

© Springer-Verlag 2001 Printed in Austria

# Glass-bearing inclusions in Nakhla (SNC meteorite) augite: heterogeneously trapped phases

M. E. Varela<sup>1</sup>, G. Kurat<sup>2</sup>, and R. Clocchiatti<sup>3</sup>

<sup>1</sup> CONICET – UNS, Depte. de Geologia, Bahia Blanca, Argentina
<sup>2</sup> Naturhistorisches Museum, Vienna, Austria
<sup>3</sup> Laboratory Pierre Süe, CEA – CNRS, Gif sur Yvette, France

With 4 Figures

Received April 10, 2000; revised version accepted October 19, 2000

#### Summary

Nakhla augite and olivine grains commonly contain glass-bearing inclusions. In contrast to olivines, augites host only one type of multiphase inclusions which consists of euhedral to subhedral augite, Ti-magnetite and pigeonite plus silica-rich glass and a bubble. No fractures surround these inclusions, making it likely that they are of a pristine composition. Heating experiments with a final temperature of  $1150 \,^{\circ}\text{C}$  were done for the first time with Nakhla augite inclusions. During heating the glass melted and crystals inside the inclusions were dissolved in the melt whereby its chemical composition changed. The quenched glass is poorer in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and richer in CaO, FeO and MgO compared to unheated inclusion glass. Our in situ analyses allowed us to estimate the initial composition of a liquid co-existing with Nakhla augite at 1150 °C and 1 atm pressure. Several features of Nakhla, such as the high Fe/Mg ratio of the augite, which is out of equilibrium with the glass, the highly variable alkali content and the Na/K ratio of the glasses are incompatible with the standard model that states that SNC meteorites are all igneous rocks formed from basaltic magmas. Our results on re-melted glasses suggest a more complex and possibly non-magmatic genesis of Nakhla. Both types of glass-bearing inclusions (those hosted by augite or olivine) could represent heterogeneously trapped mineral + glass inclusions. Those hosted by augites mimic at least in part parental melt inclusions. However, the quenched glass is out of equilibrium with the host with respect to the Fe/Mg ratio and has too much compositional variation to be representative of a parental melt.

#### Zusammenfassung

# Glasführende Einschlüsse im Augit von Nakhla (SNC-Meteorit): Heterogeneingeschlossene Phasen

Augite und Olivine im Achondriten Nakhla enthalten häufig glasführende Einschlüsse. Im Gegensatz zu den Olivinen enthalten die Augite nur einen Typ Multiphasen-Einschluß, welcher aus idiomorphem bis subidiomorphem Augit, Ti-Magnetit, Pigeonit und einem SiO<sub>2</sub>-reichen Glas mit Blase besteht. Diese Einschlüsse sind nicht von Sprüngen umgeben, was es wahrscheinlich macht, dass sie ihre ursprüngliche Zusammensetzung unverändert erhalten haben.

Erstmals wurden Schmelz-Experimente mit Endtemperaturen von 1150°C an Nakhla Augiten durchgeführt. In diesen Experimenten schmolz das Glas der Einschlüsse, löste die koexistierenden kristallinen Phasen auf und änderte dabei seine chemische Zusammensetzung. Das durch Abschrecken dieser Schmelze erzeugte Glas ist ärmer an SiO<sub>2</sub> und Al<sub>2</sub>O<sub>3</sub> und reicher an CaO, FeO und MgO als das ursprüngliche Einschlußglas. Diese in situ-Analyse erlaubt eine Abschätzung der ursprünglichen Zusammensetzung einer Schmelze im Gleichgewicht mit Nakhla Augit bei 1150 °C und 1 atm Druck. Einige Eigenschaften von Nakhla, wie das hohe Fe/Mg-Verhältnis des Augites, welches nicht im Gleichgewicht mit dem Glas ist, die variablen Alkali-Gehalte und die Na/K-Verhältnisse im Glas sind inkompatibel mit dem Standard-Modell für die SNC-Meteorite, welches diese als magmatische Gesteine basaltischer Herkunft sieht. Unsere Ergebnisse weisen auf eine komplexe, möglicherweise nicht-magmatische Entstehung von Nakhla hin. Sowohl die glasführenden Einschlüsse im Olivin als auch jene im Augit von Nakhla könnten Produkte eines heterogenen Aufsammelns von Mineral plus Glas sein. Die Einschlüsse im Augit imitieren zumindest zum Teil Schmelzeinschlüsse. Allerdings sind sie mit ihrem Fe/Mg - Verhältnis nicht im Gleichgewicht mit dem Augit und sind auch in ihrer Zusammensetzung zu inhomogen, um für ein mögliches Mutter-Magma repräsentativ zu sein.

## Introduction

The Nakhla achondrite is a member of the SNC (Shergotty, Nakhla, Chassigny) group of meteorites and is believed to be an igneous rock that formed near the surface of Mars (*Bunch* and *Reid*, 1975; *Berkley* et al., 1980; *Treiman*, 1986). Nakhla is an olivine-clinopyroxenite with augite as the major phase and a finegrained intercumulus mesostasis. Its texture is dominated by euhedral and subhedral grains of augite and is suggestive of a cumulate origin (*Bunch* and *Reid*, 1975). Detailed petrographic descriptions can be found in *Reid* and *Bunch* (1975), *Berkley* et al. (1980) and *Treiman* (1986). Augites range in size from 0.4 to 1.2 mm and have small (from 10 to  $30 \mu$ m) multiphase glass-bearing inclusions. The subhedral olivines (about 10 vol% of the rock) reach 1.4 mm in size and some of them contain large glass-bearing inclusions.

Considerable effort has been put in attempting to reach a better understanding of the processes involved in the genesis of Nakhla. However, debates about its composition and genesis continue, as models do not properly fit reality (*Treiman*, 1986; *Longhi* and *Pan*, 1989; *Harvey* and *McSween*, 1992; *Treiman*, 1993).

We present an investigation of glass-bearing inclusions in augite, which appear to be particularly useful for contributing to this ongoing discussion. Previous studies made use of inclusions hosted by Nakhla's olivine. By applying different analytical methods, *Harvey* and *McSween* (1992) and *Treiman* (1993), respectively, have obtained different chemical compositions of possible parent magmas for Nakhla. These differences are due to the many adjustments and corrections involved in the methods applied. The main assumption under which both studies were undertaken was, that glass-bearing inclusions in olivines are residuals of the parent magma, which was trapped during the growth of the host. Thus, the assemblage of glass and minerals inside inclusions were presumed to be the result of a closed-system evolution during cooling.

