatahouine diogenite is a shocked orthopyroxenite consisting mostly of unbrecciated coarse orthopyroxene crystals with fractures (*e.g.*, Lacroix 1931, 1932; Gooley and Moore 1976; Benzerara *et al.*, 2002). The orthopyroxene crystals from our sample also have a mosaic texture when observed at extinction using a polarizing microscope.

The samples considered in this study display several glass inclusions representing a homogeneous melt and contained in pyroxene and plagioclase grains. These inclusions are distributed in planar arrays transecting the host mineral grains. Figure 1a shows the distribution of glass inclusions in a host plagioclase crystal from the Dhofar 007. Comparatively large particles with high refractive index are orthopyroxene grains, which have a poikilitic texture. Distribution of glass inclusions in Johnstown and Tatahouine also is similar to that of Dhofar 007 (Fig. 1b). Moreover, the textures of glass inclusions found in our samples were revealed from backscattered electron images. For Dhofar 007 (Fig. 2a), most glass inclusions in host plagioclase crystals are rounded and up to approximately 10 microns in size. These inclusions usually contain gas bubbles formed from shrinkage during cooling, and one or more opaque grains, presumably troilite. In Johnstown, most glass inclusions in host orthopyroxene crystals are commonly multiphase with daughter crystals such as chromite, metal, and troilite. These daughter crystals are euhedral to subhedral in shape and represent a small



Fig. 1. Optical photomicrographs showing the distributions of tiny glass inclusions; (a) in a single host plagioclase crystal in Dhofar 007 cumulate eucrite, and (b) in a single host orthopyroxene crystal in Johnstown diogenite. Both with transmitted light, opened polars.

Glass inclusions in eucrites and diogenites



Fig. 2. Backscattered electron images showing glass inclusions; (a) in a host plagioclase crystal in Dhofar 007, indicating multiphase consisting of gas bubbles and one or more opaque minerals, presumably troilite, (b) in a host orthopyroxene crystal in Johnstown, containing troilite and chromite, and (c) in a host orthopyroxene crystal in Tatahouine.

proportion of the volume of the inclusion. In addition, particularly in Johnstown, these glass inclusions are elongated along the cleavage directions of the host orthopyroxene crystals. In Tatahouine, the most abundant glass inclusions are amoeboid in shape and single phase with minor troilite (Fig. 2c). Actually glass partitions of these inclusions found in our samples could be crystallized by thermal annealing and be modified a silica polymorph, such as tridymite or cristobalite.

## 3.2. Chemical compositions for inclusions

Representative major element compositions of glass and daughter minerals in

	Dhofar 007	Johnstown				Tatahouine
	Bulk	Glass	Chromite	Troilite	Bulk	Bulk
SiO <sub>2</sub> (wt %)	84.07	98.13	0.02	0.00	92.64	88.95
TiO <sub>2</sub>	1.07	0.06	0.71	0.00	0.10	0.07
$AI_2O_3$	10.26	0.12	8.78	0.00	0.59	0.54
Cr₂O₃	0.02	0.13	56.06	0.00	3.15	0.33
FeO	0.61	0.95	29.84	81.59	2.66	5.21
MnO	0.03	0.06	0.64	0.01	0.10	0.23
NiO	0.00	0.06	0.04	0.00	0.06	0.01
MgO	0.03	0.25	2.79	0.00	0.39	3.99
CaO	3.73	0.21	0.00	0.02	0.20	0.39
Na₂O	0.12	0.03	0.11	0.09	0.04	0.27
K₂O	0.06	0.00	0.02	0.01	0.00	0.01
Sum	100.00	100.00	99.00	81.72	99.91	100.00

Table 1. Selected representative analyses by EPMA for glass inclusions in Dhofar 007, Johnstown and Tatahouine.

Note: for Johnstown, the bulk composition was calculated using average volume ratios of each mineral phase.



Fig. 3. Ternary diagram showing projection of the contents (in wt%) of SiO<sub>2</sub> (Na<sub>2</sub>O+K<sub>2</sub>O), and (MgO+FeO) for bulk components of glass inclusions in the Dhofar 007, Johnstown, and Tatahouine. For purpose of comparison, the diagram includes the values of glass inclusions in other materials, determined by previous studies: Norton County, Aubres, and Chassigny (Varela, et al., 1998), Apollo samples 15598, 62295, and 67915 (Weiblen and Rodder, 1973), terrestrial upper mantle peridotites (Schiano and Clocchiatti, 1994; Schiano, et al., 1995), and the Roda diogenite (Mittlefehldt, 1994).

inclusions, acquired by EPMA, are given in Table 1. It was assumed that the each glass-bearing multiphase inclusion originally was a homogeneous melt and that the assemblage of crystals and glass presently comprising the inclusion were the result of



Fig. 4. Abundances of representative trace elements determined by LAM-ICP-MS for glass inclusions trapped in host orthopyroxene crystals from Johnstown. The abundances are normalized to the CI concentrations of Anders and Grevesse (1989).

subsequent closed system crystallization. Original melt compositions were calculated using volume ratios of individual phases and plotted on a ternary diagram projecting ratios of  $SiO_2-(Na_2O+K_2O)-(MgO+FeO)$  (Fig. 3). For the purpose of comparison, compositions of glass inclusions in aubrites, SNC meteorites (Varela, *et al.*, 1998), lunar samples (Weiblen and Rodder, 1973), Earth's upper mantle materials (Schiano and Clocchiatti, 1994; Schiano *et al.*, 1995), and the Roda diogenite (Mittlefehldt, 1994) are also plotted. The glass inclusions in Dhofar 007, Johnstown, and Tatahouine are highly silicic, similar to the other compositions that are plotted. The inclusions analyzed in the present study, however, are depleted in alkalis.

