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# Carbon in glass inclusions of Allende, Vigarano, Bali, and Kaba (CV3) olivines

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**Abstract**—Carbon contents and distribution have been measured in glass inclusions in olivines of CV3 carbonaceous chondrites by using the $^{12}C(d,p)$ $^{13}C$ nuclear reaction. All olivines from the four studied meteorites had low carbon contents ($<70$ ppm). Conversely, glasses of glass inclusions in the same olivines had highly variable carbon contents, all above 100 ppm. Glass inclusions in olivines from meteorites of the oxidized group (Allende, Kaba, and Bali) had carbon contents that varied from 100 to about 2000 ppm, whereas those from the reduced group member Vigarano were surprisingly poor in C (averaging 300 ppm). These relative abundances of carbon in these glasses of reduced and oxidized CV3 meteorites are in contrast to the abundances of interstellar SiC in these meteorites. This indicates that glass inclusions in olivines could have behaved, with respect to carbon, as closed systems that have escaped elemental exchange processes. The carbon content of the glasses is, therefore, likely to be primary and reflect the physico–chemical conditions during the formation of the host olivine and glass inclusions. The redox conditions prevailing during secondary processing of the olivines (e.g., metasomatic Fe–Mg exchange, Ca–Na exchange) appear not to have influenced the carbon distribution. Carbon could have been trapped initially as a refractory carbon species (e.g., carbide) by clear glass inclusions. Despite the fact that the nature of neither the primary nor that of the secondary C species was established, the commonly heterogeneous distribution of C in glass inclusions in olivines suggests entrapment of a solid C-bearing precursor. *Copyright © 2000 Elsevier Science Ltd*

## 1. INTRODUCTION

Carbonaceous chondrites are unique with respect to their bulk content of carbon, which can reach up to 3.5 wt% in CI chondrites. The CV3 carbonaceous chondrites are poorer in C than are the CI chondrites, with bulk carbon content varying from 0.2 to 1.2 wt% (Gibson et al., 1971). Most carbon is present as HCNO organic compounds and a minor fraction (a few 100 ppm of the bulk rock) as interstellar diamonds (Anders et al., 1989). Most of the presolar C species (organic compounds, diamonds, carbides, and others) were reprocessed in the solar nebula, and some species present in meteorites appear to have been newly formed from the breakdown products of the primary components (Hayatsu and Anders, 1981). In addition to low molecular weight compounds (hydrocarbons, amino acids), CV3 carbonaceous chondrites have most of their carbon in the form of insoluble high molecular weight carbonaceous material. Although this type of carbon has been extensively studied, there is no consensus of opinion on its structural form because there is no consensus on the amount and the nature of the elemental carbon present (e.g., amorphous C, as poorly graphitized elemental C, disordered graphite; Smith and Buseck, 1981; Kerridge, 1985). In particular, in CV3 carbonaceous chondrites a small fraction of the total carbon is present as inorganic compounds, such as carbides, graphite, and diamonds (Lewis and Anders, 1983).

Coarse-grained constituents of chondrites (e.g., chondrules, aggregates, inclusions) can keep vestigial isotopic anomalies of O and of refractory elements (e.g., Mg, Ca, Ti) that give information on the processes in the early solar system and on presolar sources. Carbon also has the potential to "remember" its presolar source and its processing in the solar nebular. The determination of carbon contents and distribution in the constituents of chondrites is essential to understand the primordial carbon chemistry and to constrain the physico–chemical conditions prevailing during mineral growth in the solar nebula. Also, because of the possible extrasolar origin of some of this carbonaceous matter (Lewis et al., 1975; Ott et al., 1981), the study of carbon in silicate phases could help to constrain the role and amount of presolar matter present during the formation of the new phases.

Recent work also showed that silicate glass inclusions in olivine from these chondrites are likely to have been primarily formed by condensation in the solar nebula (Kurat et el., 1997). Therefore, we have focused our study on the abundance and the distribution of carbon in olivine, the first major phase to condense from the solar nebula gas, and its primary glass inclusions from CV3 carbonaceous chondrites.

Carbon abundances were measured by nuclear reaction analysis (NRA). Because NRA also yields depth information, it makes possible the measurement of carbon content together with its distribution over the whole thickness of the inclusion. It also allows a distinction between carbon present in the glass and that inherited from contamination at the surface.

Previous studies using NRA were performed on chondrules, matrix, and a dark inclusion of the Allende (CV) chondrite (Van der Stap et al., 1986; Heymann et al., 1988) and in the matrix of ordinary chondrites (e.g., Makjanic et al., 1993). Recently, carbon abundances have been determined in Allende, Bishunpur, and Semarkona chondrules by using an ion microprobe (Hanon et al., 1998).

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The present data, and our preliminary results on Allende constituents (Varela et al., 1999), indicate that carbon species do not enter the structure of olivines in CV3 chondrites, but may have been trapped and preserved in the glasses of glass inclusions in olivines.

