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Glasses in coarse-grained micrometeorites

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ABSTRACT

Micrometeorites (MMs, interplanetary dust particles with 25 – 500 µm diameters) carry the main mass of extraterrestrial matter that is captured by Earth. The coarse-grained MMs mainly consist of olivine aggregates, which - as their counterparts in CC chondrites - also contain pyroxenes and glass. We studied clear glasses in four coarse-grained crystalline MMs (10M12, M92-6b, AM9, and Mc7-10), which were collected from the ice at Cap Prudhomme, Antarctica. Previous studies of glasses (e.g., glass inclusions trapped in olivine and clear mesostasis glass) in carbonaceous and ordinary chondrites showed that these phases could keep memory of the physical-chemical conditions to which extraterrestrial matter was exposed. Here we compare the chemical compositions of MM glasses and glasses from CM chondrites with that in experimentally heated objects from the Allende CV chondrite and with glasses from cometary particles. Our results show that MMs were heated to variable degrees (during entry through the terrestrial atmosphere), which caused a range from very little chemical modification of the glass to total melting of the precursor object. Such modifications include dissolution of minerals in the melted glass precursor and some loss of volatile alkali elements. The chemical composition of all precursor glasses in the MMs investigated is not primitive such as glasses in CM and CR chondrite objects. It shows signs of pre-terrestrial chemical modification, e.g., metasomatic enrichments in Na and Fe^{2+} presumably in the solar nebula. Glasses of MMs heated to very low degree have a chemical composition indistinguishable from that of glasses in comet Wild 2 particles; giving additional evidence that interplanetary dust (e.g., Antarctic MMs) possibly represents samples from comets.

1. Introduction

Micrometeorites (MMs) are the most common extraterrestrial matter collected by the Earth and constitute a class of their own with relationships to CM, CR and CI chondrites (Kurat et al., 1992, 1994) and comets (e.g., Maurette et al., 1996). Recent studies of glass inclusions in minerals and mesostasis glass in a variety of meteorites were rewarding and led to the formulation of a new model for the formation of chondritic constituents and also non-chondritic meteoritic rocks (Varela et al., 2005, 2006; Varela and Kurat 2006; Engler et al., 2007). As no such data exist for MMs, we started a study of coarse-grained crystalline types with porphyritic texture (Varela and Kurat, 2008). Glasses are very abundant in melted (e.g., cosmic spherules) and partially melted (scoriaceous) MMs (e.g., Kurat et al., 1994; Genge et al., 2008) but particular types of glasses, such as primary glass inclusions hosted by olivine and clear mesostasis glass, have not been investigated so far. With this contribution, we want to begin to fill this gap with the hope to answer some questions, such as: Are glass inclusions present in olivines of MMs? If yes, are these glasses pristine or of secondary origin? And what modifications have they experienced during atmospheric entry?

Here we present our results obtained on MMs that were collected from the Antarctic ice near Cap Prudhomme (e.g., Maurette et al., 1991), which allow us to give preliminary answers to these question.

2. Analytical techniques and samples

Major element chemical compositions of glasses were obtained with a JEOL 6400 analytical scanning electron microscope (NHM, Vienna) as well as a SX100 CAMECA electron microprobe (Department of Lithospheric Research, University of Vienna). Microprobe analyses were performed at 15 kV acceleration potential and 10 nA sample current. Analyses of minerals and glasses were performed with both, a focused (~1 µm) and a defocused beam (5 µm). The samples were first analyzed for Na with a counting time of 5 s (in order to prevent premature Na loss from glasses) followed by the analysis of all other elements with a counting time of 10 s. Basaltic and trachytic glasses (ALV 981 R24 and CFA 47; Métrich and Clocchiatti, 1989) were used as standards and the on-line ZAF program was used for corrections.

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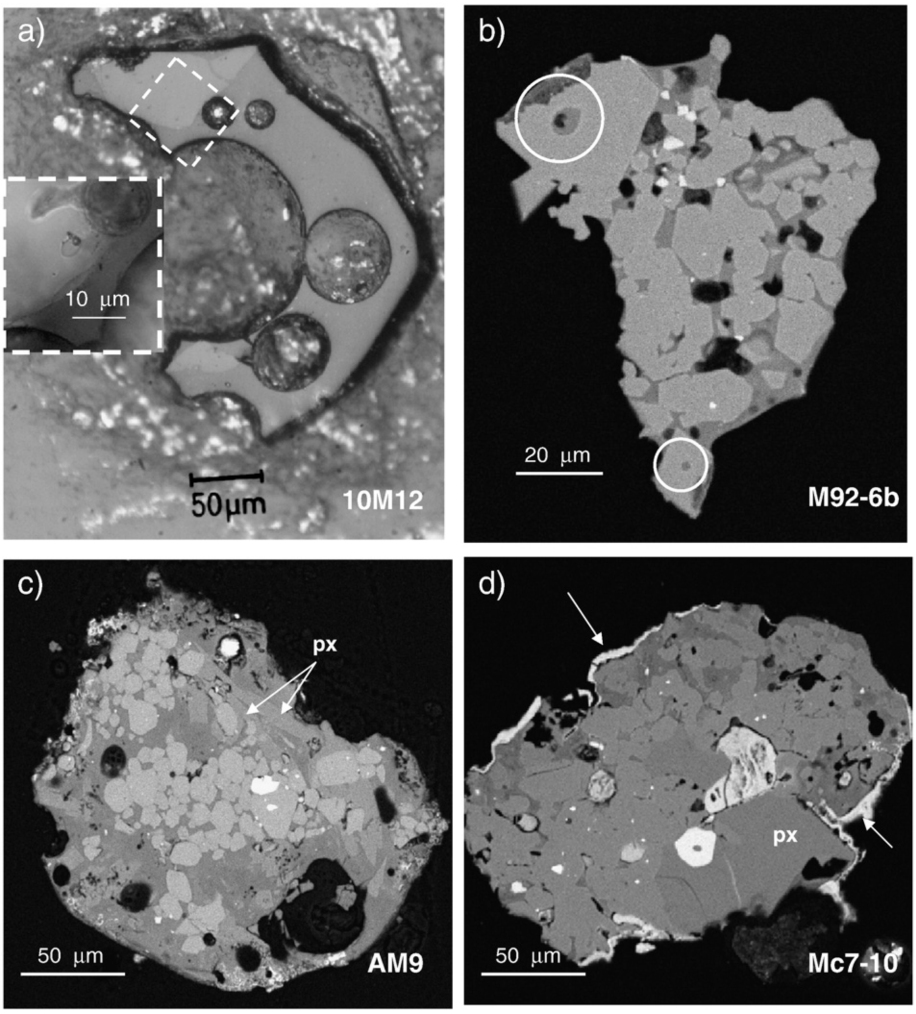

Fig. 1. a) Micrometeorite 10M12 consists of clear glass with large bubbles and two olivine crystals. One of them has a glass inclusion (inset). b) Micrometeorite M92-6b has a porphyritic texture with olivine phenocrysts set into a clear glassy matrix. Two olivines have glass inclusions. c) Micrometeorite AM9 contains aggregates of olivines, a few large augites (px) and many bubbles in abundant mesostasis glass. d) Micrometeorite Mc7-10 consists of a compact mosaic intergrowth of olivine and pyroxene (px) with small amounts of interstitial glassy mesostasis. Arrows point to the incomplete thin magnetite mantle.