Here we report on the first heating experiments performed on glass-bearing inclusions in Nakhla augite. Our data puts additional constraints on the formation conditions of this meteorite and question the widely believed igneous genesis of this meteorite.

### Analytical techniques

Analytical scanning electron microscopy was performed with a JEOL-6400 instrument (Naturhistorisches Museum, Vienna) with a sample current of 1 nA and an accelerating voltage of 15 kV. Major element compositions of minerals were measured with a Camebax CAMECA electron microprobe (Centre d'analyses Camparis, Université de Paris VI) using an accelerating voltage of 15 kV and a sample current of 40 nA. Standard correction procedures were applied. For analysis of glasses of glass-bearing inclusions, Na<sub>2</sub>O and SiO<sub>2</sub> were measured first with a counting time of 5 s and 10 s, respectively, a beam current of 10 nA and the maximum possible beam diameter. The precision for glass analyses was established by analysing basaltic (ALV 981) and rhyolitic (CFA 47) glass standards (*Métrich* and *Clocchiatti*, 1989).

Heating experiments were performed in the Laboratory Pierre Süe, Gif sur Yvette (France), in a Pt-Pt<sub>90</sub> Rh<sub>10</sub> heating stage at 1 bar pressure in a hot He atmosphere as oxygen getter (*Zapunnyy* et al., 1989). The oxygen fugacity was monitored in the outgoing gas flux with a zirconia probe and calibrated with an Ar (1% H<sub>2</sub>) gas calculated to have an oxygen fugacity of approximately  $10^{-9}$  and  $10^{-10}$  atm at 1150 °C. The system was calibrated at the melting point of Au (1063 °C). Samples were quenched to about 500 °C in less than 1 s.

# Results

## Petrography of glass-bearing inclusions

Only one type of primary glass-bearing inclusion is present in the augite of our Nakhla samples (**P**olished **T**hin **S**ections – PTS-NAKHLA, Nakhla #1 and #2, all from Naturhistorisches Museum, Vienna). These multiphase inclusions in augites have a small size (from 10 to 30  $\mu$ m), a sub-rounded or irregular shape and generally from clusters (Fig. 1A) in the pyroxene cores. Isolated inclusions located at the centre of the host are rare (Fig. 1B). Inclusions consist of glass plus  $\mu$ m-sized crystals of augite, Ti-magnetite and pigeonite, and a shrinkage bubble. Small chlorapatite and troilite grains are also present. Crystals inside inclusions are euhedral to subhedral and occupy a large part of the inclusion cavity (Fig. 1C). Inclusions in augite are generally free of surrounding fractures.

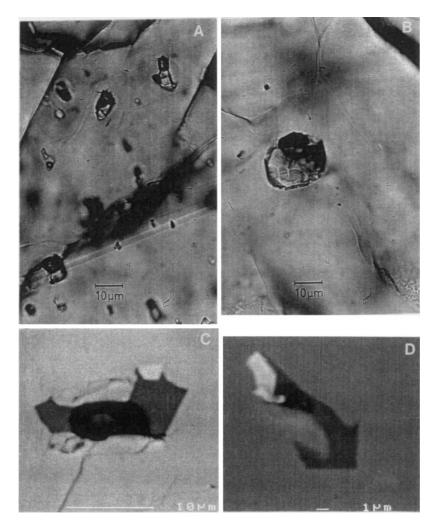


Fig. 1. A Cluster of primary multiphase inclusions in Nakhla augite with small size (from 10 to  $30 \,\mu\text{m}$ ) and sub-rounded or irregular shape. **B** Rare isolated inclusion located at the centre of the host augite. **C**, **D** Back-scattered electron images of glass-bearing inclusions in Nakhla augite. They consist of glass (dark grey), crystalline phases (grey) and a bubble

Multiphase inclusions are also present in olivines. Their sizes range from  $< 10 \,\mu\text{m}$  to  $> 300 \,\mu\text{m}$  and they contain  $\mu\text{m}$ -sized crystals of augite, Ti-magnetite, pigeonite, chlorapatite and glass (*Harvey* and *McSween*, 1992; *Treiman*, 1993). These primary inclusions are located in the centre of the host grains, generally isolated, surrounded by fractures and they do not contain a bubble. A detailed description of glass-bearing inclusions in olivines of Nakhla can be found in *Harvey* and *McSween* (1992) and *Treiman* (1993).

# Chemical composition of inclusion phases

Representative compositions of glass and crystalline phases in multiphase inclusions in Nakhla augites are given in Tables 1 and 2. Glasses are homogeneous

Table 1. Selected ASEM and EMP analyses (wt%) of the host and glass in glass-bearing inclusions in Nakhla augite

	G1	G2	G3	G4	G5	G6	GHa	GHb	GHc	GHd	GH(6)	Aug1.	Aug2.
SiO <sub>2</sub>	73.3	68.5	66.4	71.3	62.7	71.7	48.1	56.2	56.1	59.5	55.4	51.0	52.3
TiO <sub>2</sub>	_	0.8	_	0.8	0.4	0.2	2.4	0.4	0.9	0.5	1.1	0.23	0.09
$Al_2O_3$	15.7	14.5	12.8	17.1	14.2	13.3	7.2	8.8	10.8	10.5	9.4	0.67	0.70
$Cr_2O_3$	0.1	0.8	_	0.7	0.3	_	0.3	0.2	0.5	_	0.2	0.43	0.41
FeO	0.9	2.6	4.3	2.6	6.6	4.0	19.6	10.0	12.1	11.4	13.4	14.4	14.0
MnO	_	_	_	0.4	0.5	0.7	0.3	-	0.6	0.2	0.2	0.52	0.49
MgO	0.3	1.4	0.8	0.9	0.2	1.4	5.5	6.8	4.6	3.8	4.9	12.8	13.2
CaO	1.6	4.9	6.7	1.9	2.0	3.8	13.2	10.9	9.2	7.4	10.2	19.0	18.0
Na <sub>2</sub> O	4.7	3.5	4.0	3.3	5.2	3.9	2.7	5.3	2.7	2.8	3.2	0.19	0.25
$K_2O$	2.3	2.5	3.4	0.1	5.6	0.4	0.3	0.9	0.8	0.8	0.6	0.04	0.00
$P_2O_5$	0.3	_	0.7	1.0	1.0	0.5	_	-	0.9	0.5	0.3	_	_
Totals	99.2	99.5	99.1	100.0	98.7	99.9	99.6	99.5	99.2	97.4	98.9	99.3	99.4