## 2. ANALYTICAL TECHNIQUES

The carbon measurements in glass inclusions and their host olivines were carried out in the nuclear microprobe facilities of Pierre Süe laboratory (Saclay, France) by using the $^{12}C(d,p)$ $^{13}C$ reaction. The samples were irradiated with an incident deuteron beam of 1.45 MeV, and the protons were detected between 2.520 and 3.036 MeV behind a 9 $\mu$m thick Al screen with a surface barrier detector (1000–1500 $\mu$m depleted depth). The protons resulting from the $^{16}O(d,p)$ $^{17}O$ have energies of 2.486 ($p_o$) and 1.647 ($p_1$) MeV and do not contribute to the carbon energy region. At 1.45 MeV incident energy, the main interferences are due to (d,p) nuclear reactions with the major constituents of the matrix, such as $^{24}Mg$, $^{28}Si$, and $^{27}Al$. To take into account this matrix effect, we systematically measured the background on C-free silicate glasses and olivine, $[MgO/(FeO + MgO)]_{molar} = 0.90 = Mg\#$. The analyses were performed with a $5 \times 5$ $\mu m^2$ beam size and an integrated charge (Q) from 0.5 to 1 $\mu$C. The detection limits were calculated at 45 ppm C in glasses (Q = 0.5 $\mu$C) and from 30 to 75 ppm in olivines depending on its composition (Varela and Métrich, 2000). In silicate glasses (d = 2.6 to 2.7 g/cm$^3$), the analyzed depth is 8–9 $\mu$m. The C concentrations were calculated against a scapolite standard containing 6,800 ppm C (Métrich and Mosbah, 1988) and to test the validity of our measurements, carbon was analyzed in a basaltic glass to be 295 $\pm$ 45 ppm (10 measurements) by nuclear microprobe and 300 $\pm$ 35 C ppm (11 spectra) by Fourier Transform Infra-Red Spectroscopy. To minimize contamination, all our NRA analyses were performed by using a cryogenic trap.

The Fourier Transform Infra-Red spectra were obtained in reflection mode by using a Magna-IR 550 spectrometer (Nicolet, France) coupled with a Spectra-Tech microscope and equipped with a globar source, an MCT/A detector cooled with N$_2$ and a Ge-KBr beam splitter.

Major element compositions of glasses were measured with a Camebax (Centre d'analyses Camparis, Université de Paris VI) and a SX50 (Atomic Energy Commission, Buenos Aires, Argentina) CAMECA electron microprobes. Analyses were performed by using a defocused beam (5 $\mu$m), an acceleration voltage of 15 kV, a sample current of 10 nA, and counting times of 10 s. The precision was established by analyzing basaltic and trachytic glasses (ALV 981 R23 and CFA 47; Métrich and Clocchiatti, 1989) and corrections were made by using the on-line ZAF program. The samples were first analyzed for Na.

The heating stage used for high temperature experiments consisted of a small-size platinum heater (5 mm diameter) purged with purified He (Zapunny et al., 1989). Temperatures were measured with a Pt–Pt$_{90}$Rh$_{10}$ thermocouple, which was calibrated against the melting points of Ag (961°C) and Au (1063°C). The oxygen fugacity was monitored in the outgoing gas flux with a zirconia probe and calibrated with an Ar (1% H$_2$) gas calculated to have an O fugacity of approximately 10$^{-10}$ to 10$^{-9}$ atm at 1200°C.

Heating experiments and Fourier Transform Infra-Red analysis were performed at the Laboratory Pierre Süe.

## 3. SAMPLES

CV3 carbonaceous chondrites were divided into oxidized and reduced subgroups, by McSween (1977), according to their Ni contents in sulfides and the modal abundance of Fe–Ni metal and magnetite. To analyze the carbon distribution in olivines and their glass inclusions of members of both groups, we selected Allende, Kaba, and Bali (oxidized group), and Vigarano (reduced group).

Glass inclusions usually consist of glass plus a bubble, have sizes $\geq$10 $\times$ 10 $\mu m^2$, and occur in isolated olivines and olivines of aggregates or chondrules with variable FeO contents in the Vigarano, Kaba, Bali, and Allende CV3 carbonaceous chondrites [Polish Thin Sections (PTS) Vigarano, no number; Kaba, from A576; Bali J2662; Allende M5618; Allende Q and Allende, no number; all from Naturhistorisches Museum, Vienna]. The glass of these inclusions is clear or shows signs
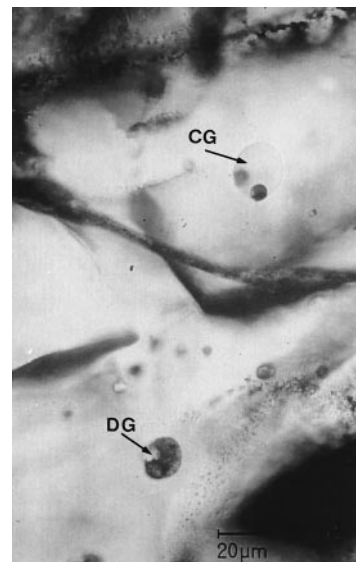


Fig. 1. Clear glass (CG) and devitrified glass (DG) inclusions coexisting in the same olivine of the Allende meteorite. (PTS, from Allende M5618). Transmitted light image.

of devitrification in a way similar to those present in terrestrial rocks (Clocchiatti, 1975). We have focused on the selection of glass inclusions by considering their occurrence (e.g., as isolated inclusions or inclusions forming clusters), the type of glass that forms the inclusion (e.g., clear or devitrified glasses), the amount of FeO present in the olivine host, and the phases associated with the glass (e.g., bubble, metal globule, troilite globule, etc.). Because of the depth-sensitivity of NRA, only inclusions thicker than 10 $\mu$m were selected.