Twenty polished sections (NHM, Vienna) of micrometeorites collected at Cap Prudhomme by expeditions led by Michel Maurette (e.g., Maurette et al., 1991), each of them containing between 5 and 15 MMs, were optically inspected. Only 4 MMs (10M12, M92-6b, AM9 and Mc7-10) were found to contain glass inclusions in olivine and/or clear mesostasis glass of a size needed for an accurate investigation.

3. Results

Micrometeorites labeled M92-6b, AM9 and Mc7-10 are of the coarse-grained crystalline type as define by Kurat et al. (1994). The most typical example of such crystalline MM is **Mc7-10**, which has a rectangular shape with about 230 µm longest dimensions. It consists of a compact mosaic intergrowth of olivine and pyroxene with small amounts of glassy mesostasis (Fig. 1d). Large and small patches of iron oxides (former metal and sulfides) and chromites are dispersed throughout the particle. This MM is incompletely covered by a thin magnetite mantle – a remnant of the fiery entry through the Earth's atmosphere (e.g., Kurat et al., 1994; Toppani et al., 2001). We previously classified this MM as one of the very rare possible ordinary chondrite (OC) particles among MMs with a relationship to H chondrites (Walter et al., 1995).

Micrometeorite **M92-6b** has an irregular shape with about 110 µm longest dimension and a porphyritic texture with olivine phenocrysts set into a clear glassy matrix (Fig. 1b). Two olivines contain glass inclusions. The mesostasis contains also abundant bubbles and a few small chromite crystals. The particle has no magnetite cover and appears to be a fragment of a former larger unit of porphyritic olivine-rich rock. We classify it as a coarse-grained crystalline MM.

Micrometeorite **AM9** has an elongated shape with about 200 µm longest dimension, contains aggregates of olivines, a few large augites and many bubbles, some plagioclase (An12) and a few sulfides (11 w% Ni) in abundant mesostasis glass (Fig. 1c). Part of its surface is rounded and only sparse magnetite coating is present in places. This MM has been previously studied by EMPA and INAA and was classified as coarse-grained crystalline MM by Kurat et al. (1994) – a coarse-grained chondritic MM (CgMM) according to Genge et al. (2008).

Micrometeorite **10M12** has the shape of a half moon with about 310 µm longest dimension (Fig. 1a). It consists mainly of clear glass with some large bubbles and two olivine crystals, one of which contains a glass inclusion. We classify this object as a broken hollow sphere. However, according to Genge et al. (2008) it could be a partially melted coarse-grained CgMM type.

Vesicles are present in all four MMs. They are large in MMs 10M12 and AM9 and small in M92-6b and Mc7-10 (Fig. 1).

All four MMs contain clear mesostasis glass. Primary glass inclusions in olivine are present in MMs 10M12 and M92-6b only. They range in size from 5 to 10 µm, are isolated and consist of clear glass and a shrinkage bubble (Fig. 1). The very small size of inclusion M92-6b-2 and the lack of a shrinkage bubble (lower center in Fig. 1b) indicate that possibly a major part of the inclusion's volume was lost during preparation.

The chemical compositions of silicate phases are given in Table 1 and glass compositions are projected in Figs. 2 (a-b) and 3 (a-k).

Glasses are Si-Al-rich with high and variable contents of MgO, FeO, CaO, Na_2O, and K_2O. The major element chemical composition of glasses of the primary glass inclusion and the mesostasis in 10M12 are Al-poor and Mg-rich and similar to each other. Only slight variations are observed in the contents of CaO, FeO and Al_2O_3 (Table 1).

The two glass inclusions in olivine of MM M92-6b show some variations in the chemical composition as compare to the glass inclusion in 10M12 in being richer in Al_2O_3 (~13 wt%) and K_2O (mean: 0.8 wt%) and poorer in MgO (mean: 5.2 wt%) and CaO (mean: 5 wt%). Mesostasis glasses in MMs M92-6b and 10M12 have different CaO and MgO contents, which are lower in M92-6b (mean: 3.8 wt% and 5 wt%, respectively) than in 10M12 (mean: 7.7 wt% and 13 wt%, respectively).

The mesostasis glass of AM9 as compared to Mc7-10 (both MMs consist mainly of olivine, glass and pyroxenes) has a low content of SiO_2 (mean: 57 wt%) and high contents of Al_2O_3 (mean: 17.7 wt%), FeO (mean: 5.2 wt%), MgO (mean: 4.6 wt%), K_2O (1.7 wt%), and a very high content of Na_2O (mean: 10.5 wt%), (Table 1).

All olivines have high contents of FeO, ranging from 16.6 to 33.3 wt%. Those present in MMs M92-6b, AM9 and Mc7-10 have variable minor element contents as follow: all three MMs have high contents of MnO (0.43 - 0.59 wt%), CaO (0.36 – 0.61 wt% in M92-6b and AM9) and Cr_2O_3 (0.35 – 0.40 in M92-6b). High-Ca pyroxene (augite) in AM9 contains some Na_2O (~1.2 wt%), is rich in Cr_2O_3 (0.5 – 1.4 wt%) and TiO_2 (~0.7 wt%) and contains only 1.3 – 1.5 wt% Al_2O_3. Low-Ca pyroxene (large euhedral crystal in lower right corner of Fig. 1d) in Mc7-10 is poor in TiO_2, Cr_2O_3 (0.2 wt%) and Al_2O_3 (0.3 wt%).

4. Discussion

Micrometeorites (MMs) - dust particles of 25 – 500 μm diameters - carry the main mass of interplanetary dust that is captured by the Earth today (e.g., Love and Brownlee, 1993; Jessberger et al., 2001). Thus, they comprise the main mass of extraterrestrial matter collected by the Earth, outweighing meteorites by a factor of >100. Micrometeorites represent a class of extraterrestrial matter that is mainly akin to CM (and to a much lesser degree to CR and CI) chondrites (all together constitute <3% of meteorite falls), but appears to be somewhat different (e.g., Kurat et al., 1994; Engrand et al., 1999). They also appear to be different from small dust particles collected in the stratosphere ("stratospheric interplanetary dust particles" – see Jessberger et al., 2001) but not from small MMs collected from Antarctic ice (Gounelle et al., 2005b). Apparently, the mineralogical differences are due to collection biases rather than different sources (e.g., Jessberger et al., 2001). Micrometeoroids – as all interplanetary dust particles - have a short life expectancy in space and because of this, among other reasons, are also likely to be mainly cometary matter replenished by comets traveling the inner solar system (e.g., Whipple, 1967; Maurette et al., 1996; Gounelle et al., 1998; Maurette, 2006). Indeed, investigation of ~1500 MMs from Greenland and Antarctica revealed a possible presence of ordinary chondrite matter, which dominates the meteorite population with ~80% of falls, of <1% (e.g., Walter et al., 1995) and only one possible achondritic particle was found so far (Gounelle et al., 2005a). Thus, the asteroid belt seems not to contribute very much to the contemporary interplanetary dust.