*G1–G6* Glass composition of unheated inclusions;  $Gh_a$ – $Gh_d$  Glass composition of heated (1150 °C) inclusions; Gh(6) Mean glass composition of heated inclusions (average of 6). *Aug1–Aug2* composition of augite hosts selected for heating experiments (EMP analysis)

Table 2. Representative composition of co-existing phases and glasses in glass-bearing multiphase inclusions in Nakhla augite (ASEM analysis)

	Glass-Bearing Inclusions										
	Aug.	Aug.	G9	Pig.	G10	Aug.	Aug.	G11	Aug.	Aug.	G12
SiO <sub>2</sub>	46.5	46.3	68.7	49.7	70.5	46.2	49.8	68.2	48.4	48.4	66.3
TiO <sub>2</sub>	0.5	0.9	n.d.	n.d.	0.4	0.3	n.d.	0.7	0.1	0.1	n.d.
$Al_2O_3$	5.2	2.8	19.9	1.9	16.4	4.7	0.7	16.4	3.6	4.2	12.4
$Cr_2O_3$	0.9	n.d.	n.d.	n.d.	n.d.	0.9	0.8	0.3	0.3	0.8	0.8
FeO	21.2	19.9	2.1	30.7	1.7	17.9	16.1	0.5	19.2	20.2	3.8
MnO	n.d.	1.8	n.d.	0.9	n.d.	0.8	0.3	n.d.	0.1	1.1	n.d.
MgO	7.8	7.4	0.8	12.9	1.4	9.4	11.1	0.5	9.7	10.5	3.9
CaO	17.5	19.2	1.2	3.0	3.7	18.7	20.9	2.5	16.3	13.5	8.1
Na <sub>2</sub> O	0.4	0.8	4.6	0.3	4.3	0.4	n.d.	6.1	0.6	1.2	3.0
K <sub>2</sub> O	n.d.	n.d.	1.2	n.d.	1.0	n.d.	n.d.	3.7	n.d.	n.d.	1.0
Totals	100	99.1	98.5	99.4	99.4	99.3	99.7	98.9	98.3	100	99.3

Crystal phases inside inclusions: Aug. augite; Pig. pigeonite; G9, G10, G11 and G12 coexisting glasses; n.d. not detected

in a given inclusion but vary in composition between inclusions: SiO<sub>2</sub> (62.7–73.3 wt%), Al<sub>2</sub>O<sub>3</sub> (12.4–20 wt%), Na<sub>2</sub>O (3–6 wt%), K<sub>2</sub>O (0.1–5.6 wt%), CaO (1.2–8.1 wt%), FeO (0.5–7 wt%) and MgO (0.2–3.9 wt%). The Fe/Mg and Na/K ratios vary from 1.2 to 49 and 0.7 to 30.6, respectively. No systematic chemical variation was detected between the glass of inclusions located in the centre and those in the rim of the augites. However, inclusions which contain different daughter crystals that occupy different proportions of each inclusion's cavity show variations in the

contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and FeO. For example, the chemical composition of glass in inclusion G5 (Table 1), where only small-sized ( $< 3 \mu m$ ) chlorapatite crystals are present, is different from that of the glass of inclusion G11, where two augite crystals co-exist with the glass (Table 2).

The chemical composition of minerals inside inclusions is given in Table 2. Clinopyroxenes range in composition from salite to augite with  $Al_2O_3$  contents between 0.7 and 5.2 wt%, respectively, and variable contents of FeO (16–20.2 wt%), MgO (7.4–11.1 wt%) and CaO (13.5–20.9 wt%). Augites have molecular compositions between  $En_{33}$ -Fs<sub>37</sub>-Wo<sub>30</sub> and  $En_{31}$ -Fs<sub>26</sub>-Wo<sub>43</sub> and Fe/Mg ratios between 1.9 and 5.3. The included augites are rich in Al and Fe as compared to the

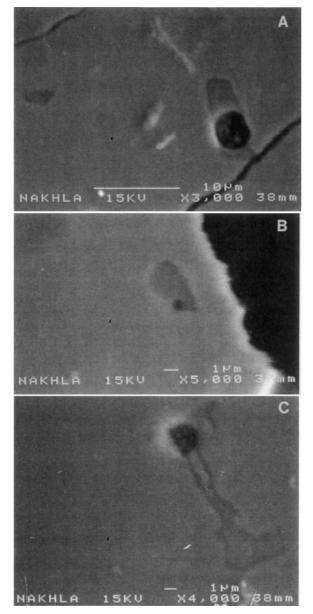


Fig. 2. Back-scattered electron scanning images of heated glass-bearing inclusions in Nakhla augites. A inclusion GH2, B inclusion GH3, C inclusion GH1: Note the absence of crystals and the thin connection still preserved in the neck of C

inclusion host (Table 1). The variation in the  $Al_2O_3$  content has to be taken with care as some beam overlap with the surrounding glass during analysis cannot be rule out.

The host augites, which were selected for the heating experiments, have molecular compositions between  $En_{37}$ -Fs<sub>24</sub>-Wo<sub>39</sub> and  $En_{38}$ -Fs<sub>24</sub>-Wo<sub>38</sub> (Table 1).

# **Heating experiments**

Heating experiments were performed with varying heating rates from 5 °C/min up to 20 °C/min. Runs lasted 8 hours each, with heating rates of 5 °C/min up to 300 °C, 2–3 °C/min up to 700 °C and 1–2 °C/min from this temperature up to the final temperature of 1150 °C. The final temperature was held for thirty minutes after which a rapid quench preserved the final composition of the melt. Multiphase inclusions in augites are free of surrounding fractures. This feature diminished the risk of early decrepitation of inclusions during heating. However, because similar heating experiments performed with Chassigny olivine with final temperatures of 1200 °C led to decrepitation of some inclusions (*Varela* et al., 1998), we decided to heat the Nakhla inclusions up to only T ~ 1150 °C. The small size of the inclusions posed some problems. This, and some oxidation that affected the host during the experiments did not allow us to observe and document precisely the dissolution processes inside inclusions and consequently, we were not able to determine specifically the temperature at which each phase has disappeared.

After quenching from the final temperature of  $1150 \,^{\circ}$ C, the inclusions turned out to be free of crystals (Fig. 2). The chemical composition of the glass in heated inclusions (Table 1) is variable: SiO<sub>2</sub> (48–59.5 wt%), TiO<sub>2</sub> (0.4–1.1 wt%), Al<sub>2</sub>O<sub>3</sub> (7.2–10.8 wt%), FeO (10–19 wt%), CaO (7.4–13 wt%), K<sub>2</sub>O (0.3–0.85 wt%) and Na<sub>2</sub>O (< 5 wt%). Molecular Fe/Mg and Na/K ratios range between 1.9 and 4.6 and 0 and 14.3, respectively.

