



doi:10.1016/S0016-7037(00)01204-8

Nitrogen microanalysis of glass inclusions in chondritic olivines by nuclear reaction

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(Received May 14, 2002; accepted in revised form September 3, 2002)

Abstract—Measured were the abundance and distribution of nitrogen in glasses of glass inclusions in olivines of CV3, CO3, CR, C4, CH3, and LL chondritic meteorites by means of the $^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$ nuclear reaction. Similar to what was observed with carbon, nitrogen is present in low concentrations (<20 ppm) in the structure of olivines but can be stored in variable amounts in glasses of glass inclusions. These primitive glasses, characterized by a Si-Al-Ca-rich composition, have highly variable nitrogen contents (30 to 1500 ppm) and highly inhomogeneous nitrogen distribution. Nitrogen contents are independent of the chemical composition of the glasses. The heterogeneous distribution is a common feature of all studied inclusions, as is evidenced by the variable contents of nitrogen in glass inclusions occurring in the same olivine grain. Nitrogen heterogeneity is suggestive of trapping of solid nitrogen carrier phases during formation of the constituents of chondrules. However, part of the originally trapped nitrogen appears to have been lost, possibly, by ulterior oxidation and subsequent transformation into volatile species. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Bulk nitrogen measurements in meteorites show that nitrogen contents vary widely “from a few parts per million in ordinary chondrites and achondrites to several hundred parts per million in enstatite chondrites and carbonaceous chondrites” (Kung and Clayton, 1978). Variations in carbonaceous chondrites range from 3200 ppm N for CI (1) to 37 ppm for C3 chondrites (Gibson et al., 1971; Kothari and Goel, 1974). In primitive ordinary chondrites (ALHA77214 type, ALHA81251-type, Mezö Madaras-type, Yamato 74191 type, ALHA77216 type, as well as some ungrouped OC) the nitrogen content varies between 0.55 to 12.9 ppm (Sugiura and Hashizume, 1992; Sugiura and Zashu, 1994; Hashizume and Sugiura, 1995; Sugiura et al., 1996, 1998). In ureilites and mesosiderites, the N contents vary from 11.5 to 27 ppm (Kothari and Goel, 1974), and in bencubbinites (Bencubbin, Weatherford, HH 237, QUE 94411, GRO 95551) from 23.1 to 59.3 ppm (Prombo and Clayton, 1985; Sugiura et al., 2000a). Finally, iron meteorites show a wide variation from 152 ppm in type IAB iron Odessa to less than 1 ppm (0.8 ppm) in the type IV iron Huizopa (Kothari and Goel, 1974; Sugiura et al., 2000b). Although the first studies on bulk nitrogen and carbon contents in carbonaceous chondrites showed that nitrogen abundance could be positively correlated with that of C (Gibson et al., 1971), subsequent studies showed that the nitrogen distribution is highly heterogeneous. The abundance of this element is not only different between samples of different meteorites, but also between samples of the same meteorite. This intrameteorite heterogeneity of nitrogen in carbonaceous chondrites was interpreted by Kerridge (1985) to be due to the variable abundance and distribution of nitrogen-bearing components within a given meteorite. Antarctic and non-Antarctic carbonaceous

chondrites show similar heterogeneities (Pearson et al., 2000); however, one of the most impressive intrameteorite inhomogeneities is that reported by Grady and Pillinger (1993) in the CR chondrite Acfer 182. With a bulk nitrogen content of only 85 ppm, the constituent microchondrules, very fine grained matrix, and dark clast have nitrogen contents of 1400, 272, and 492 ppm, respectively.

To understand the variation in nitrogen contents as well as to identify the nitrogen carrier phases, several studies (references follow below) of nitrogen isotopes have been performed. All of them show that at least three nitrogen components with different $\delta^{15}\text{N}$ contributed to the bulk isotopic composition of the meteorites, suggesting different sources for the nitrogen carrier.

Taenite is the main carrier of nitrogen in most iron meteorites unless graphite, carbides, carlsbergite (CrN), or roaldite [(Fe, Ni)₄N] are present (Sugiura, 1998; Asame et al., 1999). Carbides, taenite, or both are also the nitrogen carrier phases associated with Cr-rich sulfides in all bencubbinites (Sugiura et al., 2000a). Silicon nitride was found to be an abundant acid dissolution residue of the enstatite chondrites Indarch (EH4) and Qingzhen (EH3) and, more recently, of the Tieschitz (H3.6) and Murchison (CM) chondrites (Stone et al., 1990; Alexander et al., 1991; Russell et al., 1991; Lee et al., 1992; Besmehn and Hoppe, 2001). In interplanetary dust particles, nitrogen seems to be sited in an organic phase (Messenger et al., 1996). Also, nitrogen can be found in organic compounds of chondritic meteorites. Nitrogen isotopic compositions of macromolecular organic matter in acid residues from CI, CM, CR, and UOC show that N isotopes exhibit a large variation ($\delta^{15}\text{N} = -47\text{‰}$ to $+257\text{‰}$). However, the sites of formation of both, the heavy and light nitrogen components, remain unknown (Alexander et al., 1996). In ordinary chondrites, the fact that chondrules could have sampled a nitrogen reservoir with a signature distinct from that of the host is strongly supported by their different $\delta^{15}\text{N}$ (Murty and Marti, 1985). Also, these authors have tentatively identified a heavy and a light nitrogen

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component in a single chondrule. All these results appear to support Kerridge's (1985) conclusions that "nitrogen data are suggestive of isotopic inhomogeneity in the early solar system."

One of the main goals of this study is to advance the knowledge of the primordial chemistry of nitrogen taking into consideration the different processes responsible for the chemical fractionation of the dust of the nebula. To do so we decided to measure the content and spatial distribution of nitrogen in 48 Si-Al-Ca-rich glasses of primary glass inclusions in olivines of chondritic meteorites. These primitive glasses, considered having been formed by condensation in the solar nebula, as theoretically addressed by Yoneda and Grossman (1995) and as chemically supported by the trace element abundances reported by Kurat et al. (1997) and Varela et al. (2002a), show also a highly heterogeneous distribution of nitrogen-bearing phases during formation of glasses. The present data allow us to show that this heterogeneity may have been established during formation of the constituents of chondrules and to speculate about the possible nature of the nitrogen species stored in silicate phases of chondritic meteorites. Preliminary reports on nitrogen contents and distribution in glass inclusions in olivines have been presented at the Lunar and Planetary Science Conference (Varela et al., 1998, 1999, 2000)

2. ANALYTICAL TECHNIQUES

The nitrogen measurements in glass inclusions and their host olivines were carried out in the nuclear microprobe facilities of the Pierre Süe laboratory (Saclay, France) utilizing the $^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$ reaction. The literature concerning nitrogen nuclear microanalysis in geology is scarce. We followed the procedures developed for nitrogen analysis in minerals and glass inclusions in minerals by Mosbah et al. (1993, 1995).

Two reactions of deuterons with ^{14}N take place and can be utilized for nitrogen analysis (Table 1): $^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$ and $^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$. Counting protons instead of α_0 particles allows analysis at depth. Also, because the reaction cross section for the p reaction is superior to that for the α_0 reaction, the detection limit for the p reaction is lower than that for the α_0 reaction.

Samples were irradiated with an incident deuteron beam of 2.1 MeV with a beam current of 0.5 nA, and protons were counted behind a 9- μm screen with a surface barrier detector (1000- to 1500- μm depleted depth, Fig. 1) and a count rate of 2000 to 3000 counts per second. The analyses were performed with a $5 \times 5 \mu\text{m}^2$ beam size and an integrated charge (Q) from 0.5 to 1 μC . Nitrogen contents were quantified relative to homogeneous TiN and a glass standard. The latter ($\text{Y}_{0.12}\text{Mg}_{0.16}\text{Si}_{0.41}\text{Al}_{0.30}\text{O}_{1.40}\text{N}_{0.15}$) was provided by the Laboratoire de Chimie des Matériaux (Université Rennes) and has a nitrogen content of 3.58 ± 0.35 wt%. The value measured by nuclear reaction analysis (NRA) is 3.3 ± 0.15 wt%. Under these technical conditions, glasses of glass inclusions from Renazzo (R3-R4-R5-R6) and Allende (All3-All5-All6-All7-All8) (Table 2) were analyzed.