Our studies on MMs collected from the Earth's polar regions revealed that the dust consists of a collection of objects, which are also known from CM, CR and CI chondrites. These objects comprise aggregates of phyllosilicates and CC matrix-like phyllosilicate rocks, single minerals (olivine or low-Ca pyroxene), aggregates of Mg silicates with variable amounts of FeO (olivine and pyroxene), calcium-aluminum-rich inclusions (CAIs), and very rare chondrule fragments (Kurat et al., 1992, 1994; Hoppe et al., 1995; Kurat et al., 1996). Olivine (+/- pyroxene) aggregates are common and comprise the main mass of coarse-grained crystalline MMs. Their counterparts in CC chondrites have comparable mineral composition and phase associations, i.e., pyroxenes and glassy mesostasis can be present.

4.1. Glasses in carbonaceous chondrites (CCs)

In carbonaceous chondrites, clear glasses (with no sign of devitrification) occur either as primary glass inclusions in olivine or as mesostasis. They are characterized by having a major element composition dominated by SiO_2, Al_2O_3 and CaO with chondritic CaO/Al_2O_3 and Al_2O_3/TiO_2 ratios and low contents of alkalis, FeO and MgO (e.g., Varela et al., 2002, 2005). These glasses are also rich in refractory lithophile trace elements with abundance patterns that signal vapor fractionation. The fact that glasses do not show the chemical signature of crystallization of the minerals they are associated with has led us to propose that glasses could represent the first liquid to condense in the early solar nebula (e.g., Kurat et al., 2004; Varela et al., 2005, 2006). These liquids are an important phase for the genesis of chondritic constituents and have a cosmochemically refractory chemical composition. However, this initial composition of glasses has commonly been modified by secondary processes - as proposed by, e.g., Kurat et al. (1997), Varela et al. (2002) and Engler et al. (2007) – which resulted in a large variety of chemical compositions as represented by glasses in, e.g., oxidized CV chondrites such as Allende and ordinary chondrites.

Table 1
Major element composition of silicate phases in MMs (EMPA in wt%).

	10M12					M92-6b									
	Glass			Olivine		Glass					Olivine				
	Mesostasis	Mesostasis	GI 10M	Host GI -c-	Host GI -s-	Mesostasis	Mesostasis	Mesostasis	GI 92-6b1	GI 92-6b2	Host (GI 92-6B1)	Host (GI 92-6b2)	ol	ol	ol
SiO_2	56.0	56.9	56.9	39.4	38.9	52.7	59.8	61.1	53.8	53.7	36.8	37.1	37.1	37.0	36.7
Al_2O_3	8.1	8.2	7.6	bdl	bdl	9.2	14.4	13.9	12.3	13.5	0.06	0.02	0.03	0.04	0.02
TiO_2	0.35	0.33	0.25	0.03	0.06	0.44	0.64	0.64	0.46	0.56	bdl	bdl	bdl	bdl	bdl
Cr_2O_3	0.21	0.19	0.31	0.01	0.03	0.09	0.09	0.04	0.14	0.07	0.41	0.29	0.39	0.40	0.35
FeO	8.7	8.4	9.7	16.9	16.6	17.3	9.32	8.17	9.6	11.9	28.7	28.2	28.5	28.3	28.4
MgO	13.4	12.4	9.5	44.1	44.0	10.2	2.41	2.36	7.3	3.05	33.3	33.6	33.4	33.2	32.9
MnO	0.32	0.33	0.27	0.47	0.42	0.38	0.20	0.18	0.18	0.17	0.46	0.48	0.46	0.49	0.49
CaO	7.7	7.7	8.5	0.02	0.04	3.8	4.20	3.47	6.1	4.02	0.35	0.38	0.36	0.36	0.39
Na_2O	3.81	3.75	3.00	bdl	bdl	3.62	2.37	3.36	2.10	4.73	bdl	bdl	bdl	bdl	bdl
K_2O	0.62	0.74	0.20	bdl	bdl	0.83	1.08	0.89	0.40	1.24	0.03	0.03	bdl	bdl	bdl
Total	99.2	98.9	96.2	100.9	100.1	98.6	94.4	94.2	92.4	92.9	100.1	100.0	100.2	99.8	99.2

References: Host GI -c- (-s-): Host of glass inclusion analyzed in the center (-c-) and near de surface (-s-); ol: olivine; px: pyroxene; GI 10M: Glass inclusion 10M.

Nebular metasomatic processes during cooling have been identified to be mainly responsible for such modifications, commonly addressed as "alterations" (e.g., Varela et al., 2002, 2005, 2006; Libourel et al., 2006).

In addition, also post-formational heating events can severely modify glass compositions, mainly because re-melted glass does dissolve the co-existing minerals, which the original liquid glass precursor precipitated. Laboratory heating experiments of glass inclusions in minerals aim to reverse the post-entrapment processes that took place inside inclusions during cooling. In doing so, they bring the glass inclusions and their host to a state very close to that prevailing during entrapment. Several studies that have explored post-entrapment reactions (e.g., Gaetani and Watson, 2000) show that for incompatible (with respect to the host olivine) trace elements, the glass inclusions behave as isolated chemical system. However, this is not the case for the diffusionally readily exchangeable major elements such as Fe and Mg. For example, one of the principal processes taking place during heating is dissolution of the surrounding olivine in the liquefied glass inclusion, which modifies the initial composition of the glass by increasing the MgO and decreasing the CaO and Al_2O_3 contents (Varela, 2008). Because glass inclusions and mesostasis glasses represent different systems, it is necessary to make a distinction between the behavior of a glass inclusion - that generally behaves as a closed system - and that of the mesostasis (open systems), which are more sensible to record the latest conditions to which the object has been exposed. Thus, if objects were affected by a thermal event, we should expect the chemical compositions of inclusion and mesostasis glasses (initially Al-Ca-Si-rich) to show significant chemical changes (Varela, 2008).

Comparison of the chemical composition of glasses from MMs with that of experimentally heated chondritic glasses shall help us to estimate the degree of heating experienced by MMs during terrestrial atmospheric entry.

In addition, we shall also compare the chemical composition of MM glasses with that of the mean bulk composition of coarse-grained crystalline Antarctic MMs (Bulk CG, Kurat et al., 1994) and the bulk composition of CM chondrites (Bulk CM, Lodders and Fegley, 1998). Considering that primary glass inclusions represent the cosmochemically refractory component of chondrules, we compare also MM glass compositions with that of the mean of 36 primary glass inclusions in olivines of the CM chondrites Murchison, Acfer 094, Mighei, Murray, Yamato 82042, and Mokoia (G.I. CM). Finally, because MMs are possible samples from comets (e.g., Maurette et al., 1996), we also compare our data with those acquired from dust samples of comet Wild 2 collected by the Stardust Mission (Nakamura et al., 2008).