## 4. RESULTS

### 4.1. Petrography and Chemical Composition of Glass Inclusions and Host Olivines

#### 4.1.1. Allende (sections M5618, Allende Q, and Allende, no number)

Glass inclusions were isolated (A3, A10) or form clusters (A1, A2, A5) in olivines of aggregates or occurred as isolated inclusion in isolated olivine (A4). They were composed of either clear glass plus shrinkage bubble or brownish devitrified glass plus shrinkage bubble (Fig. 1) with sizes ranging from 10 to 20 $\mu$m. Clear glass inclusions (A3, A4, A5, A10) were rich in SiO$_2$ (47–62 wt%), Al$_2$O$_3$ (23–28.5 wt%), CaO (8.5–7.5 wt%) and have variable contents of Na$_2$O (2.8–7.5 wt%). Glass inclusion A10 was lost during removal of the gold coating before its major element contents could be obtained. Only its carbon content is given in Table 1. Devitrified inclusions (A1, A2) had higher contents of FeO and MgO and lower contents of Na$_2$O compared to clear glass inclusions.

Host olivines, ranging in size from 150 to 500 $\mu$m, were euhedral and subhedral grains in granular aggregates (Ol5, Ol11), anhedral grains in a porphyritic aggregate (Ol1, Ol3, Ol10), or isolated grains (Ol4). Their FeO and CaO contents ranged from 0.4 to 13 wt% and 0.2 to 0.8 wt%, respectively. Carbon contents of all host olivines in the Allende meteorite were <70 ppm.

The distribution of carbon with depth can be examined by comparing the proton energy peaks with those of the standard

Table 1. Major element (EMP analyses, wt%) and carbon content (NRA, ppm) of glasses in glass inclusions and host olivines from Allende, Kaba, Bali, and Vigarano CV3 meteorites.

| | A1 | A2 | $Ol_{1-2}$ | A3 | $Ol_3$ | A4 | $OL_4$ | A5 | $Ol_5$ | A10 | $Ol_{10}$ | $Ol_{11}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **ALLENDE** | | | | | | |
| $SiO_2$ | 40.4 | 37.4 | 40.6 | 47.2 | 39.7 | 46.8 | 41.3 | 62.2 | 42.2 | — | 42.4 | 40.0 |
| $TiO_2$ | 1.11 | 0.58 | 0.09 | 1.64 | 0.02 | 1.31 | 0.06 | 0.70 | — | — | 0.00 | |
| $Al_2O_3$ | 33.0 | 19.2 | 0.09 | 26.9 | 0.21 | 28.5 | 0.21 | 23.2 | 0.03 | — | 0.29 | 0.02 |
| $Cr_2O_3$ | 0.28 | 0.17 | 0.26 | 0.91 | 0.16 | 0.06 | 0.04 | 0.92 | 0.14 | — | 0.00 | bd |
| FeO | 1.75 | 11.6 | 1.47 | 0.76 | 10.4 | 0.31 | 0.57 | 0.22 | 1.36 | — | 0.40 | 13.6 |
| MnO | 0.10 | — | 0.04 | — | 0.14 | — | — | — | — | — | 0.00 | 0.17 |
| MgO | 4.80 | 21.0 | 56.5 | 0.40 | 48.5 | 0.62 | 57.2 | 0.45 | 56.2 | — | 56.1 | 45.5 |
| CaO | 18.8 | 8.3 | 0.30 | 15.4 | 0.19 | 16.8 | 0.56 | 8.60 | 0.19 | — | 0.77 | 0.25 |
| $Na_2O$ | 0.10 | 0.92 | — | 6.6 | — | 4.7 | — | 2.80 | — | — | — | — |
| $K_2O$ | bd | 0.07 | — | 0.18 | — | — | — | — | — | — | — | — |
| Total | 100.4 | 99.2 | 99.4 | 100.0 | 99.3 | 99.1 | 100.0 | 99.1 | 100.1 | — | 100.0 | 99.6 |
| C ppm | 1400 | 920 | <70 | 910 | <70 | 630 | <70 | 1600[b] 2300[c] | <70 | 170[d] 100[e] | <70 | <70 |
| Error (ppm) | ±150 | ±150 | | ±120 | | ±120 | | ±150 | | ±15 | | |

| | K2 | K3 | K4 | $Ol_{1-2-3}$ | Bali2 | Bali3 | V1 | $Ol_1$ | V2 | $Ol2$ | V6 | V7 | $Ol7$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **KABA** | | | | **BALI** | | **VIGARANO** | | | | | | |
| $SiO_2$ | 42.7 | 42.0 | 41.0 | 42.5 | 39.2 | 42.9 | 54.5 | 40.6 | 49.8 | 40.0 | 56.3 | 49.9 | 41.0 |
| $TiO_2$ | 0.98 | 1.06 | 0.88 | 0.02 | 1.10 | 1.01 | 0.44 | 0.06 | 0.98 | 0.06 | 0.87 | 1.17 | 0.07 |
| $Al_2O_3$ | 28.7 | 29.2 | 30.5 | 0.27 | 29.0 | 29.5 | 19.4 | 0.13 | 25.0 | 0.13 | 21.5 | 25.8 | 0.29 |
| $Cr_2O_3$ | 0.16 | 0.26 | 0.10 | 0.09 | bd | 0.54 | 0.67 | 0.24 | 0.32 | 0.04 | bd | bd | bd |
| FeO | 0.15 | 0.28 | 0.24 | 0.33 | 0.28 | 2.15 | 3.26 | 4.46 | 1.81 | 0.96 | 0.53 | 3.23 | 1.04 |
| MnO | bd | bd | bd | 0.06 | bd | 0.00 | bd | bd | — | 0.09 | 0.11 | 0.00 | bd |
| MgO | 3.62 | 3.19 | 3.42 | 56.1 | 2.08 | 2.56 | 2.76 | 54.3 | 1.29 | 57.6 | 0.61 | 0.77 | 57.4 |
| CaO | 22.6 | 24.0 | 23.6 | 0.53 | 23.2 | 4.65 | 5.83 | 0.23 | 5.3 | 0.33 | 13.9 | 2.19 | 0.20 |
| $Na_2O$ | bd | bd | bd | — | 4.12 | 15.4 | 11.5 | — | 13.8 | — | 5.61 | 16.3 | — |
| $K_2O$ | bd | bd | bd | — | bd | 0.43 | 0.92 | — | 0.56 | 0.00 | bd | 0.86 | — |
| Total | 98.9 | 100.0 | 99.7 | 100.0 | 99.2 | 99.1 | 99.3 | 100.0 | 98.9 | 99.3 | 99.4 | 100.2 | 100 |
| C ppm | 250 | 2090 | 610 | <70 | 16.20 | 400 | 330[a] | <70 | 390 | <70 | 220 | 240 | 44 |
| Error (ppm) | ±40 | ±100 | ±120 | | ±150 | ±30 | ±30 | | ±30 | | ±30 | ±30 | |