Heating experiments could not be made with glass-bearing inclusions in olivine because in the three samples found, inclusions were exposed at the grain's polished surface.

# Discussion

# Previous investigations of parental magma composition

Glass-bearing inclusions in major phases of nakhlites and other meteorites of possible Martian origin, like Chassigny, ALHA77005 and Y-793605 (*Jagoutz*, 1989; *Johnson* et al., 1991; *Harvey* and *McSween*, 1991b, 1992; *Treiman*, 1993; *Ikeda*, 1997) have been studied under the assumption that they represent a volume of the parent magma that was trapped during growth of the host and that the assemblage of crystals and glass in the inclusion is the result of subsequent closed-system crystallisation. The Nakhla parental magma composition has previously been evaluated from phase compositions in glass-bearing inclusions in olivines (*Harvey* and *McSween*, 1992; *Treiman*, 1993). For these calculations the authors made several assumptions: 1) once the initial melt is trapped it will follow a crystallisation path similar to that of the parent magma, 2) all inclusions contain trapped magma of

M. E. Varela et al.

-	. 0	5		1		0				
	GH(6)	D-2	Bulk Incl	А	В	С	NK3	Ν	N'	NK93
SiO <sub>2</sub>	55.4	47.4	53.7	55.9	55.7	55.3	45.8	48.9	50.5	50.2
TiO <sub>2</sub>	1.1	0.73	1.1	1.0	0.99	0.9	3.1	1.1	1.4	1.0
$Al_2O_3$	9.4	4.25	10.2	9.1	8.6	7.8	7.2	2.8	6.8	8.6
$Cr_2O_3$	0.2	0.15	0.06	0.19	0.18	0.16	ng	0.1	0.1	0.1
FeO	13.4	24.7	10.8	13.6	13.7	13.7	26.2	26.1	21.9	19.1
NiO	nd	nd	0.03	nd	nd	nd	ng	ng	ng	0.0
MnO	0.2	0.90	0.19	0.26	0.27	0.3	ng	0.7	0.4	0.4
MgO	4.9	7.89	3.91	5.4	5.8	6.6	5.70	5.2	4.3	4.0
CaO	10.2	12.9	14.0	10.8	11.2	11.9	10.4	13.8	13.0	11.9
Na <sub>2</sub> O	3.2	0.99	1.45	3.1	2.9	2.6	0.8	1.0	1.2	1.2
$K_2O$	0.6	nd	3.33	0.58	0.55	0.49	1.4	0.2	0.3	2.8
$P_2O_5$	0.3	nd	0.82	0.28	0.27	0.24	ng	ng	ng	0.7
Totals	98.9	99.9	99.6	100.2	99.9	100.3	100.6	99.9	99.9	100

Table 3. Composition of quenched glass in primary glass-bearing inclusions in Nakhla augite, of synthesized glasses and of estimated Nakhla's parental magmas

GH(6) Mean glass composition of heated inclusions, this work; *D-2* glass composition of D-2 run, *Longhi* and *Pan* (1989); *Bulk Incl* estimated bulk inclusions composition (*Treiman*, 1993); *A*, *B*, *C* glass composition GH(6) with addition of 5 vol% (A), 10 vol% (B) and 20 vol% (C) of the host augite; *NK3*, *N*, *N'*, *NK93* parent magma compositions as explained in text and shown in Fig. 4; *ng* not given; *nd* not detected

the same composition, 3) the true proportion of the phases is the one that is observed, 4) no other phases are present beside those that were identified.

*Harvey* and *McSween* (1992) used linear regression methods to estimate the true proportions of phases, including olivine, and mass-balance calculations to model the composition of the parent liquid from which these phases could have crystallised. Their calculations suggest a Fe-rich basaltic parental liquid (NK3, in Table 3).

*Treiman* (1993) also made a compositional study of glass-bearing inclusions in olivine. Twenty-four inclusions were analysed using electron microprobe by averaging series of scanned electron beam analyses. For an average inclusion composition to be meaningful, it had to be shown that all inclusions represent the same single magma. To solve this problem, *Treiman* (1993) undertook a detailed compositional study of inclusions larger than 50  $\mu$ m and concluded that all inclusions have trapped magma of a single composition. The average composition of the inclusions was then corrected for processes that occurred after entrapment (i.e., crystallisation of olivine on inclusion walls, chemical exchange with the host). The parent magma composition calculated from these inclusions (NK93, Table 3) is constrained to have augite and olivine on the liquidus and to have a molar FeO/MgO ratio of 0.207.

The chemical compositions of possible parental magmas for the SNC meteorites have also been estimated by *Longhi* and *Pan* (1989), working with augite/melt element distribution and phase equilibria constraints on synthetic systems. They used powdered glasses, which were sintered at subsolidus temperatures for one day to promote nucleation of crystals after which the temperature was raised. The final temperature was held for one or two days and then quenched (the loop was dropped into a vacuum oil bath). The D-2 run with a final temperature of 1215 °C held

during 50 h with a log  $fO_2$  of -8.3 produced the most Nakhla-like augite. For the calculation of the parent magma, their procedure was one of successive approximations. They have used the augite/liquid partition coefficient from run D-2 to calculate concentration of all the major elements oxides except K<sub>2</sub>O and SiO<sub>2</sub>. They have assumed that the K<sub>2</sub>O/Na<sub>2</sub>O ratio in the parent liquid was the same as that of the bulk rock and the SiO<sub>2</sub> was calculated by difference. Finally, they have adjusted the SiO<sub>2</sub> and CaO contents in order to bring the composition onto the olivine/augite liquidus boundary (compositions N and N', Table 3).

# Glass-bearing inclusions in augite cores

Under the assumption that Nakhla is an igneous cumulate rock, petrographic studies indicate, that olivine was the first phase to crystallise from the parent magma but it was joined at an early stage by augite (*Harvey* and *McSween*, 1992). Thus, primary inclusions in the cores of augites can represent early-trapped melts and may have a composition close to that of the parental magma.

In the following paragraphs we discuss some of the features that make glassbearing inclusions in augite a good candidate from which the chemical composition of these early melts can be estimated:

1) A rapid growth for augite cores has been inferred due to the small size of its glass-bearing inclusions by *Treiman* (1993). However, inclusions present in the core and at the surface of grains are similar not only in their sizes but also in their phase contents (glass + crystals + bubble). If a rapid growth of the crystal had occurred in the augite core, and considering the small sizes of the inclusions, glassy inclusions could be expected to be found. However, the small volumes of the inclusions trapped in the augite cores and surfaces had enough time to develop euhedral and subhedral crystals that occupy a large volume of the inclusion cavity. This suggests that growth conditions have not undergone significant changes during augite formation. Also, the compositions of inclusions located in the centre do not differ from those located near the surface of the crystals. The fact that the position of the inclusion does not reflect a certain range in magma composition could indicate, that all inclusions have trapped a melt of the same (or similar) composition. This is unusual for melt inclusions and will be discussed later.