As MMs seem to be relatives of CC constituents and did experience a heating event of unknown intensity during their entry through the Earth's atmosphere, it is very likely that the chemical composition of MM glasses was modified. This can be clearly observed in Fig. 2a between the primitive CC glasses [high Al_2O_3, low (FeO + MgO) contents] and the bulk composition of crystalline MMs (Bulk CG). The chemical composition of most CC clear glasses (glass inclusions and mesostasis) are very similar to each other – inclusive those of unheated Allende objects. In spite of the fact that MMs likely are relatives of CM chondrites, their glass compositions project far apart. However, average glass compositions of MMs project into the same area that is also populated by the average chemical composition of Allende heated glasses (glass inclusions as well as mesostasis glass, Fig. 2a, Table 2). The addition of MgO to glasses of MMs is coupled with a decrease in their CaO content that places them off the main trend defined by glasses of all CCs (e.g., trend define by the mean values of CR, CV and CM chondrites, Fig. 2b).

Although the CV3 carbonaceous chondrites (e.g., Allende, Kaba, Vigarano) are believed to have passed various types of alteration processes, including thermal metamorphism (Krot and Scott, 1995), the presence of delicate textures, chemical disequilibria (e.g., olivine fa50 co-existing with Fe-poor diopside, see, e.g., Kurat et al., 1989), and radiation damaged olivine (Zolensky et al., 1997) let such an event appear to be unlikely. This holds for most CCs – e.g., MacPherson and Davis (1997), Kurat (1997),Weisberg and Prinz (1998), and Brenker et al. (2000).

Heating experiments on glass-bearing objects of the Allende CV3 chondrite are the only ones ever performed on CC objects. Consequently, they provide the only set of data for comparisons of chemical compositions of unheated and heat-treated glasses. For a detailed description of the heating experiments please see Varela (2008).

4.2. Glasses in micrometeorites and chondrites

The data base built on analyses of about 400 glasses of primary glass inclusions in olivines of carbonaceous (CC) and ordinary chondrites (OC) documents that the FeO and MgO contents of such glasses are generally low, <4.5 and <7 wt%, respectively (Kurat, 1967; Fuchs et al., 1973; Olsen and Grossman, 1978; Varela et al., 2005, Engler et al., 2007, inset in Fig. 3a). Glasses in MMs of this study (with exception of Mc7-10 and one datum of AM9) have high contents of FeO and MgO as compared to those of CC and OC glasses (Fig. 3a). They are also higher than those of unheated mesostasis glass of Allende objects (Fig. 3b). The contents of both elements are, however, within the range of those found in experimentally heated glasses from Allende (Fig. 3b, Varela, 2008), suggesting that glasses in MMs have suffered a thermal event.

If the bulk composition of the coarse-grained crystalline MMs (Kurat et al., 1994) and that of CM chondrites (Lodders and Fegley, 1998) is taken into account, the high FeO and MgO contents of glasses in MMs 10M12 and M92-6b clearly indicate that they have been secondarily heated to high temperatures. The glass composition of CS 10M12 pro-

AM9											Mc7-10					
Glass					Olivine			Pyroxene			Glass		Olivine			Pyroxene
Mesostasis	Mesostasis	Mesostasis	Mesostasis	Mesostasis	ol	ol	ol	px	px	px	Mesostasis	Mesostasis	ol	ol	ol	px
58.5	55.3	58.8	55.4	57.3	35.8	35.6	35.8	51.8	52.4	51.8	67.4	64.6	38.7	39.5	38.7	55.7
17.2	17.6	18.3	15.0	20.3	bdl	0.03	0.02	1.32	1.54	1.37	21.3	18.8	bdl	bdl	bdl	0.3
0.43	0.29	0.46	0.52	0.33	bdl	bdl	bdl	0.69	0.84	0.64	0.05	0.07	0.04	bdl	bdl	0.2
0.00	0.04	0.07	0.06	0.05	0.19	0.11	0.10	1.40	0.54	1.41	0.00	0.04	0.16	0.02	bdl	0.2
6.1	6.6	4.74	5.1	3.41	33.3	32.4	32.6	6.5	6.4	6.6	0.40	2.97	17.6	17.2	16.9	10.5
4.55	5.5	4.29	5.9	2.79	29.3	29.7	29.8	14.2	14.6	14.1	0.29	4.99	42.3	43.2	42.7	31.3
0.24	0.22	0.17	0.25	0.10	0.49	0.59	0.55	0.25	0.27	0.25	0.04	0.09	0.43	0.44	0.46	0.5
1.41	2.69	3.67	4.54	2.66	0.48	0.61	0.58	21.9	22.4	22.1	2.53	2.62	0.02	bdl	0.02	0.7
10.16	10.77	6.82	12.71	12.09	bdl	bdl	bdl	1.24	1.16	1.18	7.38	3.32	bdl	bdl	bdl	bdl
1.82	1.54	1.84	1.32	1.52	bdl	bdl	bdl	bdl	bdl	bdl	0.77	0.73	bdl	bdl	bdl	bdl
100.4	100.6	99.1	100.8	100.5	99.6	99.1	99.5	99.3	100.2	99.5	100.2	98.3	99.3	100.4	98.7	99.4