In the course of the investigation, analytical conditions were modified to lower the detection limit for nitrogen. When a deuteron beam hits a target that contains C, N, O, Si, Mg, and Fe, several reactions occur (Table 1). The energy spectrum of secondary particles obtained contains signals from all these reactions. To minimize interferences with the nitrogen signal (Table 1), for the analysis of glasses, a 48- μm Mylar screen was placed in front of the barrier detector instead of the 9- μm Al screen, which allowed a more efficient separation of protons from α_0 particles and thus eliminated possible interferences in the nitrogen region (Fig. 1a). The integrated charge (Q) was increased from 1 to 3 μC . The nitrogen content of all glasses, with the exception of those already mentioned above, was measured by this new technique. When working with a 48- μm Mylar screen, the energy range for nitrogen lies between ~ 8 MeV and 8.706 MeV. Under these conditions, the α_0 particles due to the $^{14}\text{N}(\text{d}, \alpha)^{12}\text{C}$ reaction can be slowed

Table 1. Nuclear reactions in silicates with 2.1 MeV deuterons and possible interferences with the $^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$ reaction.

a) 9 μm Al screen			
Element	Reaction	Maximum energy reaction (MeV)	Nitrogen interference
N	$^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$	8.927	
	$^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$	8.950	yes
C	$^{12}\text{C}(\text{d}, \text{p}_0)^{13}\text{C}$	3.436	no
	$^{16}\text{O}(\text{d}, \text{p}_0)^{17}\text{O}$	2.953	no
Al	$^{27}\text{Al}(\text{d}, \text{p})^{28}\text{Al}$	6.713	no
	$^{27}\text{Al}(\text{d}, ^4\text{He}^+)^{25}\text{Mg}$	5.421	no
Mg	$^{24}\text{Mg}(\text{d}, \text{p}_0)^{25}\text{Mg}$	6.252	no
	$^{24}\text{Mg}(\text{d}, ^4\text{He}^+)^{22}\text{Na}$	0.114	no
	$^{25}\text{Mg}(\text{d}, \text{p})^{26}\text{Mg}$	9.848	yes
Si	$^{25}\text{Mg}(\text{d}, ^4\text{He}^+)^{23}\text{Na}$	5.568	no
	$^{28}\text{Si}(\text{d}, \text{p}_0)^{29}\text{Si}$	7.457	no
	$^{28}\text{Si}(\text{d}, \text{p}_1)^{29}\text{Si}$	6.237	no
	$^{28}\text{Si}(\text{d}, ^4\text{He}^+)^{26}\text{Al}$	0	no
	$^{29}\text{Si}(\text{d}, \text{p}_0)^{30}\text{Si}$	9.519	yes
Ca	$^{29}\text{Si}(\text{d}, \text{p}_1)^{30}\text{Si}$	7.384	no
	$^{29}\text{Si}(\text{d}, ^4\text{He}^+)^{27}\text{Al}$	4.901	no
Ca	There is no nuclear reaction		
Fe	There is no nuclear reaction		
b) 48 μm Mylar screen			
Element	Reaction	Maximum energy reaction (MeV)	Nitrogen interference
N	$^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$	8.706	
	$^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$	5.994	no
C	$^{12}\text{C}(\text{d}, \text{p}_0)^{13}\text{C}$	2.916	no
	$^{16}\text{O}(\text{d}, \text{p}_0)^{17}\text{O}$	2.359	no
Al	$^{27}\text{Al}(\text{d}, \text{p})^{28}\text{Al}$	6.426	no
	$^{27}\text{Al}(\text{d}, ^4\text{He}^+)^{25}\text{Mg}$	0	no
Mg	$^{24}\text{Mg}(\text{d}, \text{p}_0)^{25}\text{Mg}$	5.947	no
	$^{24}\text{Mg}(\text{d}, ^4\text{He}^+)^{22}\text{Na}$	0	no
	$^{25}\text{Mg}(\text{d}, \text{p})^{26}\text{Mg}$	9.646	yes
Si	$^{25}\text{Mg}(\text{d}, ^4\text{He}^+)^{23}\text{Na}$	0	no
	$^{28}\text{Si}(\text{d}, \text{p}_0)^{29}\text{Si}$	7.196	no
	$^{28}\text{Si}(\text{d}, \text{p}_1)^{29}\text{Si}$	5.931	no
	$^{26}\text{Si}(\text{d}, ^4\text{He}^+)^{26}\text{Al}$	0	no
	$^{29}\text{Si}(\text{d}, \text{p}_0)^{30}\text{Si}$	9.311	yes
Ca	$^{29}\text{Si}(\text{d}, \text{p}_1)^{30}\text{Si}$	7.121	no
	$^{29}\text{Si}(\text{d}, ^4\text{He}^+)^{27}\text{Al}$	0	no
Ca	There is no nuclear reaction		
Fe	There is no nuclear reaction		

Reference: energies before the screens are: 9.014 MeV and 9.901 MeV for $^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$ and $^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$ reactions, respectively.

down (from 8.950 to 5.994 MeV; for detail, see Table 1). The nuclear reactions with all other elements (e.g., C, O, Mg, Al, Si) will give reaction products with a maximum energy that will not interfere with the $^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$ proton energy (Table 1). The interference due to $^{25}\text{Mg}(\text{d}, \text{p})^{26}\text{Mg}$ and $^{29}\text{Si}(\text{d}, \text{p}_0)^{30}\text{Si}$ Si have minimum effects because they involve only rare isotopes (Table 1).

If measurement of trace quantities of nitrogen would have been performed without any screen (neither the 9- μm Al nor the 48- μm Mylar) and with keeping the count rate at 2000 to 3000 c/s, it would have been necessary to reduce the intensity of the primary beam and to work with very long acquisition times. Working with screens allows data acquisition at a low count rate (with zero dead time) and to measure trace quantities of nitrogen in a reasonable time span. The nitrogen concentrations were measured against two standard glasses. The first, [YLaNAI + SiO₂], provided by the Laboratoire Pierre Süe (concentrations in mol%: SiO₂, 55; Al₂O₃, 9; AlN, 18; La₂O₃, 9; Y₂O₃, 9), has a nitrogen content of 2.4 ± 0.12 wt%. The second, [SiAlCaMg + N], provided by the Centre de Recherches Petrographiques et

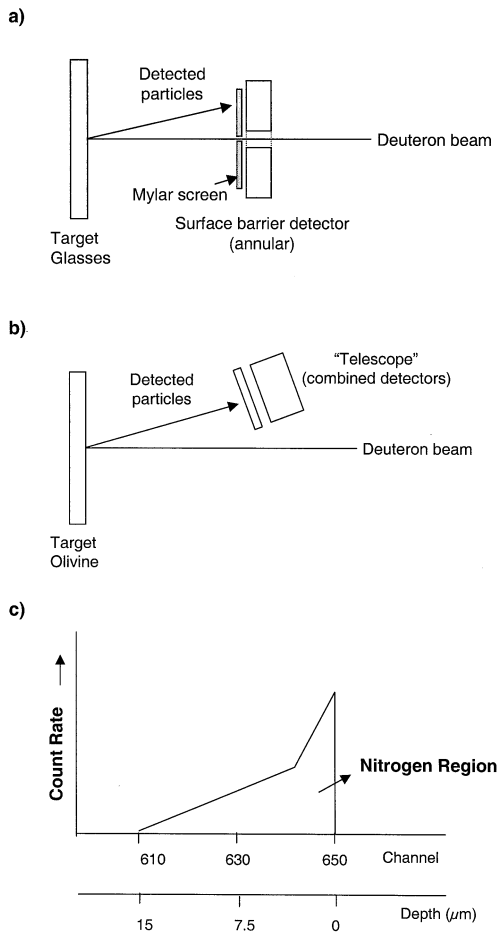


Fig. 1. Scheme of the nitrogen reaction technique. (a) The deuteron beam passes through the annular detector, and a 48- μm Mylar screen is placed in front of the surface barrier detector, which allows separation of p_0 from α_0 particles. (b) For measurements of nitrogen concentrations in olivine, a second detector was placed in front of the surface barrier detector (telescope mode) to produce a slowdown of protons from the $^{25}\text{Mg}(d, p)^{26}\text{Mg}$ reaction. (c) Idealized proton energy spectrum for the reaction $^{14}\text{N}(d, p)^{15}\text{N}$, where an homogeneous nitrogen concentration is assumed, showing the correspondence between channel number and depth. For analysis glasses of glass inclusions, the nitrogen signals were integrated to 10- μm depth.