2) Pigeonite is present in glass-bearing inclusions in augite (Table 2). It has high contents of  $Al_2O_3$  and MgO and lower contents of FeO as compared to those of pigeonites in the mesostasis. Its  $X_{Fe}$  ( $X_{Fe} = Fe/(Fe + Mg)$ ) of 0.75 is very near the value 0.72, which is considered to mark the lower limit of the stability of pigeonites at one atmosphere pressure (*Lindsley*, 1983). Considering the primary occurrence of the glass-bearing inclusions in augites and the  $X_{Fe}$  value of its pigeonites, glass inclusions must have been quenched from temperatures above 825 °C. That is the lowest temperature at which a Fe-rich pigeonite is stable (*Lindsley*, 1983). Similarly, due to the presence of Fe-rich pigeonite in Nakhla and Governador Valadares, a similar conclusion was reached by *Harvey* and *McSween* (1991a), i.e. that these meteorites could have been quenched from temperatures above 860 °C.

3) The Nakhla olivines and augites are not in equilibrium with respect to their Fe/Mg ratios. Explanations for this have been attempted by several authors. According to *Treiman* (1986), the large olivine, or the olivine and augite cores

(*Treiman*, 1990), could represent xenocrysts. *Longhi* and *Pan* (1989) and *Harvey* and *McSween* (1991a) argued that both minerals may have formed from the same magma but have been disturbed by later diffusive addition of Fe to different degrees, with olivine having been more affected than the augite. If this is so, we cannot exclude the possibility that this process could also have affected glass-bearing inclusions that occur in olivine cores. However, augite cores appear to have been nearly unaffected by that diffusion event and their Fe/Mg ratio is likely to represent that of the parental magma (*Harvey* and *McSween*, 1991a).

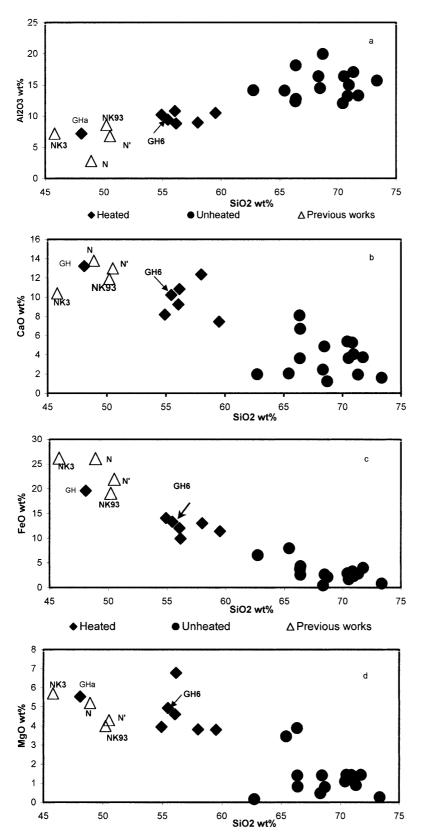
In summary, augites could have had a relatively rapid growth, trapped small amounts of (parental?) melt, which was subsequently quenched to glass-bearing inclusions. These primary glass-bearing inclusions are free of inside and outside fractures. This fact not only argues in favour of an uncontaminated composition of the inclusions but also argues against any shock alteration. Also, the fact, that augite cores are less affected by secondary diffusive addition of Fe than olivines, diminishes the risk of alteration of its glass inclusions.

# Results of heating experiments are incompatible with trapping of a homogeneous melt

Heating experiments allow the reversal of processes that took place inside inclusions during cooling. If a homogeneous melt is trapped, it will form a closed system and subsequently evolve by precipitation of crystalline phases (daughter crystals) and the residual glass will represent the final stage of the evolution and its chemical composition will be characterised by high contents of SiO<sub>2</sub> and alkalis (see unheated glass inclusions, Table 1 and Fig. 3). Heating this type of inclusion will cause melting of the glass and dissolution of crystalline phases (e.g. crystals inside inclusion and the augite that has crystallised onto the inclusion walls). That will change the chemical composition of the glass, which will become richer in FeO, MgO and CaO and poorer in SiO<sub>2</sub> compared to the unheated glass. The results of heating experiments do indeed show, that the chemical composition of the quenched glass has changed. It became poorer in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and richer in CaO, FeO and MgO, compared to the unheated glass (Table 1).

The binary diagrams of Fig. 3 show that the compositions of the inclusions, except for one (GHa), fall within a cluster with similar contents of SiO<sub>2</sub>, FeO, MgO, Al<sub>2</sub>O<sub>3</sub> and CaO. The shape of GHa, its bubble size and its chemical composition, low content of SiO<sub>2</sub> (48 wt%) and high contents of TiO<sub>2</sub> (2.4 wt%), FeO (19.6 wt%), and CaO (13.2 wt%), indicate that GHa could be the product of a necking-down process. Necking-down of an elongated inclusion will develop bulges separated by a thin neck. These two new inclusions with a connecting tube (Fig. 2C) will have the

Fig. 3. Representative major element variation diagrams of glass in unheated and heated glass-bearing inclusions in Nakhla augite. GH(6) is the experimentally derived average composition of the liquid co-existing with Nakhla augite a 1150 °C and 1 atm pressure. Model parent magma compositions are: NK3: *Harvey* and *McSween* (1992); N: *Longhi* and *Pan* (1989); N' and NK93: *Treiman* (1993); **a** Al<sub>2</sub>O<sub>3</sub> vs SiO<sub>2</sub>, **b** CaO vs SiO<sub>2</sub>, **c** FeO vs SiO<sub>2</sub>, **d** MgO vs SiO<sub>2</sub>



total volume of the original single inclusion but different surface/volume ratios. Moreover, if any phase change (e.g. formation of a bubble + crystal) has occurred before the necking-down, the new inclusions will have chemical and mineralogical compositions different from those of the normal inclusions (*Roedder*, 1984), similar to what is observed in GHa.

In principle, the results of heating experiments seem to indicate, that the primary multiphase inclusions in Nakhla augites could be the results of a closed-system evolution of a trapped melt. The average composition of all heated inclusions (GH(6) in Table 1) characterises the composition of a liquid co-existing with Nakhla augite at  $1150 \,^{\circ}$ C and 1 atm pressure.