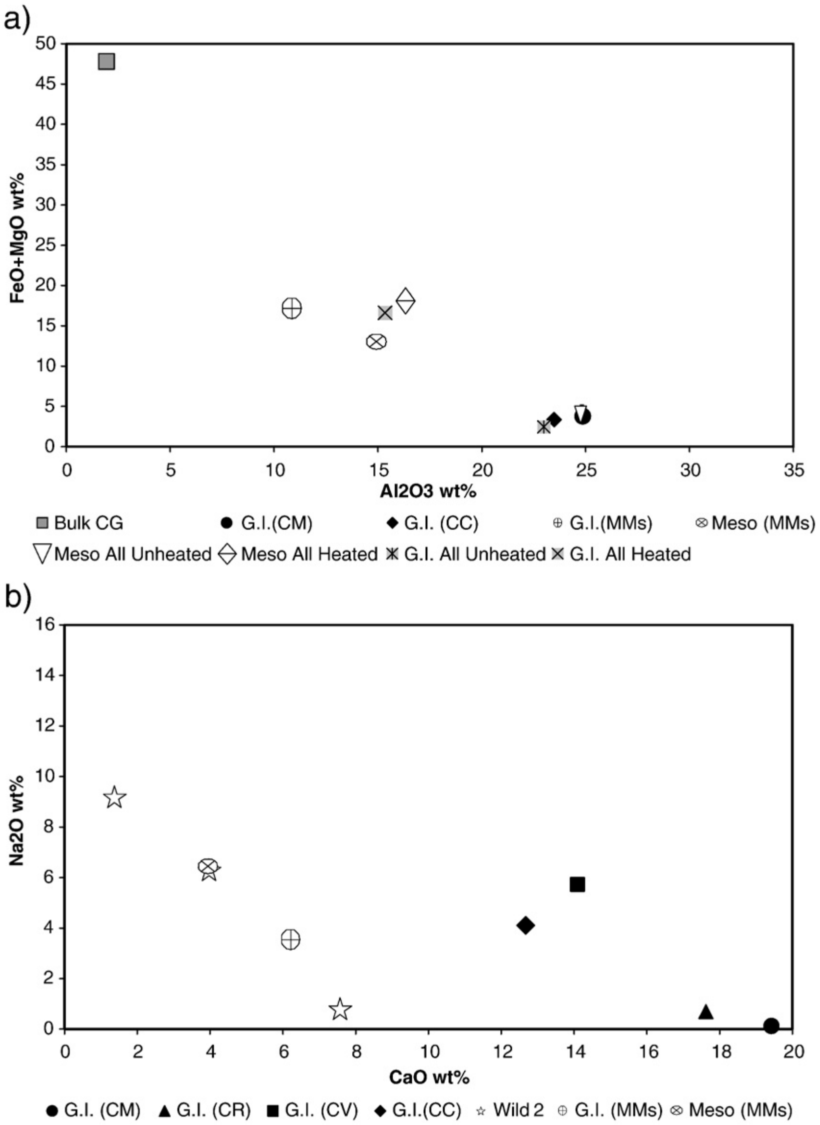

Fig. 2. a) (FeO + MgO) vs. Al_2O_3 mean contents of glasses of glass inclusions (G.I.) in CM chondrites (CM), carbonaceous chondrites (CC, includes data on CR-CM-CV-CO3-CO4-C4-C2), micrometeorites (MMs), Allende unheated (All Unheated), Allende heated (All Heated), as well as mesostasis of micrometeorites (Meso MMs). Bulk CG used here and in the following diagrams refers to bulk composition of coarse-grained crystalline Antarctic MMs (Kurat et al., 1994). G.I. (CM) used here and in the following diagrams refers to the mean of 36 primary glass inclusions in olivines of the CM chondrites Murchison, Acfer 094, Mighei, Murray, Yamato 82042 and Mokoia. b) Na_2O vs. CaO mean contents of glasses in glass inclusions (G.I.) of CM, CV, CR, and other CCs and MMs, mesostasis in micrometeorites (Meso MMs) and glasses in particles from comet Wild 2. Wild 2, used here and in the following diagrams refers to glasses in dust samples of comet Wild 2 collected by the Stardust Mission (Nakamura et al., 2008).

glass composition) with the bulk composition of crystalline MMs (representing mainly olivine and some pyroxene). This indicates dissolution of olivine and pyroxene in a melted precursor mesostasis. Also, the composition of the glass from 10M12 is similar to that of glasses of Allende chondrules which were experimentally heated to high temperature (1450 °C). Thus, from the high contents of FeO and MgO in 10M12 we can conclude that it likely experienced total melting.

As was previously mentioned, the addition of FeO and MgO to the glass (e.g., by dissolution of olivine) will decrease the initial Al_2O_3 and CaO contents as is documented by the negative correlation between (FeO + MgO) and Al_2O_3 (Figs. 2a and 3c) contents. Glasses in MMs seem to project close to a mixing line between two compositions: one close to the mean of 36 Ca-Al-rich pristine glass inclusions in olivines from CM chondrites [G.I. (CM)] and the bulk compositions of coarse–grained crystalline MMs [Bulk (CG)] and CM chondrites [Bulk (CM)]. However, the fit is not perfect and most glass compositions project below that mixing line indicating either a non-pristine original composition or another chemical modification in addition to the dissolution of Fe-Mg silicates. A similar negative (FeO + MgO) vs. Al_2O_3 correlation is also observed with compositions of unheated and heated glasses of the Allende CV3 chondrite (Fig. 3d). A clear conclusion can be drawn from these elemental projections: MM glasses have high FeO and MgO contents because they represent liquids which dissolved variable quantities of Fe-Mg silicates in a heating event. The highest T apparently was encountered by CS 10M12, followed by MMs M92-6b, AM9 and Mc7-10. Glasses from Mc7-10 project closest to the pristine and refractory Al-rich glass composition.

The CaO content of glasses should - similar to the Al_2O_3 content – also be negatively correlated with the MgO and FeO contents (Varela, 2008). However, MgO (and FeO) and CaO contents of glasses in MMs are positively correlated (Fig. 3e). This is clearly different from the negative correlation shown by the heated glasses of Allende (Fig. 3f). The latter form a mixing line between a refractory component rich in CaO and poor in MgO [e.g., the G.I. (CM)] and the bulk of CM chondrites (Bulk CM). Because the most severely experimentally heated Allende glasses project onto the same place as do 10M12