Geochimiques (CRPG), Nancy, (concentrations in wt%: SiO_2 : 55.81; Al_2O_3 , 15.63; MgO , 13.25; CaO , 15) has 4557 ± 460 ppm N (Humbert, 1998). This second standard, with nitrogen contents close to those measured in glasses, was useful to make a precise determination of the error involved when measuring nitrogen at ppm levels. By using the first glass (N content of 2.4 ± 0.12 wt%) as the standard, we have determined nitrogen contents of the Nancy glass by NRA of 4100 ± 200 ppm. The error, using an integrated charge of 7 μC , was estimated to be $\sim 5\%$.

For glasses, the nitrogen contents usually are integrated to a depth of 15 to 18 μm . Many inclusions are 10 to 15 μm in depth (estimated depth by optical microscopy). To avoid any contribution from the Mg interference from the host olivine beneath the inclusion, we have considered only the nitrogen signal from the first 10 μm from the surface. As can be seen in the illustration of the nitrogen spectrum (Fig. 1c), this will practically comprise the whole nitrogen region.

To measure nitrogen concentration in olivines, we used the telescope mode where two detectors are combined. The second detector was placed in front of the surface barrier detector to count the α_0 particles of the reaction $^{14}\text{N}(d, \alpha_0)^{12}\text{C}$ with acquisition times of 4 to 5 h per point

(Fig. 1b). The purpose of the second detector is to minimize the Mg interferences from the Mg-rich matrix. It produces a differential slowdown of particles from the reaction $^{25}\text{Mg}(d, p)^{26}\text{Mg}$ with respect to those from the $^{14}\text{N}(d, p)^{15}\text{N}$ reaction. This new procedure shifts the Mg interference to low energies (Fig. 2). The detection limits were estimated to be 10 ppm nitrogen in glasses and 20 ppm in olivines.

Major element compositions of glasses were measured with Camebax (Centre d'analyses Camparis, Université de Paris VI), SX50 (Atomic Energy Commission, Buenos Aires, Argentina) and SX100 (Institute of Petrology, University of Vienna) CAMECA electron microprobes. Analyses were performed with a defocused beam (5 μm), 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 471; Métrich and Clocchiatti, 1989), and corrections were made with the online program.

3. SAMPLES

The nitrogen content of glasses of glass inclusions was measured in polished thin sections of the chondrites listed in Table 3. We have selected the glass inclusions considering their occurrence (e.g., isolated or cluster inclusions), the type of glass that forms the inclusions (e.g., clear glass or devitrified), and the phases associated with the glass (e.g., bubbles, crystals, globules). Primary glass inclusions occur as isolated inclusions or form clusters in olivines of aggregates, of chondrules, and in isolated olivines and generally consist of glass and a bubble. They vary in size from 80 to 10 μm (Fig. 3). The glass is mostly clear, with only one inclusion showing signs of devitrification (glass inclusion A128/2 from Acfer 128, Table 2). The associated phases present in glass inclusions—in addition to the glass—are spinel crystals (inclusions HAH5, A128/1 and glass 1A, from Hammadah al Hamra 073, Acfer 128 and Allende DI 4884-2B, respectively, Table 2) and a Fe-Ni globule (inclusion V2 from Vigarano, Table 2).

4. RESULTS

4.1. Petrography and Chemical Composition of Glasses of Glass Inclusions

4.1.1. CO3 Carbonaceous chondrites

All glass inclusions consist of clear glass plus a bubble, except for the glass inclusion DAG 005(3m) (from Dar al Gani 005), which consists of clear glass plus a bubble and a spinel crystal. They are hosted by olivines in aggregates (glass inclusions: DAG 289(2b); DAG 083(3d)-DAG 083(4); DAG 005(2b)-DAG 005(3a)-DAG 005(3g)-DAG 005(3m)-DAG 005(5)) with FeO and CaO contents varying from 2.1 to 12.7 wt% and 0.1 to 0.2 wt%, respectively. Glass inclusion DAG083(3a) in a chondrule is hosted by an olivine that has FeO and CaO contents of 0.66 and 0.59 wt%, respectively. Glass inclusions DAG 291(8a) and DAG 289(4b) are hosted by isolated olivines with low FeO (0.33 and 0.44 wt%, respectively) and high CaO (0.68 and 0.44 wt%, respectively) contents. The nitrogen content of all glass inclusions varies from 44 to 1030 ppm (Table 2).

4.1.2. CV3 Carbonaceous chondrites

4.1.2.1. Allende. Glass inclusions occur isolated (All3, All7, All8) or in clusters (All5, All6) in olivines of aggregates or in an isolated olivine (AllH1). Inclusion sizes vary from 10 to 30 μm . They consist of clear glass plus bubble and they are rich in

Table 2. Major elements (wt%) and nitrogen content (ppm) in glasses of glass inclusions in olivine of chondritic meteorites.