The GH(6) composition is richer in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O and poorer in FeO, MgO and CaO than the glass of run D-2 of *Longhi* and *Pan* (1989) (see Table 3). These differences in the chemical composition of the glasses obtained in the GH(6) and D-2 run (Table 3) are to be expected as they have been performed with different starting material and under different conditions. As to the starting material, *Longhi* and *Pan* (1989) have used synthetic glasses with the estimated composition of parent D calculated by *Treiman* (1986) while we made in situ re-melting of the natural inclusions trapped in Nakhla augite cores. With respect to the experimental conditions, our heating experiments have a lower final temperature and were performed in much less time than the previous authors' experiments (in our experiments the final temperature of 1150 °C was kept for 8 h). The duration of our experiment was sufficient for dissolution of the crystalline phases inside inclusions.

As we have already mentioned, previous estimates of the chemical composition for the possible parent magmas of SNC meteorites were made to pass the plausibility tests based on a variety of assumptions. Thus, corrections were made in such a way as to yield a magma composition with the expected MgO/FeO ratio. The Fe-Mg partition coefficient,  $K_d(Fe) = [(FeO/MgO)_{aug}/(FeO/MgO)_{Liq}]$ , as experimentally determined by us for the possible melt composition GH(6) and its augite host is 0.398, very much higher than the experimentally determined value for terrestrial basaltic systems and for the presumed SNC meteorite parent magma. According to Longhi and Pan (1989), the latter varies between 0.179 and 0.293, depending on the Wo content of the pyroxene. Recent investigations of melt inclusions (e.g. Danushevsky and McNeill, 2000) show, that equilibration between inclusion glass and host crystals during cooling changes the glass composition, mainly in the contents of SiO<sub>2</sub>, MgO and FeO. However, our data, although having been acquired at high temperature, clearly indicate, that equilibrium was not attained between the melted inclusion and the host augite and that very likely there never was chemical equilibrium between these phases. Heating temperatures above 1150 °C will result in increasing dissolution of the augite host from the inclusion wall but will not improve the situation. Previous investigations of inclusions in Nakhla olivines indicated that the rind zone constitutes 13 vol% of the inclusions (Treiman, 1993). Close inspection shows that a rind zone is not visible in the small inclusions in augites, suggesting that the host layer occupies a small volume of the inclusion cavity. However, by adding 5, 10 and 20 vol%, respectively, of augite (core composition) to the experimentally determined melt composition (A, B and C, Table 3), the calculated augite-melt  $K_d$  (Fe) for these liquids of 0.43, 0.46 and 0.52, respectively, are also out of equilibrium.

The fact that the  $K_d(Fe)$  of the liquid experimentally obtained by heating a piece of this meteorite does not agree with that of previously estimated compositions based on theoretical grounds could be strong evidence for the inclusions being the result of heterogeneous trapping, a case very similar to that of glass-bearing inclusions in olivine of Chassigny (*Varela* et al., 2000).

Another unexpected result is that the experimentally determined GH(6) composition is not olivine-normative. This suggests that the melt was not saturated with olivine at the moment of formation of the inclusions. As the inclusions are present in the cores of augites, no olivine could have been in equilibrium with the melt during crystallisation of the augites. However, Nakhla does contain about 10 vol% of olivine and this situation is in clear contrast to previous estimations of the Nakhla parent magma composition, which considered that the parent magma was saturated with olivine when the cores of augites formed.

The GH(6) quenched melt composition has a high Na<sub>2</sub>O content as compared to previously estimated parent magma compositions for Nakhla (Fig. 4). In all our experiments, the quenched glass is always enriched in Na<sub>2</sub>O with respect to K<sub>2</sub>O (see, Table 1 and the binary diagram of Fig. 4), except for one inclusion, which has no detectable Na<sub>2</sub>O content and 0.5 wt% K<sub>2</sub>O. Individual glasses have highly variable Na/K ratios, a feature that is not typical for parental melt inclusions. One particular feature of GH(6) is its high content of Na<sub>2</sub>O, likely a direct consequence of the dissolution of a Na phase present in the glass-bearing multiphase inclusions in Nakhla augite.

In summary, glass-bearing inclusions in augites from Nakhla

- have a quartz-normative composition when homogenised in melting experiments,
- cannot be in equilibrium with olivine, which is a requirement for the Nakhla parental liquid as Nakhla contains about 10 vol% olivine,
- are not in equilibrium with the host augite with respect to their Fe/Mg ratio, and
- have highly variable Na/K ratios as well as highly variable absolute alkali contents, all incompatible with trapping of a homogeneous parental melt.

# Heterogeneous trapping

Inclusions in Nakhla olivine occur isolated in the centre of grains in contrast to those in augite, which are very small, widespread in the host and almost always form clusters. All inclusions in augite comprise an assemblage of crystalline phases + glass + bubble. Those hosted by olivine match Chassigny multiphase inclusions, which consist of crystalline phases + glass, but lack bubbles. Multiphase inclusions in olivines consist of radiating crystals of augite, alkali feldspar and pigeonite and of euhedral crystals of Ti-magnetite in a silica-rich glass (for details see *Treiman*, 1993). This arrangement of crystals, which nucleated on the inclusion walls and grew inward, forms the "vitrophyric texture" of *Harvey* and *McSween* (1992).

In the three samples examined by us, neither an olivine nor an augite showed co-existence of both types of inclusions. Each mineral carries its specific type of primary glass-bearing inclusion with its characteristic texture. This fact could suggest differences in the physico-chemical conditions under which each mineral was formed.

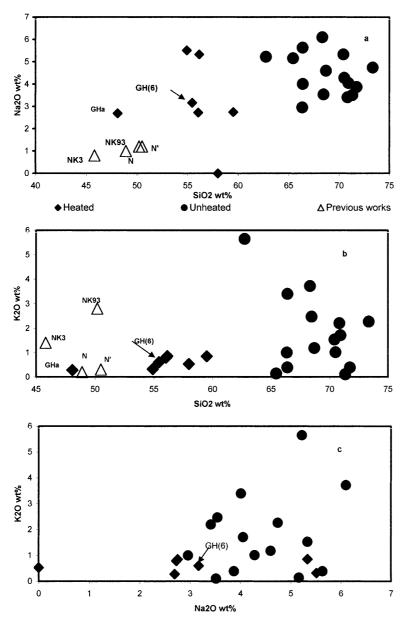


Fig. 4. Alkali element variation diagram of glass in unheated and heated glass-bearing inclusions in Nakhla augite. **a** Na<sub>2</sub>O vs SiO<sub>2</sub>, **b** K<sub>2</sub>O vs SiO<sub>2</sub>, **c** Na<sub>2</sub>O vs K<sub>2</sub>O

According to *Treiman* (1993), the first step in the crystallisation of Nakhla is an early growth of augite, which was preserved as euhedral grains in inclusions in olivines. After that "a period of changing physical conditions (moderately rapid cooling and/or decompression) led to the growth of olivine and augite in disequilibrium shapes, skeletal for olivine, and spongy for augites". Melt inclusions were trapped as both crystals filled in. Accordingly, the entrapment of these inclusions took place in a quiescent magma chamber. However, the question that arises, is, if both minerals are formed at the same time (or close in time) in a

relatively closed and quiescent system, how can both minerals be affected by different physico-chemical conditions that allow the entrapment of so different types of inclusions in each other?