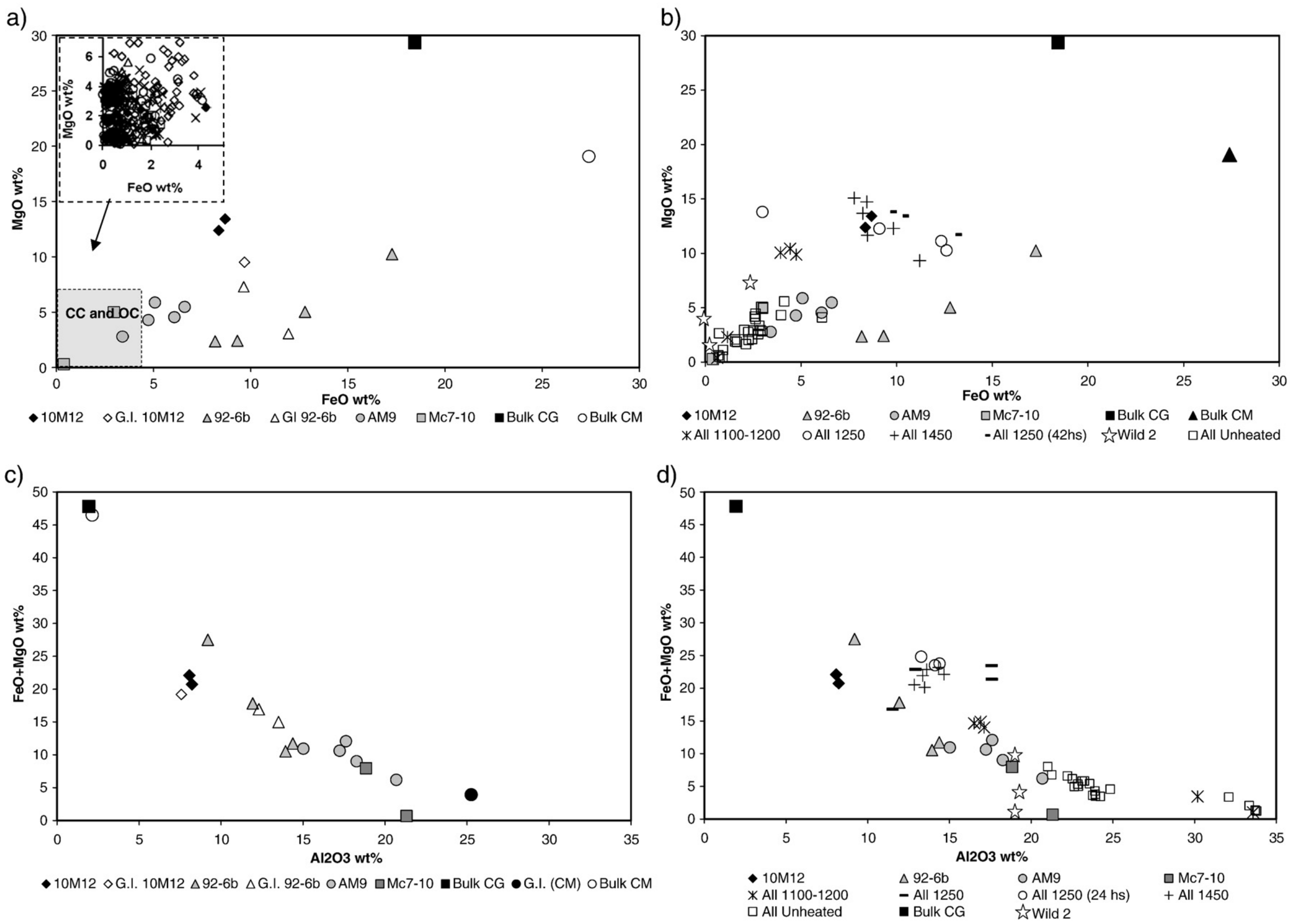

Fig. 3. a) FeO vs. MgO contents of glasses in MMs. Inset shows the FeO vs. MgO contents of inclusion glasses in CCs and OCs. Bulk CM used here and in the following diagrams refers to bulk composition of CM chondrites (Lodders and Fegley, 1998). b) FeO vs. MgO contents of glasses in MMs, unheated and heated mesostasis glasses from the Allende CV3 chondrite (Varela, 2008). Numbers indicate the final temperature of heating experiments, for example: All 1250 (24 hs) refers to glasses heated to a final temperature of 1250 °C that was kept during 24 hs. All Unheated used here and in the following diagrams refers to Allende unheated mesostasis glass (Varela, 2008). c) (FeO + MgO) vs. Al_2O_3 contents of glasses in MMs and d) compared to heated and unheated glasses from the Allende CV3 chondrite, the Bulk CG MMs and Wild 2 dust. e) MgO vs. CaO contents of glasses from MMs, and f) compared to heated and unheated mesostasis glass from Allende CV3 chondrite, Bulk CG, Bulk CM, and Wild 2 dust. g) CaO vs. Al_2O_3 contents of glasses in MMs, and h) compared to heated and unheated mesostasis glass from Allende CV3 chondrite, Bulk CG, Bulk CM, G.I. (CM), and Wild 2 dust. i) Na_2O vs. CaO contents of glasses in MMs and j) compared to heated and unheated mesostasis glass from Allende CV3 chondrite, Bulk CG, Bulk CM, G.I. (CM), and Wild 2 dust. k) TiO_2 vs. Al_2O_3 contents of glasses in MMs and heated and unheated mesostasis glass from Allende CV3 chondrite, Bulk CG, Bulk CM, G.I. (CM), and Wild 2 dust.

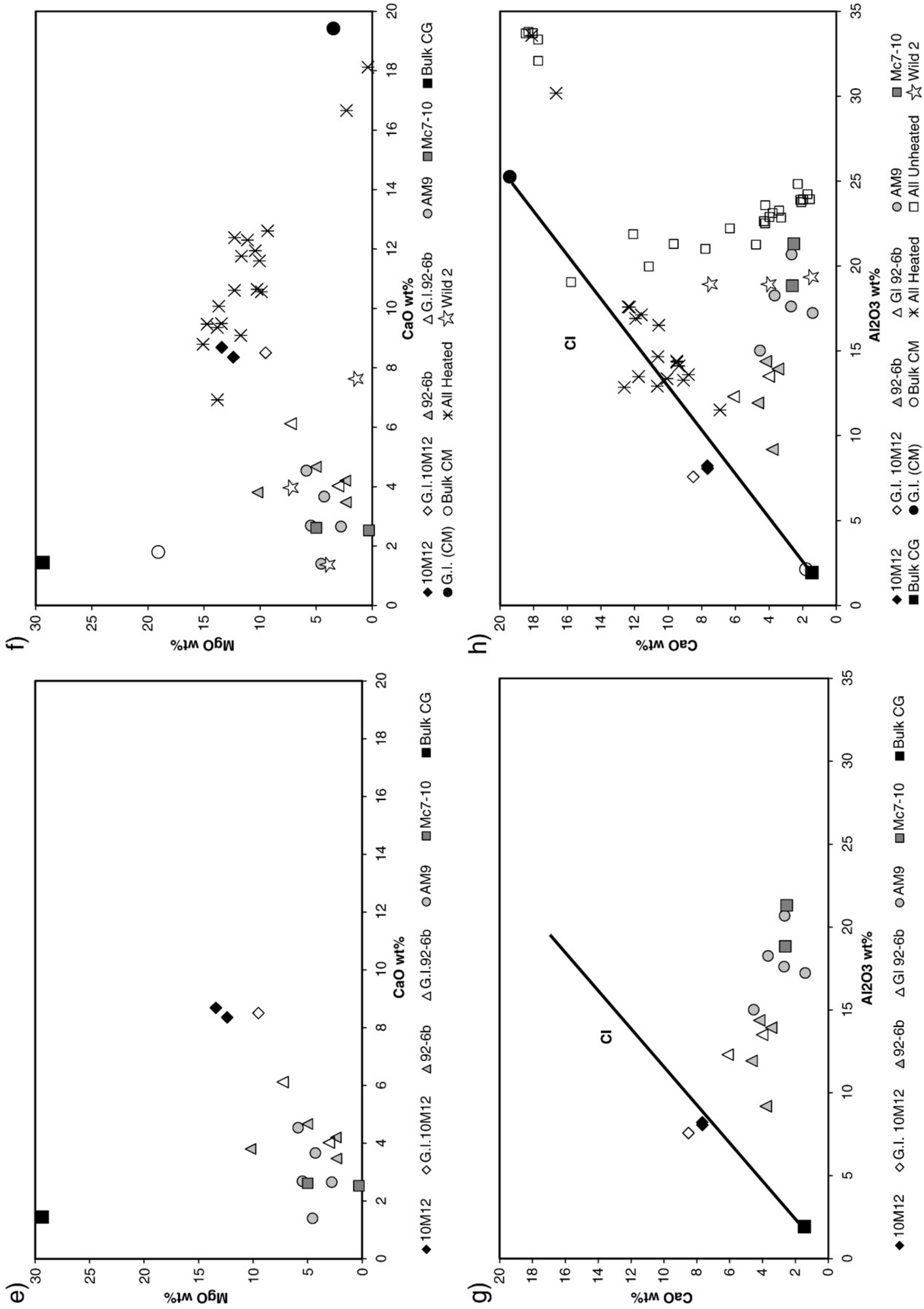

Fig. 3 (*continued*).