	CO3 Dar al Gani (DAG)											CV3 Bali, Kaba, Vigarano, Allende- Ningqiang															
	291 (8a)	289 (2b)	289 (4b)	083 (3a)	083 (3d)	083 (4)	005 (2b)	005 (3a)	005 (3g)	005 (3m)	005 (5)	Bali 1	Kaba 2	Kaba 3	Kaba 4	Vig 2	Vig 6	Vig 7	Vig 10	All 3	All 5	All 6	All HI	All 7	All 8	Ning 1	
SiO ₂	56.2	46.0	65.0	53.7	52.6	58.4	55.6	61.0	54.4	59.0	51.1	38.7	42.7	42.0	41.0	49.8	56.3	49.9	47.2	47.2	62.2	52.7	41.8	52.1	50.4	81.9	
TiO ₂	1.27	0.97	0.51	0.54	1.24	0.71	0.76	1.12	1.34	1.53	1.30	1.07	0.98	1.06	0.88	0.98	0.87	1.17	1.31	1.64	0.70	0.94	1.18	0.04	0.78	0.31	
Al ₂ O ₃	34.9	30.3	19.1	23.2	20.6	19.3	21.1	25.4	25.6	27.6	26.9	31.0	28.7	29.2	30.5	25.0	21.5	25.8	26.8	26.9	23.2	23.4	28.6	22.7	22.8	10.2	
Cr ₂ O ₃	n.d.	0.28	0.24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.18	0.16	0.26	0.10	0.32	n.d.	n.d.	0.45	0.91	0.92	0.71	0.07	0.59	0.56	0.09	
FeO	0.63	1.02	1.74	0.81	0.84	0.49	0.63	1.68	1.23	1.44	1.78	0.40	0.15	0.28	0.24	1.81	0.53	3.23	0.89	0.75	0.22	0.26	0.37	0.49	0.41	0.78	
MnO	n.d.	n.d.	n.d.	0.11	0.05	n.d.	0.02	0.04	n.d.	0.01	0.04	n.d.	0.02	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	0.04	
MgO	0.32	0.92	3.52	6.03	0.87	0.48	3.74	2.16	3.71	0.61	2.68	1.77	3.62	3.19	3.42	1.29	0.61	0.77	1.30	0.40	0.45	0.31	0.84	0.30	1.16	1.10	
CaO	0.8	6.9	4.1	11.1	13.9	13.6	12.4	3.2	7.0	1.8	5.5	19.3	22.6	24.0	23.6	5.3	13.9	2.2	15.2	15.4	8.6	12.9	21.9	16.3	16.4	1.9	
Na ₂ O	4.57	13.7	5.5	3.16	8.1	6.6	4.61	3.97	5.3	5.9	10.8	6.4	n.d.	n.d.	n.d.	13.8	5.6	16.3	7.4	6.6	2.80	7.5	5.9	6.6	6.6	0.84	
K ₂ O	0.30	0.82	0.48	n.d.	0.35	0.19	0.09	0.22	0.57	0.57	0.56	n.d.	n.d.	n.d.	n.d.	0.56	n.d.	0.86	0.15	0.18	n.d.	0.03	0.11	n.d.	0.03	1.21	
total	99.0	100.3	100.2	98.7	98.6	99.8	99.1	98.8	99.0	98.4	100.6	98.7	98.9	100.0	99.7	98.9	99.4	100.2	100.6	100.0	99.1	98.9	100.7	99.9	99.1	98.4	
N	368	44	150	46	448	74	1030	143	590	130	337	170	190	30	200	85	150	180	490	90	520	1130	630	1160	44	1250	
error	75	9	30	9	90	15	100	30	60	25	65	35	40	6	40	15	30	35	50	18	50	110	60	115	9	125	
(+/- ppm)																											
Size (μm)	20	20	10	20	15	15	20	20	15	15	50	15	10	10	10	20	15	40	20	15	15	10	30	20	10	20	
	CV3 Allende DI		CO4 Hammada al Hamra 073		CH3 Acfer 214					CR Renazzo- Acfer 182 - EL Djouf 001										LL3.1 Bishunpur							
	2C	1A	HAH073 (6)	HAH073 (5)	A214/ 1	A214/ 2	A214/ 3	A214/ 4	A214/ 5	R1	R2	R3	R4	R5	R6	A182/ 1	A182/ 2	A182/ 3	ED001/ 2	Bish 1	Bish 2	Bish 5					
SiO ₂	47.5	47.7	50.5	47.7	56.2	41.9	59.9	52.0	51.0	44.0	57.7	42.0	58.5	50.8	56.7	46.6	64.7	51.6	66.2	74.7	69.4	73.1					
TiO ₂	1.31	1.16	0.84	1.27	0.67	1.56	0.83	0.44	0.61	1.19	0.12	1.32	1.36	1.26	0.58	1.21	0.55	1.25	0.20	0.38	0.59	0.39					
Al ₂ O ₃	24.1	22.0	26.8	25.0	16.8	27.0	18.0	24.2	23.6	26.4	19.0	27.7	18.6	29.6	19.4	23.9	14.7	22.9	17.5	12.3	10.7	10.3					
Cr ₂ O ₃	0.53	0.32	0.02	0.18	1.43	0.12	0.49	0.25	0.29	0.16	0.37	0.32	0.49	0.24	0.23	n.d.	n.d.	0.65	0.50	0.11	0.87	0.65					
FeO	0.29	0.67	1.08	1.08	2.78	0.12	2.32	2.46	2.16	0.10	0.68	0.74	0.47	1.62	0.32	0.83	0.95	1.47	0.45	1.99	2.72	1.61					
MnO	0.02	0.05	0.04	0.07	0.09	0.02	0.08	0.00	0.13	0.02	0.18	bd	0.34	0.04	0.04	0.01	0.02	n.d.	n.d.	0.04	0.18	n.d.					
MgO	0.63	0.65	2.47	3.79	3.30	2.63	0.79	5.34	2.88	3.29	3.19	4.79	3.15	0.59	3.19	4.08	4.55	4.23	2.98	1.27	1.97	0.96					
CaO	18.9	17.7	7.2	8.8	11.0	24.0	9.2	4.36	5.0	24.2	18.3	22.0	17.0	1.0	19.2	21.8	12.3	17.8	13.1	8.2	9.4	8.7					
Na ₂ O	6.1	6.8	7.1	11.3	4.93	1.55	7.8	10.3	13.9	n.d.	n.d.	n.d.	0.18	14.2	0.04	0.02	0.14	n.d.	0.07	n.d.	3.65	2.79					
K ₂ O	0.07	0.23	1.09	0.67	0.28	n.d.	0.57	0.72	1.05	n.d.	n.d.	n.d.	n.d.	0.54	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.23	0.17					
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	1.11	0.22	0.53	0.02	0.05	n.d.	n.d.	0.25	0.26	0.03	0.21	0.03	n.d.	0.07	n.d.	0.09	0.11	0.29					
total	99.5	97.3	97.1	99.9	98.6	99.2	100.5	100.1	100.7	99.4	99.5	99.1	100.4	99.9	99.9	98.5	97.9	100.0	101.1	99.1	99.8	99.0					
N	94	94	322	100	43	70	200	316	540	760	1152	350	480	240	190	52	150	720	63	610	700	1500					
error	20	20	65	20	10	15	40	65	55	75	110	70	50	50	40	10	30	70	13	60	70	150					
(+/- ppm)																											
Size (μm)	20	20	20	15	30	40	15			30	30	80	25	30	25	60	40	30	20	15	50	10					

References: Names of glass inclusions have been shorten to: Dar al Gani : DAG; Vigarano: Vig.; Allende: All; Ningqiang: Ning.; Allende dark inclusion: Allende DI; Hammada al Hamra 073: HAH073; Acfer 214: Acfer; Renazzo: R, Acfer 182: A, El Djouf: ED and Bishunpur. Bish.

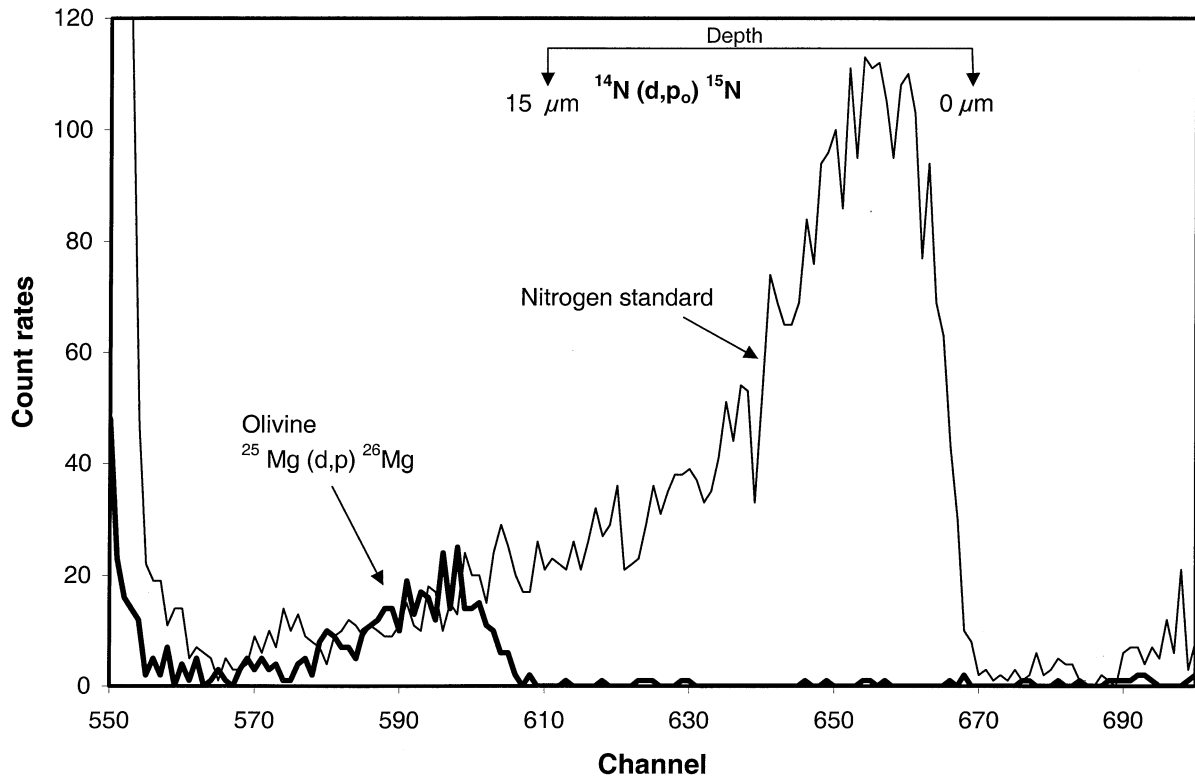


Fig. 2. $^{14}\text{N}(d, p)^{15}\text{N}$ spectra of the standard glass [$\text{YLaNaI} + \text{SiO}_2$] and the standard San Carlos olivine. The Mg interface due to the $^{25}\text{Mg}(d, p)^{26}\text{Mg}$ nuclear reaction leads to a strong increase in the count rates in the low-energy region of the nitrogen spectrum.