bd = below detection limit [For glasses (10 nA sample current) the detection limits are $Na_2O$ = 0.06 wt%, $K_2O$ = 0.07 wt%, $Cr_2O_3$ = 0.1 wt%, MnO = 0.1 wt%; for olivine (40 nA sample current) the detection limit of MnO and $Cr_2O_3$ are 0.04 wt%. — = non detected.

[a] = measurement at the glass/globule interface.
[b] = measurement in the glass.
[c] = measurement at the glass/olivine interface.
[d] = includes contribution of some carbon from the bubble.
[e] = measurement in the centre of the inclusion; $Ol_{1-2}$ = host olivine of glass inclusions 1 and 2.

(Fig. 2). The reference spectrum of the scapolite illustrated a homogeneous distribution of carbon with depth. The incipient development of a second peak within the devitrified glass inclusion (A1) in olivine of the Allende meteorite indicated a heterogeneous distribution with a high concentration of carbon in the deepest part of the inclusion (Fig. 2). Variable concentration of carbon was also observed in the elongated inclusion (A5) from the center (1600 ppm C) toward the glass/olivine interface (2900 ppm C; Table 1).

Carbon contents varied from one inclusion to another, from 920 and 1400 ppm in devitrified inclusions (A2–A1) and from 1600 to 100 ppm for clear glass inclusions (A3–A4–A5–A10; Table 1).

In glass inclusion A10, two measurements were performed, and one of them did overlap the bubble zone. Because this area was exposed at the surface, we cannot exclude some contamination increasing the carbon counts in this way (Table 1).

### 4.1.2. Kaba (from specimen A 576)

The studied glass inclusions K2, K3, and K4 occurred as a cluster in a single olivine grain (Fig. 3). They were composed of clear glass plus a shrinkage bubble. All inclusions had similar chemical compositions that varied somewhat: $SiO_2$ (40.9–42.7 wt%), $Al_2O_3$ (28.7–30.5 wt%), and CaO (22.6–24 wt%). The host olivine had a CaO content of 0.53 wt% and a very low FeO content (0.33 wt%). The carbon content of the glass inclusions varied from 250 to 2090 ppm. Analyses at the glass/olivine interface in K4 (K4, Table 1) showed no detectable variation in carbon contents. The host olivine contained <70 ppm C (Table 1).

### 4.1.3. Bali (section J2662)

Two glass inclusions from this sample were analyzed. They were part of an inclusion cluster in the same olivine. Bali2 consisted of clear glass plus a bubble and was characterized by having $SiO_2$ (39 wt%), $Al_2O_3$ (29 wt%), and CaO (23 wt%). Bali3 consisted of highly devitrified brownish glass characterized by similar contents of $SiO_2$ and $Al_2O_3$ with respect to Bali2, but a much higher content of $Na_2O$ (15 wt%) and a lower content of CaO (4.6 wt%). The carbon contents of Bali2 and Bali3 were 1600 and 400 ppm, respectively (Table 1). No
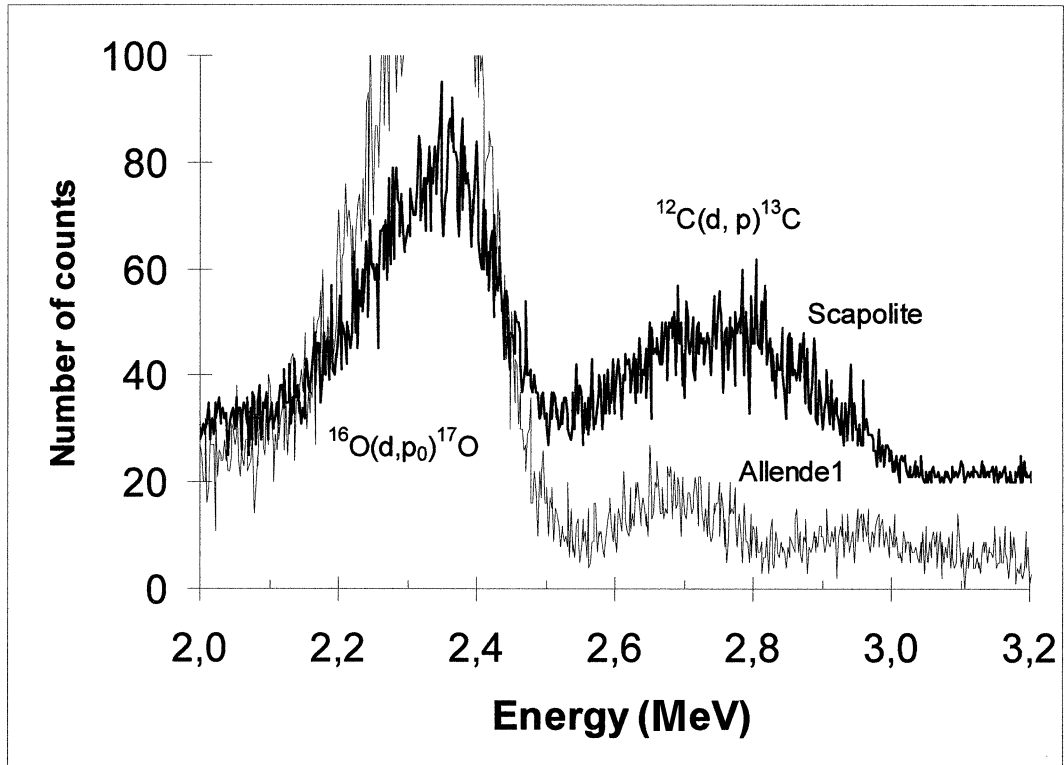
Fig. 2. $^{12}C(d,p)$ $^{13}C$ spectra of the standard scapolite (in which carbon distribution is homogeneous) and the glass inclusion (All1) in olivine from Allende meteorite (showing the heterogeneous carbon distribution with depth). The integrated charges were 0.5 and 1 $\mu C$, respectively.