Why have inclusions always nucleated a bubble in augite but not in olivine? We cannot argue for a rapid cooling of the host phase, because in that case and, considering the small size of augite inclusions, totally glassy inclusions would be expected to form, which is not the case.

The petrography of the glass-bearing inclusions in addition to the experimental results of re-melted glasses suggests that both types of glass-bearing inclusions (those hosted by augite and olivine, respectively) could represent heterogeneously trapped phases. In principle, and due to the dissolution of crystals inside inclusions in augites during heating, inclusions hosted by augites mimic at least in part parental melt inclusions.

#### Evidences contradicting the standard petrogenetic model

In the standard petrogenetic model, SNC meteorites are all igneous rocks inferred to have been formed from basaltic magmas (*Treiman*, 1993). However, several features are difficult to account for with this model.

(1) The differences between glass-bearing inclusions in similar rock types:

If Nakhla and Chassigny are igneous rocks (pyroxenite and dunite, respectively) formed by similar processes, why are the results of heating experiments on their primary glass-bearing inclusions so different?

A recent study of the Chassigny meteorite showed that glass inclusions in olivine cannot be the residual after a closed-system evolution of a melt but rather represent heterogeneously trapped precipitates from a fluid at sub-solidus temperatures (*Varela* et al., 2000). Heating experiments show that crystalline phases inside Chassigny inclusions were not dissolved in the melted glass and that the chemical composition of the quenched glass after heating to final temperatures of  $1200 \,^{\circ}$ C had a chemical composition similar to that of the original glass. This situation, totally different from that encountered in inclusions in Nakhla augite, suggests that these two rocks cannot be the product of a simple magmatic process.

(2) Our results questioned the fact of considering Nakhla an igneous rock:

Recent studies of basalts from Mt. Etna (*Clocchiatti* et al., 1998) show, that single phenocrysts do contain inclusions of markedly different compositions. The range in composition is sufficiently large, so that the entrapped melts could not have been in equilibrium with one another. The olivines host glass inclusions with alkalic to transitional melts. This variation in melt composition is accompanied not only by a chemical zonation of the host but also by a specific position of these inclusions in the host (the interior of the crystal includes alkalic inclusions while the outer rim includes de transitional ones). This chemical variation of the trapped melts is explained by *Clocchiatti* et al. (1998) as being due to different degrees of partial melting of a uniform source. The lack of equilibrium observed between host and melts in Nakhla is difficult to be attributed to a similar process as that describe above as both types of inclusions in Nakhla (hosted by augites and olivine, respectively) have similar composition (compare Bulk Incl of *Treiman*, 1993, and

GH(6) in Table 3) and, as we have already mentioned, the composition of inclusions in augite does not vary systematically with position within the host.

This situation clearly indicates that no chemical fractionation of the parent of the augites took place while they grew. This is possible, if the mass of the reservoir is much larger than that of the crystals precipitated. Such a situation is not typical for magmatic systems because major minerals of the final rock must represent a major component in the melt and crystallisation of that phase must quickly lead to fractionation of the remaining liquid. In addition, the variable alkali abundances in the inclusion glasses do not fit a magmatic model. The binary diagrams of Fig. 4 show a slightly developed (in the case of Na<sub>2</sub>O) or totally absent (in the case of K<sub>2</sub>O) correlation of alkali abundances with that of SiO<sub>2</sub>. This, however, is difficult to account for by entrapment of a former homogenous melt that evolved as a closed system during cooling. The absence of fractures around inclusions argues against the idea that alkali contents could have been disturbed in a secondary process. Thus, this variability must have its roots in the very beginning, during augite and inclusion formation.

Nakhla seems not to be the result of a simple petrogenetic process. If Nakhla is an igneous cumulate rock, how can we reconcile the GH(6) composition, based on in situ heating experiments of glass-bearing inclusions in augites cores, with a possible parental magma? Can an olivine-clinopyroxenite, with 10 vol% of olivine, be formed from a quartz-normative initial liquid?

Nakhla is, may be, not an igneous cumulate rock. This possibility has also certain implications in the controversial radiometric dating of this meteorite. The apparently young ages obtained from internal isochrons (e.g. *Bogard* and *Nyquist*, 1979; *Nakamura* et al., 1982) could be due to a disturbance of the Rb/Sr chronometer rather than a melting event, as the melt needs to be depleted and the cumulates enriched in incompatible elements (*Jagoutz*, 1997; *Jagoutz* and *Jotter*, 1999). Nakhla (as well as Chassigny) is full of surprising features. It contains a light N component (delta <sup>15</sup>N ~ -30 per mil) which also is similar to a component known from ordinary chondrites (*Wright* et al., 1992; *Mathew* et al., 1998). In addition, organic matter in Nakhla is similar to that present in carbonaceous (CM) chondrites (*Jull* et al., 1999).

All these evidences suggest, that Nakhla is possibly not an igneous rock formed from a basaltic magma. However, details on how this rock was formed remain speculative. Nakhla could have been formed by agglomeration of minerals from two different sources with glass-bearing inclusions in augites and olivines representing heterogeneously trapped mineral + glass (or glass precursors). In this way, the variability of alkali abundances at the moment of inclusion formation could be achieved.

# Conclusions

The first in situ heating experiments performed on glass-bearing inclusions in Nakhla augite allow us to give the initial composition of a possible liquid coexisting with Nakhla augite at 1150 °C and 1 atm pressure. Glass-bearing inclusions in augite homogenise in the heating experiment and dissolve all crystalline phases. They thus mimic a parental melt that has subsequently evolved as a closed system during cooling. In spite of being stable in contact with the host, the experimentally derived liquid is out of equilibrium with the augite host (Fe/Mg distribution). It is quartz-normative and thus also out of equilibrium with olivine, a major phase of the Nakhla rock and it is highly inhomogeneous in its contents of alkalis. Therefore, the glass-bearing inclusions in Nakhla augite likely are heterogeneously trapped solids (e.g. pyroxene, magnetite, phosphate and sodium-rich phases) and liquids. These results question the validity of igneous models put forward for the origin of Nakhla.