SiO_2 (62.2 to 41.8 wt%), Al_2O_3 (22.7 to 26.9 wt%), and CaO (8.6 to 21.9 wt%), and they have variable contents of Na_2O (2.8 to 7.5 wt%) (Table 2).

Aggregates in Allende dark inclusion DI 4884-2B contain fluffy nontransparent and transparent olivines (Kurat et al., 2000). Glass inclusions are present in two transparent olivines of two different aggregates. The glass inclusion glass 2C consists of clear glass plus a bubble and is hosted by a euhedral olivine that is poor in FeO (0.8 wt%) and rich in CaO (0.4 wt%). Glass 1A consists of clear glass plus two spinel crystals (Al_2O_3 , 66.8 wt%; Cr_2O_3 , 4.5 wt%; MgO , 25.6 wt%, FeO, 3.2 wt%) and a bubble. The subhedral host olivine has FeO and CaO contents of 5.1 and 0.25 wt%, respectively. Both glass inclusions are 20 μm in size; they are Si-Al-Ca rich, with Na_2O contents of 6.1 and 6.8 wt%, respectively (Table 2). The nitrogen content in glasses of glass inclusions in olivines of Allende and Allende DI varies from 44 to 1160 ppm.

4.1.2.2. *Vigarano*. Glass inclusions in olivines of aggregates occur in clusters (V2, V7, V10) or as isolated inclusions (V6) with sizes between 10 and 40 μm . They consist of clear glass plus a shrinkage bubble and only inclusion V2 shows, in addition, a Fe-Ni globule.

Glasses are rich in SiO_2 (47.2 to 56.3 wt%) and Al_2O_3 (21.5 to 26.8 wt%) and have variable contents of CaO (2.2 to 15.2 wt%) and Na_2O (5.6 to 16.3 wt%) (Table 2). The nitrogen content varies from 85 to 490 ppm. The glass inclusion V10 is particularly interesting because the bubble, placed in the center of the cavity, was not exposed during polishing. This allows the

measurement of the nitrogen content in the glass—490 ppm (corresponding to the first 5 μm in depth)—and that in the bubble—2100 ppm (this is an equivalent content calculated considering a matrix with the glass composition). The FeO content of the host olivines of all glass inclusions in Vigarano meteorite varies from 0.4 to 4.5 wt%.

4.1.2.3. *Bali, Kaba, and Ningqiang*. Glass inclusions Bali1 (15 μm in size) and Ning1 (20 μm in size) are isolated inclusions in olivine of an olivine aggregate and in an isolated olivine, respectively. Those from the Kaba chondrite (Kaba2, Kaba3, Kaba4) form a cluster in a single olivine grain and are 10 μm in size. Glasses from Kaba and Bali are rich in SiO_2 (38.7 to 42.7 wt%), Al_2O_3 (28.7 to 31.0 wt%), and CaO (19.3 to 24.0 wt%). The Na_2O content of glasses varies from 6.4 wt% in the glass of Bali1 to nondetectable contents (<0.02 wt%) in glasses of the Kaba inclusions. Glasses from Ning1 are extremely rich in SiO_2 (81.9 wt%), rich in Al_2O_3 (10.2 wt%), and have alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 2.05$ wt%) similar to that of CaO (1.9 wt%). The nitrogen content of all glass inclusions in these meteorites varies from 30 to 1250 ppm (Table 2). Host olivines of Bali1 and Kaba (2-3-4) are poor in FeO, 0.52 and 0.33 wt%, and rich in CaO, 0.51 and 0.53 wt%, respectively.

4.1.3. CO4 Carbonaceous chondrites

Two glass inclusions were measured in Hammadah al Hamra 073 (HAH073). The inclusion HAH073(6) shows signs of devitrification and is an isolated inclusion in an aggregate

Table 3. List of polished thin sections studied.

	Type	Name	Provenance
Carbonaceous Chondrites	CO3	Dar al Gani 083	NM, Vienna
		Dar al Gani 289	NM, Vienna
		Dar al Gani 291	NM, Vienna
	CV3	Dar al Gani 005	NM, Vienna
		Allende M5618	NM, Vienna
		Allende Q	NM, Vienna
		Allende	NM, Vienna
		Allende DI 4884-2B	AMNH, New York
		Kaba, from A576	NM, Vienna
	CO4	Ningqiang	NM, Vienna
		Bali, from J2662	NM, Vienna
		Vigarano	NM, Vienna
	CH3	Hammadah al Hamra 073	NM, Vienna
	CR	Acer 214	NM, Vienna
		Renazzo L3812	NM, Vienna
Renazzo L3428		NM, Vienna	
Acer 182		NM, Vienna	
EI Djouf 001		AMNH, New York	
Ordinary Chondrite	LL	Bishunpur	NM, Vienna

olivine with FeO and CaO contents of 17.1 and 0.11 wt%, respectively. Glass inclusion HAH073(5) that consists of clear glass plus a spinel crystal and a bubble is hosted by an isolated olivine (FeO and CaO content of 9.3 and 0.64 wt%, respectively). Both glasses are rich in SiO₂ (47.7 and 50.5 wt%) and Al₂O₃ (25.0 and 26.8 wt%) and have alkali contents (Na₂O + K₂O: 8.2 and 12 wt%) higher than their CaO content (7.2 and 8.8 wt%, respectively). The nitrogen contents are 322 and 100 ppm, respectively (Table 2).

4.1.4. CH3 Carbonaceous chondrites

Glass inclusion A214/1, 30 μm in size, consists of clear glass plus a bubble and a metal globule. It occurs as an isolated inclusion in the center of a euhedral olivine (FeO, 15.9; CaO, 0.1 wt%) of an olivine aggregate. Glass inclusions A214/3 and A214/2 consist of clear glass and a shrinkage bubble. A214/2 is hosted by an euhedral olivine (FeO, 0.25; CaO, 0.66 wt%) in a chondrule and A214/3 is hosted by an isolated olivine (FeO, 20.3; CaO, 0.21 wt%). Nitrogen contents were also obtained from interstitial glasses (A214/4 and A214/5) in a barred chondrule. These interstitial glasses are free of any sign of crystallization.

All glasses are rich in SiO₂ (41.9 to 59.9 wt%) and Al₂O₃ (16.8 to 27.0 wt%) and have variable contents of CaO (4.36 to 24 wt%) and Na₂O (1.55 to 13.9 wt%). Nitrogen contents of glasses in glass inclusions range from 43 to 200 ppm; those in interstitial glasses are 316 and 540 ppm (Table 2).

4.1.5. CR Carbonaceous chondrites

Glass inclusions from Renazzo (R1, R2, R3, R4, R5, R6) and EI Djouf 001 (ED001/2) consist of clear glass and a shrinkage bubble, and their size ranges from 20 to 80 μm. Those of Acfer 182 are as follows: A182/1, 60 μm in size, is composed of clear glass plus a bubble and a spinel crystal; A182/2, 40 μm in size, consists of devitrified glass plus a bubble; and A182/3 is 30 μm in size and consists of clear glass plus a bubble.

Glasses of all inclusions are rich in SiO₂ (42.0 to 66.2 wt%), Al₂O₃ (14.7 to 29.6 wt%), and CaO (12.3 to 24.2 wt%), except for inclusion R5, which is poor in CaO (1.0 wt%). Glasses in olivines of these CR chondrites have very little or nondetectable contents of Na₂O, except for inclusion R5 that has a high Na₂O content (14.2 wt%) (Table 2). All glass inclusions are hosted by aggregate olivines with FeO and CaO contents varying from 0.54 to 2.5 wt% and 0.64 to 0.18 wt%, respectively. Nitrogen contents vary from 52 to 1152 ppm.