enrichment of C at the glass/olivine interfaces could be detected. The host olivine had a very low content of FeO (0.4 wt%) and a high content of CaO (0.58 wt%).
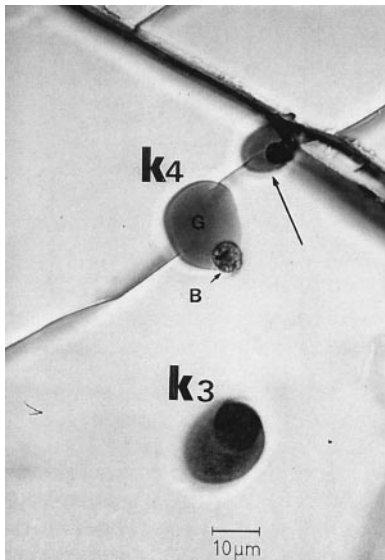


Fig. 3. Clear glass inclusions forming a cluster in a Kaba olivine (PTS, section J2662). The cluster consists of the analyzed inclusions K3 and K4 and a small inclusion (arrow), which is cut by a microfracture that also cuts through the K4 inclusion. G: Glass; B: Bubble. Transmitted light image.

### 4.1.4. Vigarano

Glass inclusions V1, V2, and V7 occurred as clusters in olivine of aggregates. Inclusions V1 and V2 were composed of clear glass plus a shrinkage bubble plus a Fe–Ni globule. The latter phase was absent in inclusion V7. The glasses had high contents of $SiO_2$ (49–55 wt%), $Al_2O_3$ (19.4–25.8 wt%) and $Na_2O$ (11.5–16 wt%) and low contents of CaO (2.2–5.8 wt%; Table 1). The host olivines had FeO and CaO contents varying from 0.96 to 4.46 wt% and 0.20 to 0.33 wt%, respectively. Carbon contents of V1, V2, and V7 glass inclusions were 330, 390, and 240 ppm, respectively. The carbon content of the host olivines was below the detection limit of 70 ppm (Table 1).

The glass inclusion V6 was an isolated inclusion in an aggregate olivine and consisted of clear glass plus a bubble. Its chemical composition differed form those of the previous ones by being rich in CaO (14 wt%) and poor in $Na_2O$ (5.6 wt%). The carbon content of the glass was 220 ppm.

Carbon analyses at the interface between glass and a Fe–Ni globule (V2) and that at the center of inclusion (Table 1) did not reveal any carbon enrichment.

## 5. DISCUSSION

### 5.1. Carbon in Olivines: The Redox Conditions

The contents of FeO in olivines can be used to evaluate the redox conditions prevailing either during their formation or during secondary metasomatic alteration. To evaluate how this variation could have controlled the carbon distribution, we performed carbon analyses in olivines with variable FeO contents.
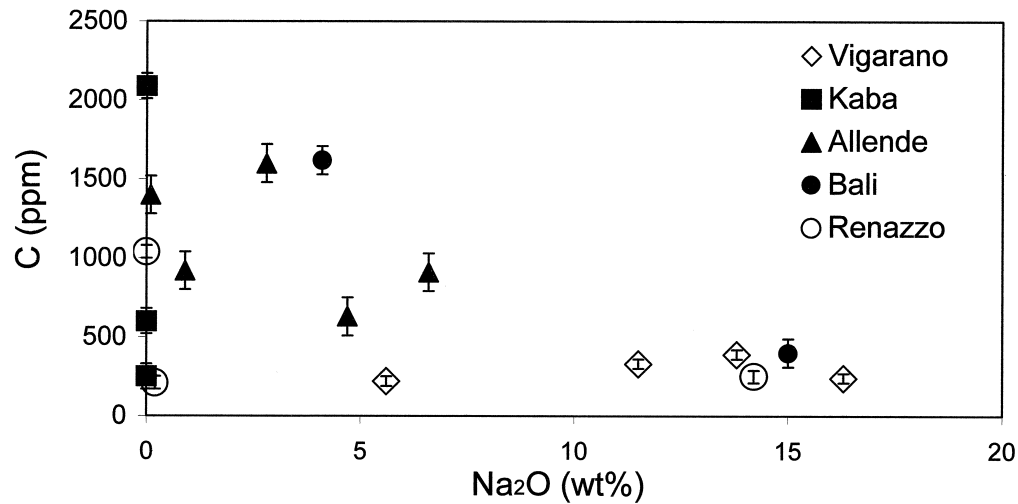
Fig. 4. The variation of carbon (ppm) with Na$_2$O (wt%) contents in the glasses of glass inclusions in olivine from Allende (249), Kaba (53), Bali (50), and Vigarano (?). Renazzo glass inclusion data are given for comparison (from Varela et al., 1998).