The relatively large glass inclusions in Johnstown were analyzed using LAM-ICP-MS. Figure 4 compares the abundances of representative trace elements in the inclusions and those of the host orthopyroxenes. The abundances of La, Ce, Pr, and Nd in the inclusions from Johnstown could be determined above the detection limits, because they have higher concentrations than the host orthopyroxene. For Dhofar 007, the inclusion sizes were extremely small, and, hence, the trace element contents are qualitatively represented (Fig. 5). In Fig. 5, the abundances represent mixtures of the inclusions and the matrix anorthite. The silica content of anorthite is approximately 50 wt% and that of the inclusion is almost 100 wt%, thus the silica-rich data in Fig. 5 mean a value of the inclusions with the lowest contamination by the matrices. Abundances of Rb, Sr and Ba are positively correlated with SiO<sub>2</sub> (Fig. 5a–c), whereas abundances of Pb are negatively correlated (Fig. 5d). These relationships could indicate a slight enrichment of Rb, Sr and Ba and the absence of significant quantities of Pb in the silica-rich inclusions.

## 4. Discussion

The glass inclusions in Dhofar 007, Johnstown, and Tatahouine have highly silicic compositions and are depleted in alkalis as compared with those in other meteorites. Although silicate melts can be produced by low-degree partial melting of peridotites, the resultant melts have not highly silicic composition but only basaltic, and contain a high



Fig. 5. Trace element variation diagrams for glass inclusions added to matrix plagioclase crystals from Dhofar 007.

concentration of incompatible elements (Kushiro, 1975; Baker *et al.*, 1995). The inclusions analyzed in the present study are almost pure silica and are not very rich in incompatible elements. Thus, these inclusions appear to be produced by another formation mechanism. Schiano *et al.* (1995) suggest that silicic-rich glasses in the Earth's upper mantle could be generated from a very low degree of partial melting of mafic minerals. A dehydrogenation of nominally anhydrous mafic minerals by heating or depressurization has also been proposed as a possible formation mechanism (Varela *et al.*, 1998). However, in contrast to the results reported here, formation of silica-rich melts in clinopyroxene-bearing rocks by both mechanisms should be accompanied by enrichments of alkali and incompatible elements. In addition, a highly silicic melt (~100% SiO<sub>2</sub>) should react with olivine during the migration of melt, so the formation of the present inclusions requires generation in an olivine-absent system.

A highly silicic melt can be produced in the early stages of incongruent melting of clinopyroxene, as estimated from melting experiments of clinopyroxene (Doukhan *et al.*, 1993; Raterron *et al.*, 1995). In addition, the melt generated from orthopyroxene is expected to be lower in contents of incompatible elements than that produced from clinopyroxene-bearing rocks such as basalt, because of low abundances of incompatible

elements in orthopyroxene as compared with clinopyroxene. Therefore, our results are consistent with a silica-rich melt generated from the incongruent melting of olivineabsent orthopyroxenite. For Dhofar 007, formation of the inclusions in host plagioclase might be considered by capturing incongruent melts of orthopyroxenite from insights into their major compositions. It remains unclear if the melting event that formed these secondary inclusions resulted from thermal heating or from shock-induced breakdown of pyroxene.

Based on the above evidence from these inclusions, they cannot have originated from a late stage residual melt on the parent body. The occurrence of these secondary glass inclusions, outlining healed fractures in a single crystal, suggests migration of melts after the crystallization process. Although the migration of highly silicic melts generally is considered to be difficult because of high viscosity, the viscosity of the original melts of the glass inclusions analyzed might have decreased because of the enrichment in sulphur.

Consideration of the data reported above allows an interpretation of the possible petrogenesis of these glass inclusions. First, silica-rich melt penetrated into fractures in the host mineral. Later annealing healed the fracture and tiny droplet glass inclusions remained. Then, the daughter minerals precipitated from the inclusion melt during cooling, and, finally, the remaining silicic melt solidified. By this time, the glass inclusions were modified to the shape of negative crystals, which were elongated along the cleavage direction of the host mineral orthopyroxene. In the case of Tatahouine, host minerals and inclusions later were deformed by strong shock metamorphism, and the glass inclusions have amoeboid shapes and are arranged in non-crystallographic planar arrays.

## 5. Conclusions

We investigated textural and compositional characteristics of the glass inclusions found in a cumulate eucrite and two diogenites. These secondary inclusions are highly silica-rich and sulphur-rich, and have low abundances of incompatible elements. These inclusions might have formed from the melts produced by incongruent melting of orthopyroxene. Petrogenesis of primary inclusions remains unclear.