4.1.6. LL Ordinary chondrite

Glass inclusions in Bishunpur (Bish1, Bish2, Bish3) olivine are composed of clear glass and a bubble and are 10 to 50 μm in size. Glasses are very rich in SiO₂ (69.4 to 74.7 wt%) and have lower contents of Al₂O₃ (10.3 to 12.3 wt%) and CaO (8.2 to 9.4 wt%) as compared with glass inclusions in carbonaceous chondrites. The content of Na₂O is low (<3.65 wt%). All glass inclusions are isolated in olivines of aggregates with FeO contents varying from 8.4 to 16.9 wt%. They show high nitrogen contents varying from 610 to 1500 ppm.

4.2. Nitrogen Content of Host Olivines

To avoid matrix effects during nitrogen measurements in olivines, we have selected olivines from aggregates exposed at



Fig. 3. Clear glass inclusion in olivine of the Allende meteorite (polished thin sections [PTS] Allende M5618). The big inclusion with a shrinkage bubble is accompanied by several smaller-sized inclusions and by trails of very small secondary, nonglassy inclusions. Transmitted light image.

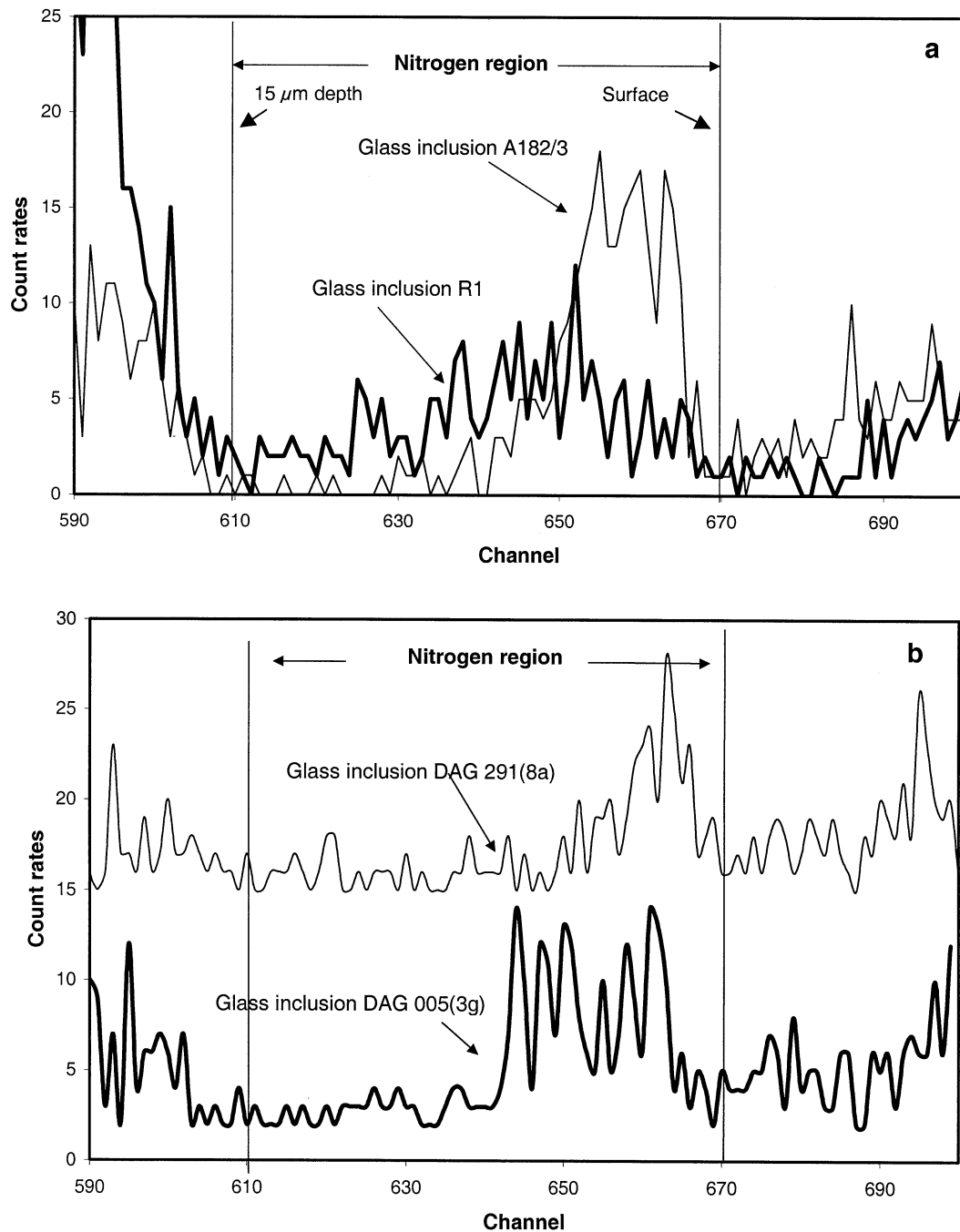


Fig. 4. $^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$ spectra of nitrogen in glasses of (a) glass inclusions A182/3 and R1 (from Acfer 128 and Renazzo chondrites, respectively) and (b) glass inclusions DAG 291(8a) and DAG 005(3g) (from Dar al Gani 291 and Dar al Gani 005 chondrites, respectively). Note the low count rates for nitrogen near the surface of glass inclusions R1 and DAG 005(3g).

both sides of a thick ($500\ \mu\text{m}$) Renazzo sample. The locations where analyses were done were selected with an optical microscope to be fracture-free. To diminish at maximum the possible alterations introduced by sample preparation, the sample was polished with $0.2\ \mu\text{m}$ Al_2O_3 and alcohol. The FeO content of olivines varies from 2.5 to 6.2 wt%. We have also measured the nitrogen content in pyroxenes present in the same

aggregate. Pyroxenes do not host glass inclusions but they constitute—with olivines—the principal mineral phases in aggregates or chondrules. The two pyroxenes analyzed show very small variation in their chemical composition (averages): SiO_2 (60.7 wt%); MgO (34.9 wt%); FeO (3.65 wt%), and Cr_2O_3 (0.62 wt%). The nitrogen content of olivines and pyroxenes is below the detection limit of 20 ppm.

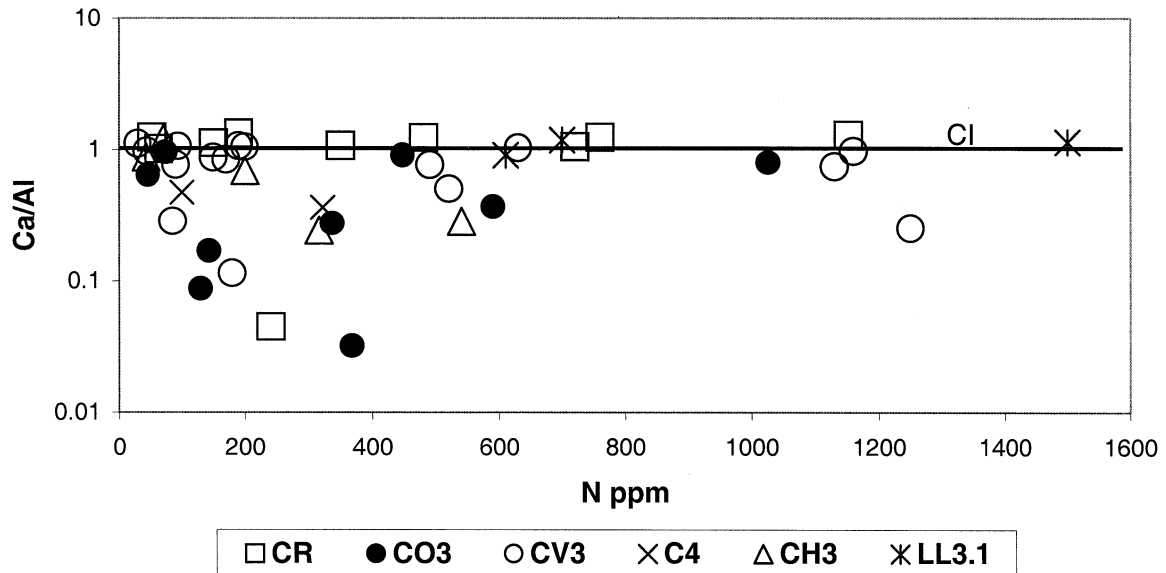


Fig. 5. The variation of N content (ppm) with Ca/Al ratio in glasses of glass inclusions in olivines of CR, CO3, CV3, C4, CH3, and LL3.1 chondrites. CI = Ca/Al ratio of CI chondrites.