Our results of point analyses of olivines show that, for either isolated olivines with the lowest FeO contents (~0.30 wt%) or for those with high FeO contents (11.8 and 13.6 wt%) forming chondrules, carbon is always below the detection limit (30–70 ppm) depending on analytical conditions (Table 1). Thus, no correlation can be established between the FeO content of olivines and its carbon contents. The FeO content in the constituents of chondrules is likely to be of a secondary nature and the product of metasomatic exchange reaction with the ambient vapor (Kurat, 1988; Dohmen et al., 1997). Therefore, the variable FeO content in olivine is likely not related with a reduction promoted by the initial amount of carbon grains present, as proposed by Hanon et al. (1998). In such a model, the carbon grains in an environment in which they are not stable should have been accreted together with oxidized silicates. Furthermore, if the high carbon content of FeO-poor chondrules is due to a reduction process, the original carbon content must have been much higher than that measured after the reduction process took place. Also, reduction of Fe$^{2+}$-bearing silicates should create Ni-poor metal, what is not observed in Type I chondrules, which contain metal with primitive Fe/Ni and Ni/Co ratios. Thus, reduction of oxidized mineral assemblages for the formation of the Fe-poor silicates in carbonaceous chondrites appears to be highly unlikely, especially also in view of the primitive composition of the Fe-poor olivines and their glass inclusions (Kurat et al., 1997; 1989a,b; Dohmen et al., 1998).

The redox conditions prevailing during olivine formation, or during the secondary processes that could have governed the variation in FeO content of olivines, do not have a direct relationship with the carbon contents of olivines (Varela and Métrich, 2000).

## 5.2. Heterogeneous Carbon Distribution: Within a Single Glass Inclusion and From One Inclusion to Another

Highly variable amounts of carbon within a single inclusion as indicated by $^{12}$C(d,p) $^{13}$C spectra (Fig. 2) seem to be a particular feature of glass inclusions in olivines of the Allende meteorite. Variable C contents have also been found in terrestrial environments. However, these inhomogeneities were shown to be due to carbon films deposited in microcracks that crosscut the glass inclusions (Mathez and Delaney, 1981). We cannot rule out that something similar could have happened in glass inclusions in meteorites, but then the heterogeneous distribution should also be present in all inclusions and especially in those such as K4, which are visibly bisected by a microfracture (Fig. 3). However, the carbon distribution in glasses of the Kaba, Bali, and Vigarano meteorites was homogeneous, in spite of belonging to the same oxidized CV3 chondrite group as Allende and which are believed to have been formed by similar processes. This first result suggests that either the physico–chemical conditions prevailing during Allende formation or the postformation processes (e.g., alteration) could have differed from those that had affected Kaba, Bali, and Vigarano, leading to a heterogeneous carbon distribution in the Allende glass inclusions.

Highly variable contents of carbon were also measured in glasses of primary glass inclusions (Fig. 4). No variation in the carbon contents was observed between clear glass and devitrified glass inclusions because their contents vary from 100 to 2,300 ppm and 400 to 1400 ppm, respectively. We may note that the variation in carbon contents measured in glass inclusions hosted by different olivines of the same aggregate and in inclusions present in the same olivine (e.g., Kaba and Bali) are similar to the bulk C content of individual chondrules (~300 to ~3900 ppm, Hanon et al., 1998).

Our results clearly indicate that carbon is always present in low concentrations in olivines of the CV3 meteorite, but with variable amounts in the glasses of glass inclusions. Therefore, glass inclusions appear to be suitable for hosting carbon in chondrules.

## 5.3. Effects of Secondary Processes in Glasses

### 5.3.1. Metosomatism

The secondary processes that probably affected the constituents of all chondrites are exchange reactions that replace

elements in the solid by others from the vapor (Kurat, 1988). It is, therefore, interesting to know whether such secondary metasomatic processes, which apparently caused a replacement of Ca by Na, could, to some extent, also have affected the carbon contents of glasses.

Glasses of primary glass inclusions are characterized by highly refractory (Al–Ca-rich) compositions. Their content of $Na_2O$ is generally low (<4 wt%), and the $K_2O$ content is usually below the detection limit (0.07 wt%). Examples of this are the glass inclusions in olivine from the Kaba meteorite and some from the Allende meteorite, having the most refractory composition. However, some glass inclusions have $Na_2O$ contents >10 wt% (e.g., V1, V2, V7, Bali3; Table 1). Thus, sodium seems to be a good tracer of the alkali metasomatism events. However, no correlation between the carbon and $Na_2O$ contents in the glasses of glass inclusions could be established (Fig. 4). For example, about 900 ppm C was measured in the glass inclusions (A2 and A3) of Allende olivines, which have $Na_2O$ contents of 0.9 and 6.6 wt%, respectively. Moreover, the lowest and highest contents of carbon in the glasses of all glass inclusions in olivines were found in inclusions from Kaba (K2 and K3), where the $Na_2O$ content was below the detection limit. A similar situation was previously reported from glass inclusions in olivine of the Renazzo CR chondrite (Fig. 4), where glasses with highly different $Na_2O$ contents (0.2 and 14 wt%) had similar carbon contents (~200 ppm; Varela et al., 1998).