#### Acknowledgments

The authors wish to thank to Prof. A. Fujiwara, Dr. H. Yano, Dr. M. Abe and Dr. S. Hasegawa, for constructive discussion and information, to Dr. P.C. Buchanan and Dr. A. Pun for helpful reviews that greatly improved the quality of this manuscript.

#### References

Baker, M.B., Hirschmann, M.M, Ghiorso, M.S. and Stolper, E.M. (1995): Compositions of near-solidus peridotite melts from experiment and thermodynamic calculations. Nature, 375, 308–311.

Anders, E. and Grevesse, N. (1989): Abundances of the elements: meteoritic and solar. Geochim. Cosmochim. Acta, 53, 197–214.

- Benzerara, K., Guyot, F., Barrat, J.A., Gillet, P. and Lesourd, M. (2002): Cristbalite inclusions in the Tatahouine achondrite: Implications for shock conditions. Am. Mineral., 87, 1250–1256.
- Binzel, R.P. and Xu, S. (1993): Chips off Asteroid 4 Vesta: Evidence for the parent body of basaltic achondrite meteorites. Science, 260, 186–191.
- Doukhan, N., Doukhan, C., Ingri, J., Jaoul, O. and Raterron, P. (1993): Early partial melting in pyroxenes. Am. Mineral., 78, 1246–1256.
- Floran, R.J., Prinz, M., Hlava, P.F., Keil, K., Soettel, B. and Wanke, H. (1981): Mineralogy, petrology, and trace element geochemistry of the Johnstown meteorite: a brecciated orthopyroxene with siderophile and REE-rich components. Geochim. Cosmochim. Acta, 45, 2385–2391.
- Gaffey, M.J. (1997): Surface lithologic heterogeneity of asteroid 4 Vesta. Icarus, 127, 130-157.
- Gooley, R. and Moore, C.B. (1976): Native metal in diogenite meteorites. Am. Mineral., 61, 373-378.
- Halter, W.E., Pettke, T. and Heinrich, C.A. (2002): Major to trace element analysis of melt inclusions by laser-ablation ICP-MS: methods of quantification. Chem. Geol., 183, 63–86.
- Kurosawa, M., Jackson, S.E. and Sueno, S. (2002): Trace element analysis of NIST SRW 614 and 616 glass reference material by laser ablation microprobe-inductively coupled plasma-mass spectrometry. J. Geostand. Geoanal.; Geostand. Newsl., 26, 75–84.
- Kushiro, I. (1975): On the nature of silicate melt and its significance in magma genesis: Regularities in the shift of the liquidus boundaries involving olivine, pyroxene and silica minerals. Am. J. Sci., 275, 411– 431.
- Lacroix, A. (1931): Sur la chute recente (27 Juin 1931) d'une meteorite asiderite dans l'Extreme Sud tunisien. C.R. Acad. Sci., Paris, **193**, 305-309.
- Lacroix, A. (1932): La meteorite (diogenite) de Tatahouine, Tunisie (27 Juin 1931). Bull. Soc. Fr. Mineral., 55, 101–122.
- Metzler, K., Bobe, K.D. Palme, H., Spettel, B. and Stöffler, D. (1995): Thermal and impact metamorphism of the HED parent asteroid. Planet. Space Sci., 43, 499–525.
- Mittlefehldt, D.W. (1994): The genesis of diogenites and HED parent body petrogenesis. Geochim. Cosmochim. Acta, 58, 1537-1552.
- Papike, J.J., Shearer, C.K., Spilde, M.N. and Karner, J.M. (2000): Metamorphic diogenite GRO95555: mineral chemistry of orthopyroxene and spinel and comparisons to diogenite suite. Meteorit. Planet. Sci., 35, 875–879.
- Raterron, P., Ingri, J., Jaoul, O., Doukhan, N. and Elie, F. (1995): Early partial melting of diopside under high pressure. Phys. Earth Planet. Iner., 89, 77–88.
- Schiano, P. and Clocchiatti, R. (1994): Worldwide occurrence of silica-rich melts in sub-continental and sub-oceanic mantle minerals. Nature, 368, 621–624.
- Schiano, P., Clocchiatti, R., Shimizu, N., Maury, R.C., Jochum, K.P. and Hofmann, A.W. (1995): Hydrous, silica-rich melts in the sub-arc mantle and their relationship with erupted arc lavas. Nature, 377, 595– 600.
- Varela, M.E., Kurat, G., Clocchiatti, R. and Schiano, P. (1998): The ubiquitous presence of silica-rich glass inclusions in mafic minerals: Examples from Earth, Mars, Moon and the aubrite parent body. Meteorit. Planet. Sci., 33, 1041-1051.
- Weiblen, P.W. and Rodder, E. (1973): Petrology of melt inclusions in Apollo samples 15598 and 62295, and of clasts in 67915 and several lunar soils. Proc. Lunar Sci. Conf., 4th, 681–703.
- Yamaguchi, A., Taylor, G.J. and Keil, K. (1996): Global crustal metamorphism of the eucrite parent body. Icarus, **124**, 97-112.