5. DISCUSSION

The nuclear reaction technique has been applied to the study of glasses of glass inclusions for three essential reasons: (1) it has an excellent spatial resolution, (2) it is a nondestructive technique, and (3) it has a good sensitivity and allows measuring low nitrogen concentrations (<100 ppm).

5.1. Nitrogen Distribution in Glasses of Glass Inclusions

Because NRA also yields depth information, it permits the measurement of nitrogen content and its distribution at the depth from which protons from the reaction still reach the detector. Nitrogen is present in variable amounts in glasses of primary glass inclusions with a variable distribution within the inclusion. Figure 2 shows a typical nitrogen spectrum, with the nitrogen region limited between channel 670 (corresponds to the energy of protons coming from the surface of the target: 0 μm depth) and channel 610 (corresponds to 15 μm depth; Fig 1c). When we compare the nitrogen spectra obtained from glass inclusions (Fig. 4) to that of the standard glass (Fig. 2), we observe that inclusion A182/3 shows a typical nitrogen spectrum but inclusion R1 is shifted to the low-energy regions (or low channel number) showing low nitrogen contents near the surface. Similarly, the nitrogen signal from glass inclusions DAG 005(3g) is also shifted to lower energy regions as compared with DAG 291(8a). This shift, showing that few or no nitrogen is detected near the target surface, is independent of the total amount of nitrogen as is observed in glass inclusions Acfer 182/A3 and R1, which have similar nitrogen contents (Table 2). Because the surface of the inclusion is an artificial one, created by cutting and polishing the sample, the absence of nitrogen in the first few micrometers near the surface of the glass (e.g., DAG 005(3g)) seems difficult to attribute to an original feature; rather, it may be related to loss of nitrogen when the inclusion was exposed to different chemical condi-

tions. A possible cause for such a loss could be changing redox conditions. It is known that large amounts of nitrogen can be chemically dissolved in a glass under proper conditions. This chemical solubility increases (by a factor of 10^4 to 10^5 compared with physical solubility) with increasingly reducing conditions (Mulfinger, 1966). If a glass incorporated nitrogen under reducing conditions, it can release it if conditions become more oxidizing, which is the explanation for the presence of bubbles rich in nitrogen in industrial glasses (Mulfinger, 1966). A similar process may also have worked in glass inclusions in chondritic olivines, as it is suggested by the glass inclusion in the Vigarano chondrite (V10), where high quantities of nitrogen are present in the bubble. This, along with the trace element data on glasses of glass inclusions (Kurat et al., 1997; Varela et al., 2002a), clearly indicates formation of these glasses under reducing conditions. The release of nitrogen from a freshly cut glass surface (only possible if N is present as a volatile species) as well as the detection of a N-rich bubble in the Vigarano sample (V10) seem to indicate a change from reducing to more oxidizing conditions.

Variation in the nitrogen content can also be observed in glasses of glass inclusions hosted by the same olivine (e.g., Kaba2, Kaba3; Table 2). These inclusions have similar refractory (Si-Al-Ca)-rich compositions, and considering their primary occurrence in the very same host, it is likely that they were formed during similar redox conditions. However, they have different nitrogen contents.

Generally, such heterogeneous distribution of nitrogen from one inclusion to another is a feature that characterizes practically all types of glass inclusions in olivines. This indicates that the intrameteorite heterogeneities mentioned previously can occur at a very small scale and were established during formation of a single olivine grain. This indicates heterogeneous trapping of solid nitrogen carrier phases. High resolution transmission electron microscopy could eventually produce evi-

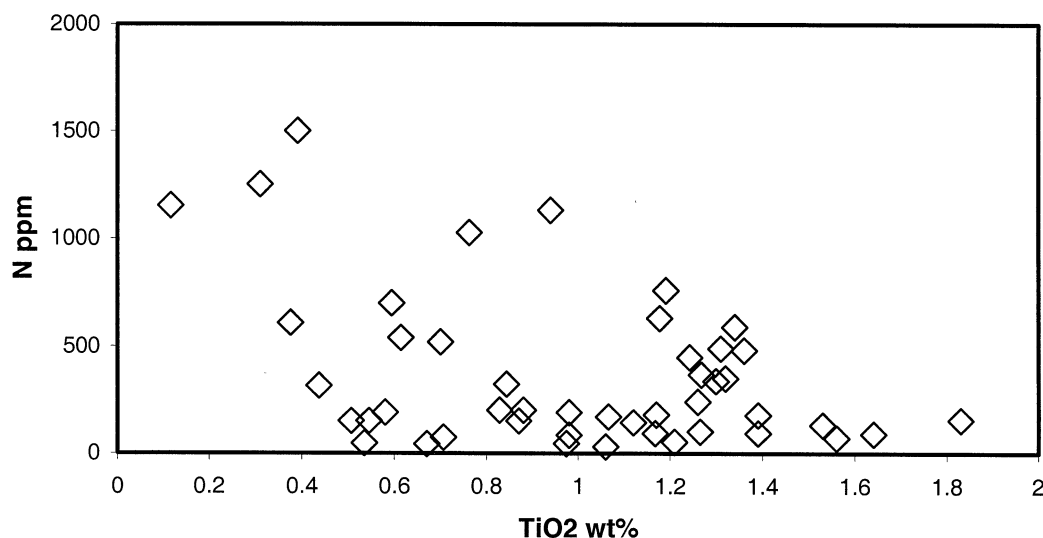


Fig. 6. Variation of nitrogen (ppm) with TiO_2 (wt%) content in glasses of glass inclusions in olivines.

dence for the existence of nanometer-sized nitrogen compounds.

5.2. Nitrogen in Olivines

Because glass inclusions are formed contemporaneously with the host, the presence of nitrogen in olivines is another parameter to take into account. As was outlined above, it was necessary to develop a new method to analyze the nitrogen content in Mg-rich phases to minimize the Mg interference in the nitrogen energy region. In the previous section, we explained that the protons produced at the surface of the target will have higher energy, and those produced at deeper levels (the result of the many interactions with target atoms) will have lower energies as they reach the detector. The Mg interference due to the $^{25}\text{Mg}(\text{d}, \text{p})^{26}\text{Mg}$ nuclear reaction produces protons with energies similar to those constituting the lower energies region of the nitrogen spectrum. Thus, if the Mg interference is not shifted from the nitrogen region, its presence will increase the count rates of nitrogen in the low-energy part of the nitrogen region. This increment, considered to be only the result of nuclear reactions, led us to misunderstand our first results and to overestimate the nitrogen content in olivines (Varela et al., 1998). The new procedures (the telescope mode, explained in the analytical techniques and illustrated in Fig. 1b) allowed shifting the Mg interference to lower energies, thus providing a clean nitrogen signal (Fig. 2).

Our new results indicate that for all types of olivines (e.g., isolated olivines, olivines of chondrules and aggregates) with variable FeO contents (showing formation under different redox conditions), the nitrogen content is below the detection limit of 20 ppm. This result is similar to that obtained for carbon in olivines (Varela and Métrich, 2000) and seems to indicate that nitrogen, as well as carbon, have not entered the structure of olivine during the primary formation processes. The very low contents of nitrogen and carbon in olivines of chondritic meteorites appear to be structurally controlled. Because nitrogen can only be accepted in trace amounts in the

structure of olivines, the influence of the host in causing the variable amounts of nitrogen contained in glasses is likely to be negligible.

5.3. Chemical Composition of Glasses

With this result in mind, our discussion will now be concentrated on elucidating whether the variable contents of nitrogen in glasses can be either a primary feature (e.g., heterogeneous trapping of nitrogen during glass formation) or could be the result of secondary processes that affected glasses of glass inclusions.