A particular situation was present in Vigarano, where glass inclusions in olivines from the same or from different chondrules with highly variable contents of $Na_2O$ had similarly low contents of carbon (Table 1 and Fig. 4). This indicates that the secondary process that modified the $Na_2O$ contents did not directly affect the carbon content. Thus, it is unlikely that the low carbon concentrations could be a residue, but it is possible that it could be inherited from the initial conditions prevailing during formation of Vigarano glass inclusions.

Besides CaO and $Na_2O$, $SiO_2$ is also present in variable amounts in the glasses of the glass inclusions in olivine. In the Kaba meteorite, glass inclusions with similar $SiO_2$ contents had highly variable C contents. Conversely, for similar C contents (e.g., 1400, 1600, and 1620 ppm, in inclusions A1, A5, and Bali2, respectively) the $SiO_2$ content varied from 39.2 to 62.2 wt%. Thus, no correlation can be established between the carbon content of glasses and their silica content.

In summary, the alkali metasomatic process does not affect carbon in glass inclusions from Kaba and Vigarano chondrites. Although we cannot firmly conclude that alkali metasomatism has not influenced the carbon contents in Allende glass inclusions, the C distribution is still highly heterogeneous and, possibly, primary. Similar heterogeneous distributions have been found in three glass inclusions hosted by the same olivine from the Kaba meteorite. These inclusions likely formed during similar redox conditions and have a similar Si–Al–Ca-rich composition, but highly different carbon contents. This strongly suggests heterogeneous trapping of solid carbon carrier phases.

### 5.3.2. Devitrification

Another process that could have affected carbon distribution in glass inclusions is devitrification. Devitrification in terrestrial glass inclusions is produced when large numbers of crystal nuclei developed in the glass, giving it a granular appearance. The nucleation processes depend on several parameters, such as the cooling rate, the viscosity, and the chemical composition of the silicate melt. If the devitrified inclusions have been preserved without any chemical exchange after entrapment, homogenization of the glass, that is, melting of nuclei, can be obtained by heating the samples to appropriate temperatures (Clocchiatti 1975, Roedder 1984).

However, the different attempts to homogenize the devitrified inclusions in olivines of the Allende meteorite were in vain. No changes were observed in either the size of the bubble or in the extent of devitrification after long-time heating experiments (36 h) with final temperatures of 1200–1250°C. This absence of evolution during temperature experiments may be related to either chemical exchanges that modified the initial composition of the glass during the metasomatic processes or to these experiments having been performed at atmospheric pressure. Also, we cannot rule out the possibility that devitrified inclusions in meteoritic phases could be formed by a heterogeneous trapping of crystal nuclei during a primary process governed by other parameters than those that led to devitrification of glasses in terrestrial rocks.

The possible relationship between devitrification and carbon contents has been investigated by analyzing devitrified inclusions in olivines from the Allende (A1 and A2) and Bali (Bali3) meteorites. Our analyses show that devitrified inclusions and clear glass inclusions may have a similar range of carbon contents despite their different major element compositions (Table 1). It has to be noted that C concentrations determined by using the $^{12}C(d,p)$ $^{13}C$ NRA are representative of the whole carbon content independent of its chemical state.

A previous study of carbon in the glasses of glass inclusions in olivines of the Allende meteorite performed with a Raman microprobe in reflected light mode Makjanic et al., 1989; Makjanic 1990) showed that carbon was not present in any other form but graphite in more than 40% of the devitrified inclusions. Makjanic et al. (1989) concluded that carbon could very likely be an impurity that is responsible for the devitrification and, therefore, graphite precipitated when the glass became oversaturated with respect to carbon. However, that clear glass inclusions show similar or even much higher contents of carbon than the devitrified ones argues against this hypothesis.

Our results show that carbon is concentrated in glasses of both types of inclusions (glassy and devitrified) in olivine, and its abundance varies within the same range in the different types of inclusions.

Considering that the Fourier Transform Infra-Red analysis failed to detect CO, $CO_3$, and $CO_2$ signals in the glasses of both clear glass and devitrified inclusions, and considering also the absence of graphite lines in clear glass inclusions (Makjanic et al., 1989), carbon could have been initially trapped as very fine-grained dust, possibly as carbide (e.g., SiC). During the devitrification process this species can be affected, and the break-down product could be graphite as detected by Raman analysis in devitrified inclusions.

## 5.4. Have Glass Inclusions Behaved as Closed Systems?

One question to be addressed concerns the ability of glass inclusions in olivine to keep the carbon trapped during their

formation and subsequent processing. All constituents of chondrules (e.g., olivines, pyroxenes, and glasses) must have been affected by the high temperature events during chondrule formation, somewhat changing their primitive composition. Regardless of the modification processes involved (either related to a nebular, e.g., Palme and Wark, 1988; Palme et al., 1991, or to an asteroidal origin, e.g., Housley and Cirlin, 1983) the chondrite composition, as well as the composition of the constituents, will be modified. However, glass inclusions are mostly well protected by the host and could have behaved as closed systems that were not affected by these processes.