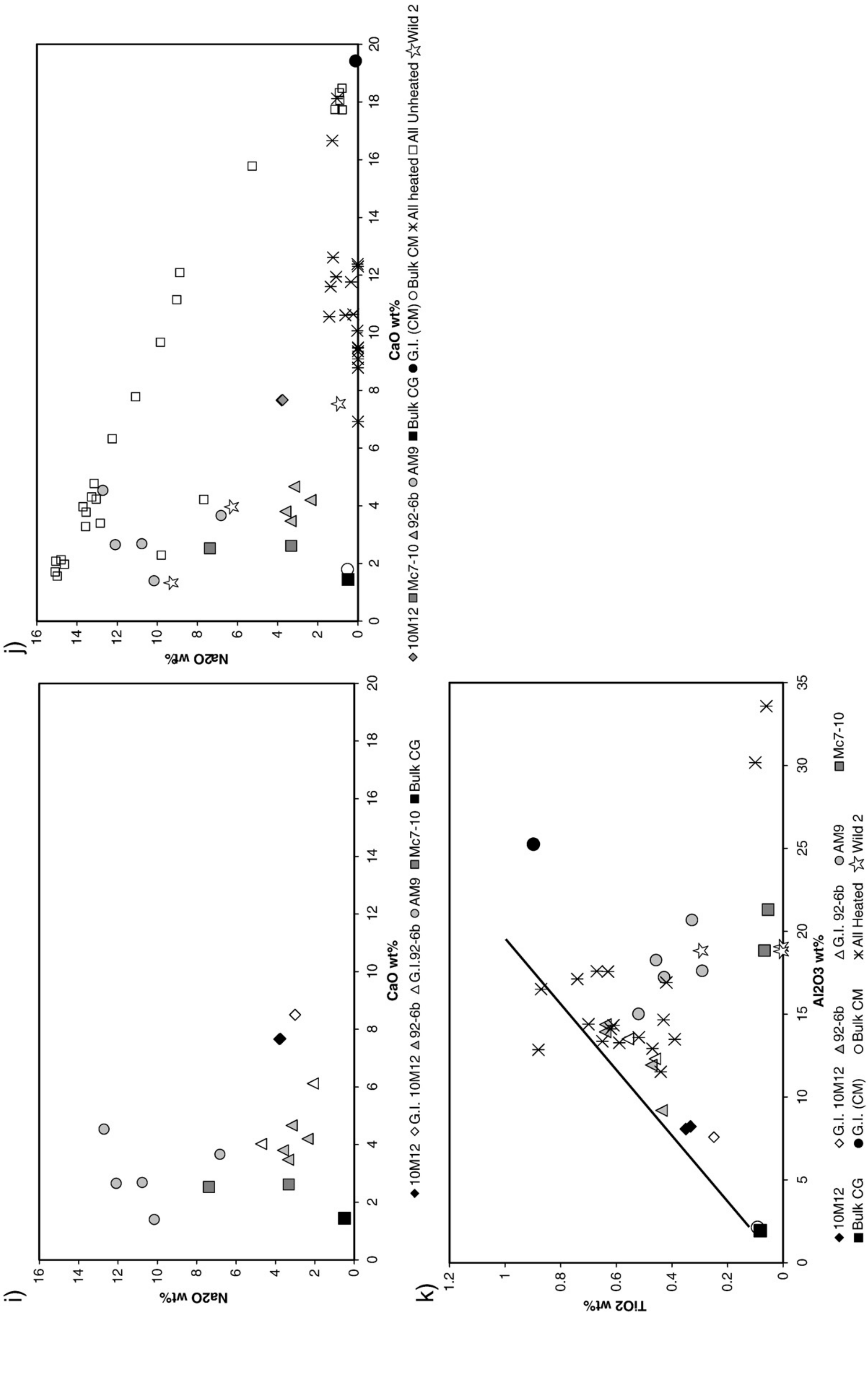

Fig. 3 (*continued*).

glasses, our conclusion from above is supported, namely that 10M12 is the most strongly heated sample investigated. The chemical compositions of all glasses project off the G.I. (CM) – Bulk CM mixing line – which is an indication of a non-primitive starting composition. In fact, all glasses from MMs have a positive correlation between their MgO and CaO contents, indicating mixing between a Mg-poor and possibly Ca-poor precursor and a component similar in composition to 10M12 glass (and Allende glasses heated to 1450 °C). Apparently, none of the MM glasses could have been derived from a primitive precursor poor in volatile elements (Fig. 3f). Consequently, we have to conclude that MM glasses mostly had modified ("altered") glass (or crystalline mesostasis) precursors.

Considering these findings, it is not surprising that in MM glasses CaO and Al_2O_3 contents are not in chondritic proportion (Fig. 3g). Only the glass compositions of the most strongly heated CS 10M12 project close to the chondritic CaO/ Al_2O_3 ratio line. Also, most highly heated Allende glasses project close to the chondritic line (Fig. 3h). Apparently, the chondritic CaO/ Al_2O_3 ratio of Allende glasses was established in the heating event (Varela, 2008). All MM glasses, except CS 10M12, apparently were not heated strongly enough to experience modification to a similar extent. Again we have to conclude that MM glasses have non-primitive, modified pre-heating precursors (glass or crystalline mesostasis). They also have experienced varying heating intensities during atmospheric entry, which caused dissolution of varying amounts of chondritic matter in the liquefied glass precursor.

The contents of Na_2O and CaO in MM glasses are either not or slightly negatively correlated (Fig. 3i). Glasses of primary glass inclusions and clear mesostasis glass in CCs are very poor in Na_2O and rich in CaO and Al_2O_3 (e.g., Fuchs et al., 1973; Olsen and Grossman, 1978) in a chondritic CaO/ Al_2O_3 proportion [e.g., G.I. (CM) – Varela et al., 2002, 2006]. However, this ratio can be modified by metasomatic exchange of Ca for Na between glass (or the precursor liquid) and the solar nebula (e.g., Varela et al., 2005, 2006). The final product of this process seems to be very Na-rich glasses (or crystalline counterparts), which are common in some meteorites (e.g., CV3 chondrites and unequilibrated OCs – e.g., Kurat, 1967; Kurat and Kracher, 1980; Varela, 2008). The negative correlation between Na_2O and CaO contents in glasses from these chondrites gives evidence for that process. In Fig. 3j we show as an example the projections of unheated and heated glass compositions from Allende objects. Clearly, the unheated Allende glasses have modified chemical compositions, which were created by a metasomatic Na-for-Ca exchange process. That results in a mixing line in the Na_2O vs. CaO contents projection between the pristine glass composition (Na-free and Ca-rich, G.I. (CM)] and the final product, a nepheline-rich glass (Na-rich, Ca-poor). This process is a characteristic solar nebula process that can be traced not only in glasses of CCs and unequilibrated OCs but also in achondrites and silicate inclusions in iron meteorites (Varela et al., 2003; Kurat et al., 2003, 2007). Glasses from MMs all project far below the metasomatic exchange line represented by non-heated glasses in Allende objects in Fig. 3j. The effect of heating must be mostly volatilization of Na, as is demonstrated by the compositions of heated Allende glasses (All heated in Fig. 3j), which all project near the baseline. Consequently, we have to conclude that all MM glasses come from Na-bearing precursors and probably have lost some Na during atmospheric entry. This means that precursors were present, which have seen nebular metasomatic chemical modification.

Although MM glasses seem to have experienced a heating event, their Na_2O content is still high (2.4 - 12.7 wt%) if compared to that of the heated glasses of Allende (Fig. 3i-j). This seems to be simply a consequence of the duration of the heating event, which in the case of MMs, lasted only seconds but took hours for the Allende objects in the heating experiment.

The Al_2O_3/TiO_2 ratio of glasses in MMs is sub-chondritic (Fig. 3k) – similar to that of most glasses in chondrites, inclusive primary glasses in CM chondrites. Also not unexpected is that the composition of heated glasses of Allende approach the chondritic line – as do those of glasses of CS 10M12 and MM M92-6b. Glass compositions of MM Mc7-10 project far from the chondritic line indicating that their composition is close to the original composition they had in space. We can again conclude that MM Mc7-10 is the least heated sample in our study and CS 10M12 the most intensely heated one. Particles AM9 and M92-6b fill in between with the former closer to the low-T end than the latter.