Secondary processes can affect glasses of glass inclusions in a similar way as they do the constituents of chondrites. These processes involve a replacement of elements from the solid by others from the vapor (e.g., replacement of Ca by Na, exchange of Mg^{2+} by Fe^{2+} or of Al^{3+} by Cr^{3+} ; e.g., Kurat, 1988). Glasses of the primary glass inclusions are characterized by a highly refractory (Al-Ca-rich) composition. Those from the CR-type chondrites, Kaba (CV3) and inclusion Bish1, have Na_2O contents below the detection limit. All other glass inclusions have glasses with highly variable contents of Na_2O (Table 2).

A recent study (Varela et al., 2002a) of glasses of glass inclusions in the CR-type chondrite group (Renazzo, El Djouf 001, Acfer 182) showed that glasses of glass inclusions have, generally, a chondritic $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. However, the Na-rich glasses in the CR-type chondrite group have a disturbed $\text{CaO}/\text{Al}_2\text{O}_3$ ratio indicating a replacement (secondary) of Ca by Na (Varela et al., 2002a). Conversely, this exchange reaction seems not to have occurred in other primitive glasses of glass inclusions. Glasses from Allende DI (1A, 2C) as well as from LL3.1 chondrite Bishunpur (Bish2, Bish5) and some of CH3 chondrites Acfer 214 (A214/1, A214/2) are also rich in Na, but have a chondritic or near-chondritic Ca/Al ratio, which makes a metasomatic Ca-Na exchange unlikely. The fact that the incorporation of Na has not altered the Ca/Al chondritic ratio of glasses clearly suggest that this element was incorporated into

the glasses as a primary element during formation of the inclusions (Varela et al., 2002b). The presence of Na as a primary element indicates a change in the physicochemical conditions, in particular the persistence of low temperatures that allowed condensation of Na (~ 950 °C). Nevertheless, as it is explained below, the fact that Na can be incorporated as primary element or be the result of secondary processes seems not to have affected the amount of nitrogen that can be stored in glasses.

Primary glass inclusions hosted by a transparent olivine from Allende dark inclusion have contents of Na₂O of 6.1 and 6.8 wt%, respectively, chondritic Ca/Al ratios (suggestive of incorporation of Na during glass inclusions formation) and low contents of nitrogen. The glass inclusion AllH1, hosted by an isolated olivine in Allende (hundreds of microns away from the dark inclusion) has a similar content of Na₂O (5.9 wt%) and a chondritic Ca/Al ratio but is enriched six times in nitrogen compared with those in the dark inclusion olivine. Allende inclusions All3, All7, and All8 have subchondritic Ca/Al ratios and the same content of Na₂O (6.6 wt%), but very different contents of nitrogen (44, 90 and 1160 ppm, respectively, Table 2). A similar situation is observed in the glass inclusions of the CO3 chondrite group.

Our results show that for the majority of the glass inclusions in olivines from the CR type, LL, and the CV3 chondrite groups with chondritic or near-chondritic Ca/Al ratio, nitrogen can be present in variable amounts (Fig. 5). The variable amounts of nitrogen stored in glasses seems to be a primary feature established at the moment of formation of the inclusion.

However, for this hypothesis to be correct, we have to be sure that glass inclusions have behaved as essentially closed systems with respect to nitrogen. Comparison of the CR chondrites Acfer 182 and Renazzo shows that they have very different bulk nitrogen contents (Acfer 182 with 85 ppm and Renazzo between 500 and 800 ppm, Kerridge, 1985; Grady and Pillinger, 1993) with Renazzo being six to nine times richer in nitrogen. However, the amount of nitrogen stored in glasses of glass inclusions appertaining to these meteorites remains within a similar order of magnitude (from 50 to 700 ppm N in Acfer 182; from 190 to 1150 ppm N for Renazzo) with a mean nitrogen content for Renazzo (530 ppm) less than two times that in Acfer 182 (300 ppm). Microchondrules in the carbonaceous chondrite Acfer 182 are enriched in nitrogen (1400 ppm) relative to the whole rock (85 ppm, Grady and Pillinger, 1993). Conversely, nitrogen concentrations in individual chondrules of the ordinary chondrite Bjurböle are lower (between 2.4 and 11.4 ppm) than those of the whole rock (26.72 ppm N, Murty and Marti, 1985). However, glasses of glass inclusions in olivines from both, carbonaceous chondrites and the ordinary chondrite Bishunpur, have comparable nitrogen concentrations (Table 2).

An interesting result is the high content of nitrogen in interstitial glasses of a barred chondrule of the Acfer 214 CH3 chondrite (A214/4, A214/5, Table 2). Nitrogen contents are even higher than those of glass inclusions in an olivine of an aggregate, in an olivine in a chondrule and in an isolated olivine of the same chondrite (Table 2). Mesostasis glasses in barred olivine chondrules usually behave as open systems as they are exposed to alteration and/or evaporation processes (e.g., Varela et al., 2002c). However, temperatures that have affected this

specific chondrule appear to have been low enough to avoid evaporative loss of nitrogen from the glass. Other possibilities also to be considered are, for example, that conditions were reducing during heating or that the chondrule glass lost nitrogen but because the initial contents of nitrogen were very high, some could still be detected.

However, searching for the nitrogen carrier within the glass is a frustrating task, because oxidation of the most likely precursor phases—Si, Al, and Ti nitrides—will not leave a detectable trace. An example of this is the highly variable and uncorrelated concentrations of TiO₂ and nitrogen (Fig. 6), which indicates that Ti was mainly condensed as a refractory oxide, as is documented by the chondritic Ti/Al ratio of most glasses.

Trapping of refractory nitrogen species by the condensing liquids (which later were chilled to glasses) seems to be a possibility to explain the enormous variability of N contents in glasses. Such very fine grained dust could have contained nitrides that were subsequently oxidized and transformed into volatile species (N₂) that could have diffused toward and concentrated into the bubble. This may explain, among other things, also the case of the Vigarano Vig10 inclusion where high quantities of nitrogen were detected in the bubble suggesting that a diffusion process occurred after the breakdown of a possible solid precursor.

6. CONCLUSIONS

Nitrogen contents and distribution in 48 glasses of primary glass inclusions in olivines of CV3, CO3, CR, C4, CH3, and LL chondrites were measured by means of the ¹⁴N(d, p)¹⁵N nuclear reaction. Nitrogen contents of anhydrous silicates are low and nitrogen is preferentially accumulated in glasses of primary glass inclusion of olivines. The contents of nitrogen stored in glasses are highly variable (30 to 1500 ppm) for all chondrite groups.

The chemical compositions of the glasses appear not to play an important role in controlling the variable amounts of nitrogen that can be stored in glasses. The variable content of nitrogen collected in glasses of glass inclusions, either in the same olivine or in olivines of the same chondrule or aggregate, show that nitrogen can be heterogeneously sampled during the growth of the constituents of chondrules, as seems also to be indicated by isotope data. Glasses of primary glass inclusions seem to be reliable phases where nitrogen can be stored and preserved.

The heterogeneous distribution of nitrogen in glasses suggests incorporation through solid precursor phases. Subsequent oxidation and transformation to a volatile species could provoke nitrogen release, diffusion, or both. Trapping of reduced refractory nitrogen species by the glasses seems to be a good mechanism for accumulating nitrogen in silicates at a very early stage of formation of chondrules and other constituents of chondrites.

Acknowledgments—We thank the nuclear microprobe team of Laboratoire Pierre Süe for constant assistance during measurements, B. Marty, Nancy, for providing a sample of the standard glass, T. Ntaffos for help with microprobe analyses, and J. P. Duraud and Nicole Métrich for their constant interest and help. This article benefited from the constructive reviews by Monica Grady and two anonymous reviewers

and by the thorough editorial assistance of associate editor U. Ott. This work was supported by LPS, postdoctoral fellowships CIES and CEADRI (LPS and CEA, France) to M.E.V., FWF and Oskar und Friederike Ermann-Fonds, Austria, and CONICET and Fundación Antorchas, Argentina.

Associate editor: U. Ott

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