As previously mentioned, CV3 carbonaceous chondrites have been divided into two groups, reduced and oxidized, with the members of the reduced subgroup probably being more primitive (Krot et al., 1995). As has been shown by Huss and Lewis (1995), the abundance of interstellar SiC decreases from reduced to oxidized CV3 chondrites, with Vigarano and Allende at the extremes of this range. This variation in the abundance of presolar grains in several of the CV3 chondrites was interpreted to be due to thermal processing (Krot et al., 1995). If glass inclusions were affected by these processes, we would expect a similar variation in their carbon contents, that is, decreasing contents from Vigarano (reduced group) to Allende (oxidized group). However, the mean carbon content of glass inclusions indicates a totally different situation. Vigarano glasses are markedly depleted in carbon ($\sim$300 ppm) with respect to those from Allende ($\sim$930 ppm), Kaba ($\sim$980 ppm), and Bali ($\sim$1000 ppm). These average carbon contents, which have to be taken with care due to the wide variation of carbon contents of glass inclusions within each meteorite, may record the initial heterogeneity prevailing during the formation of the constituents of CV3 chondrites.

### 5.5. Trapping of Fine-Grained Dust

The different points discussed up to now suggest that the variation of carbon contents in the glasses of glass inclusions in olivines could be related to an early process. Carbon was possibly heterogeneously trapped during glass inclusion formation, and its concentration was not altered during subsequent high temperatures events. If this hypothesis is correct, then we have to consider the possible mechanisms that could have formed these inclusions.

Debates have focused on two mechanisms being responsible for the origin of these inclusions: nebular and magmatic processes. The nebular hypothesis considers glass inclusions to be of primitive condensate origin from the early solar nebula (Fuchs et al., 1973). On the other hand, the magmatic hypothesis considers them to be residua of a melt from which the host olivine grew (Roedder, 1981).

Because of trace element abundances in a Ca–Al-rich glass inclusion in a Renazzo olivine, Kurat et al. (1997) gave strong evidence in favor of its primitive origin by condensation in the solar nebula. The analyzed inclusions were rich in refractory lithophile elements and had a flat CI-normalized pattern at about 10–15 $\times$ CI. These features indicate that the glass inclusion could not have been derived from a partial melting event nor from expulsion of incompatible elements from the host olivine. Also, the formation of glass inclusions by condensation has been theoretically addressed by Yoneda and

Grossman (1995). According to these authors, glass inclusions (referring to the glass inclusions present in olivines of the Murchison CM2 chondrite) "could represent condensate liquids that were in equilibrium with forsterite at $P^{tot} = 0.3$ atm or at dust/gas enrichment factors of $\sim$70 at $P^{tot} = 1 \times 10^{-3}$ atm." These dust-enriched regions should also be very oxygen-rich and, thus, carbon should be present as oxidized species (e.g., $CO_2$ or $CO_3^{2-}$). Carbon is mainly dissolved as $CO_2$ in silicic melts (Holloway and Blank, 1994) and as carbonate ions in basaltic and Ca-rich silicate melts with a strong dependence on CaO and $SiO_2$ contents (Dixon, 1997). In any case, its solubility limit in silicate melts is lower than a few ppm at 1100°C and very low $P_{CO2}$. The high C concentration and its heterogeneous distribution in the glasses of glass inclusions in CV3 chondrite olivines suggest that C could have been initially trapped as refractory C phases (e.g., carbides) in primitive condensates.

If glass inclusions are formed by condensation from a solar nebula gas by a process similar to that of liquid phase epitaxy, then they could represent the liquid that aided the growth of olivine from the vapor (Kurat et al., 1997). This process is common in industrial crystal production and allows the growth of crystals from the vapor through a thin liquid layer between the vapor and the growing crystal. The surface of the liquid has a large accommodation coefficient and is, therefore, a preferred site for deposition, and the liquid facilitates the ordered crystal growth (e.g., Givargizov, 1987). In the case of glass inclusions in meteoritic olivines, the liquid surface in contact with the crystal will act as an accommodation surface, and elements that are not accepted in the olivine structure will remain in the liquid, which subsequently will become a glass inclusion. In this way, elements such as Al, Ca, the rare earth elements, and also C, will be enriched in the primary glass inclusions. In addition, the most refractory primary glass inclusions have a cosmic Ca/Al ratio ($\approx$1) and cosmic ratios of other refractory lithophile elements (Kurat et al., 1997). If C was incorporated as a condensed refractory C species, this would imply that the regions where glass inclusions formed must have had a C/O ratio of $\sim$1 (Larimer and Bartholomay, 1979), that is, two times the solar ratio of 0.42 (Anders and Grevesse, 1989).

The carbon contents of the glasses of glass inclusions in CV3 chondrite olivines could be equivalent to the approximate amount, which has been stored during formation by condensation under nebula conditions.

### 6. CONCLUSIONS

Our results indicate that carbon has been preferentially trapped in glasses of primary glass inclusions during olivine growth. The variable redox conditions that could have affected olivines and their primary glass inclusions during secondary processing did not influence carbon contents of glasses of glass inclusions, nor did the $Fe^{2+}$ and alkali metasomatisms, which affected the olivines of most CV3 chondrites. Carbon contents in glasses were higher in the meteorites of the oxidized group (Allende, Bali, and Kaba $\sim$900–1000 ppm) than in those of one of the reduced group (Vigarano $\sim$ 300 ppm) and, thus, clearly show that glass inclusions in olivines can, with respect to carbon, behave a relatively closed systems. The total carbon content of glasses does not seem to be affected by postformation modification processes that have been changed CV3 chondrite constituents. Carbon could have been trapped as a refrac-

tory carbon species during formation of the inclusions, perhaps, during a liquid phase epitaxy growth mechanism. The heterogeneous trapping of carbon in Kaba and Allende glass inclusions in olivine is an argument in favor of the entrapment of solid precursors. The fact that carbon in glass inclusions appears not to be a residue after secondary processes suggests that carbon contents in glass inclusions can represent the variable amounts that have been stored during formation by condensation under nebular conditions.

*Special handling:* C. Koeberl

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