Evidently, our (very small) sample of glasses from only 4 MMs does not contain an originally pristine refractory precursor rich in CaO and Al_2O_3 and free of volatile elements (e.g., Na) such as those common (but not exclusively) in CM and CR chondrites. The similarity of the chemical composition of primary inclusions and mesostasis glasses (Table 1) indicates a high degree of melting of particles 10M12 and M92-6b and mixing (dissolution) of Fe, Mg silicates and also chondritic matter. This is also supported by the chemical composition of olivines, which for the cosmic spherule (CS) 10M12 indicates crystallization from a melt that had the composition of the glass (Table 1). Other olivines appear to be out of equilibrium with their glasses, which could be an indication of preservation of some relictic features or simply a consequence of the fast crystallization process.

4.3. Glasses in comet Wild 2 dust

Nakamura et al. (2008) reported the first petrographic description and phase analyses of "chondrulelike objects" collected by the

Table 2
Averaged EMP analyses of glass inclusions in olivines and mesostasis glass in carbonaceous chondrites and micrometeorites (in wt%).

	Glass inclusions in olivines					Mesostasis glass		
	Mean CC *250*	All unheated *82*	Mean MMs *3*	All heated *28*	Mean OC *70*	All unheated *25*	All heated *16*	Mean MMs *12*
SiO_2	54.2	52.0	55.0	51.7	63.7	49.9	52.0	58.7
TiO_2	0.83	0.92	0.42	1.07	0.68	0.79	0.55	0.39
Al_2O_3	23.5	23.0	10.9	15.3	16.3	24.8	16.4	15.0
Cr_2O_3	0.36	0.52	0.18	0.42	0.53	0.36	0.32	0.07
FeO	0.90	0.86	10.6	**6.1**	2.05	2.35	8.0	7.2
MnO	0.04	0.04	0.21	0.13	0.07	0.02	0.18	0.21
MgO	2.47	1.59	6.5	**10.5**	3.45	2.76	11.0	5.7
CaO	12.7	13.8	6.2	11.0	6.4	7.9	11.1	3.97
Na_2O	4.11	6.2	3.51	2.70	5.94	9.84	0.42	6.41
K_2O	0.49	0.14	0.65	0.15	0.99	0.13	0.06	1.10
P_2O5	0.11	0.15	nd	0.62	0.13	nd	0.07	
Total	99.62	99.2	94.2	99.7	100.3	98.7	100.1	98.7

References: CC: Carbonaceous Chondrites; OC: Ordinary Chondrites; MMs: Micrometeorites; All: Allende; 250: number of analyzed objects.

Stardust Mission from comet Wild 2. The particles appear to be fragments of former larger units and consist of olivines and pyroxenes either in glassy mesostasis or poikilitically intergrown. These rock and mineral fragments resemble in some respect crystalline MMs of our collection. In particular, our least heated crystalline MM Mc7-10 (possibly related to H chondrites) has olivine and pyroxene compositions, which are very similar to those of Wild 2 particle Torajiro. The correspondence between MM Mc7-10 and Torajiro includes FeO contents of olivine (17.2 vs. 19.0 wt%) and low-Ca pyroxene (10.5 vs. 9 wt%) as well as the FeO/MnO ratios of olivines (39 vs. 24) and low-Ca pyroxenes (21 vs. 18). The other Wild 2 particles analyzed by Nakamura et al. (2008) have phases that are poorer in FeO than those in our small sample of MMs. However, such phase compositions are very common among MMs (e.g., Presper et al., 1992; Kurat et al., 1994; Gounelle et al., 2005b). The only exception is the low-iron-manganese-enriched (LIME) pyroxene (FeO/MnO<1) of particle Gen-chan. Such Mn-rich silicates are common in IDPs (Klöck et al., 1989) but apparently absent in small and large MMs. Thus, the chemical compositions of olivines and pyroxenes in Wild 2 cometary dust generally resemble the IDP and MM phase compositions – in agreement with the prediction made by Maurette et al. (1996) and Gounelle et al. (1998).

Nakamura et al. (2008) also analyzed the mesostasis glass of three Wild 2 particles. They project into the multi-dimensional space occupied by glass compositions in MMs and chondrites (Fig. 3). Because Wild 2 particles presumably are not secondarily heated for a sufficiently long time to allow dissolution of olivine and pyroxene (the impact deceleration took only μ-seconds and likely was explosive, e.g., Maurette and Kurat, 2006), they are all poor in MgO and FeO – like all glasses in chondrites and in MM Mc7-10 (Fig. 3a,b). Their Al_2O_3 content is high, but not high enough for projecting into the pristine glass composition space (Fig. 3c,d). Again, a correspondence between Wild 2 glasses and those in MM Mc7-10 (and also AM9) is observed in this and all other elemental projections (Fig. 3e-k). Interestingly, the Wild 2 glass compositions all project into compositional space occupied by chemically modified MM glasses. This is particularly evident in Fig. 3j (Na_2O vs. CaO), where their compositions project neither into the field of pristine chondritic glasses, nor onto the Na-for-Ca exchange line (as represented by Allende chondrite glasses), nor into the terminal modification space (Na-rich upper left corner in Fig. 3j). Apparently, Wild 2 glasses experienced – like glasses of MMs of this study – chemical modification ("alteration"), presumably in the nebula as evidenced by high Na contents (Fig. 2b).

Nakamura et al. (2008) found that olivines and pyroxenes in Wild 2 comet particles have oxygen isotope compositions similar to those of chondrules in CCs, which they interpret to "suggests that chondrules have been transported out to the cold outer solar nebula and spread widely over the early solar system". We can add that Wild 2 particles compositionally very well match MMs, samples of the most abundant matter collected by the Earth today, and that they experienced the very same nebular processing which MMs and constituents of CCs and OCs suffered in the cooling early solar nebula. The similarity covers not only the major and minor element phase compositions but also their O isotope composition (e.g., Hoppe et al., 1995; Engrand et al., 1999; Gounelle et al., 2005b).

5. Conclusions

Glasses in MMs are chemically modified ("altered") to varying degrees and record:

1) Heating to variable degrees during deceleration in the terrestrial atmosphere from very low (particles Mc7-10 and AM9) to high (MM M92-6b) temperatures and total melting of the precursor object (MM 10M12).
2) This heating is documented by dissolution of variable amounts of Fe, Mg silicates and matter of chondritic chemical composition in the melts (glass precursor).
3) None of the MMs investigated in this study originally contained pristine refractory glass such as the primitive Ca, Al-rich glass of CM and CR chondrite constituents. The precursor compositions of all glasses in the MMs investigated were chemically modified – comparable to nebular metasomatic modifications omnipresent in many CCs and all OCs (and other meteoritic matter).
4) Dust collected by the Stardust mission from comet Wild 2 carries glasses with chemical compositions indistinguishable from those present in MMs, which were not heated to high temperatures. Genuine dust from comet Wild 2, therefore, appears to resemble the omnipresent interplanetary dust. This dust has seen the full spectrum of metasomatic processes, which were active in the early solar nebula.

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