## Acknowledgements

We acknowledge the constructive reviews of J. C. Bridges, J. Longhi, H. McSween and N. Arndt, which helped to improve this manuscript. CONICET in Argentina, FWF in Austria, and LPS in France have financially supported this work.

#### References

- Berkley JL, Keil K, Prinz M (1980) Comparative petrology and origin of Governador Valadares and other nakhlites. Proc Lunar Planet Sci Conf 11: 1089–1102
- *Bogard DD, Nyquist LE* (1979) Ar-39/Ar-40 chronology of related achondrites. Meteoritics 14: 356
- Bunch TE, Reid AM (1975) The nakhlites, part 1. Petrography and mineral chemistry. Meteoritics 10: 303–315
- *Clocchiatti R, Schiano P, Ottolini L, Bottazzi P* (1998) Earlier alkaline and transitional magmatic pulsation of Mt Etna volcano. Earth Planet Sci Lett 163: 399–407
- *Consolmagno G, Britt DT* (1998) The density and porosity of meteorites from the Vatican collection. Meteoritics Planet Sci 33, 6: 1231–1243
- Danyushevsky L, McNeill A (2000) Experimental and petrological studies of melt inclusions: techniques, advantages and problems. Workshop on Melt inclusions, Grenoble, France
- Harvey RP, McSween HY Jr (1991a) Petrogenesis of the nakhlite meteorites: evidences from cumulate mineral zoning. Geochim Cosmochim Acta 56: 1655–1663
- Harvey RP, McSween HY Jr (1991b) Parental magma of the nakhlites: clues from the mineralogy of magmatic inclusions. Meteoritics 26: 343
- *Harvey RP, McSween HY Jr* (1992) The parent magma of the nakhlite meteorite: clues from melt inclusions. Earth Planet Sci Lett 111: 467–482
- *Ikeda Y* (1997) Petrology and mineralogy of the Y-793605, Martian meteorite. Antarctic Meteorite Res 10: 13–40
- Jagoutz E (1989) Sr and Nd isotopic systematics in ALHA77005: age of shock metamorphism in shergottites and magmatic differentiation on Mars. Geochim Cosmochim Acta 53: 2429–2441
- Jagoutz E (1997) Isotopic constraints on differentiation and evolution of SNC meteorites. Lunar Planet Sci Conf XXVIII: 651–652
- *Jagoutz E, Jotter R* (1999) SNC meteorites: relatives finally finding each other (Abstract). Meteoritics Planet Sci 34 [Suppl]: A59
- Johnson MC, Rutherford MJ, Hess PC (1991) Chassigny petrogenesis: melt inclusions intensive parameters and water contents of Martian (?) magmas. Geochim Cosmochim Acta 55: 349–366
- Jull AJT, Beck JW, Burr GS, Gilmour IA, Sephton MA, Pillinger CT (1999) Isotopic evidence for abiotic organic compounds in the martian meteorite Nakhla (Abstract). Meteoritics Planet Sci 34 [Suppl]: A60

- 172 M. E. Varela et al.: Glass-bearing inclusions in Nakhla (SNC meteorite) augite
- Lindsley DH (1983) Pyroxene thermometry. Am Mineral 68: 477-493
- *Longhi J, Pan V* (1989) The parental magma of SNC meteorites. 19<sup>th</sup> Proc Lunar Planet Sci Conf: 451–464
- *Mathew KJ, Kim JS, Marti K* (1998) Martian atmospheric and indigenous components of xenon and nitrogen in the Shergotty, Nakhla, and Chassigny group meteorites. Meteoritics Planet Sci 33: 655–664
- *Métrich N, Clocchiatti R* (1989) Melt inclusions investigation of the volatile behaviour in historic basaltic magmas of Etna. Bull Volcanol 51: 185–198
- Nakamura N, Unruh D, Tatsumoto M, Hutchison R (1982) Origin and evolution of the Nakhla meteorite inferred from Sm-Nd and U-Pb systematics and REE, Ba, Sr, Rb and K abundances. Geochim Cosmochim Acta 46: 1555–1573
- *Ott U, Begemann F* (1985) Are all the "martian" meteorites from Mars? Nature 317: 509–512
- *Reid AM, Bunch TE* (1975) The nakhlite, part II. Where, when and how. Meteoritics 10: 317–325
- Roedder E (1984) Fluid inclusions. Rev Mineral 12: pp 644
- *Treiman H* (1986) The parental magma of the Nakhla achondrite: ultrabasic volcanism on the shergottite parent body. Geochim Cosmochim Acta 50: 1061–1070
- *Treiman H* (1990) Complex petrogenesis of Nakhla (SNC) meteorite: evidence from petrography and mineral chemistry. Proc 20<sup>th</sup> Lunar Planet Sci Conf: 273–280
- *Treiman H* (1993) The parent magma of the Nakhla SNC meteorite, inferred from magmatic inclusions. Geochim Cosmochim Acta 57: 4753–4767
- Varela ME, Clocchiatti R, Kurat G, Massare D (1998) Glass-bearing inclusions in the Chassigny olivine: heating experiments suggest non-igneous origin (Abstract). Meteoritics and Planet Sci 33 [Suppl]: A158
- Varela ME, Kurat G, Mosbah M, Clocchiatti R, Massare D (2000) Glass-bearing inclusions in olivine of the Chassigny achondrite: heterogeneous trapping at sub-solidus temperatures. Meteoritics Planet Sci 35: 39–52
- Wright IP, Grady MM, Pillinger CT (1992) Chassigny and nakhlites: carbon bearing components and their relationship to martian environmental conditions. Geochim Cosmochim Acta 56: 817–826
- Zapunnyy SA, Sobolev AV, Bogdanov AA, Slutskiy AB, Dmitriyev LV, Kunin LL (1989) An apparatus for high-temperature optical research with controlled oxygen fugacity. Geochem Int 26: 120–128

Authors' addresses: *M. E. Varela*, CONICET – Universidad Nacional del Sur, Dpte de Geologia, San Juan 670, (8000) Bahia Blanca, Argentina, e-mail: evarela@criba.edu.ar; *G. Kurat*, Naturhistorisches Museum, Postfach 417, A-1014 Vienna, Austria; *R. Clocchiatti*, Laboratory Pierre Süe, CEA-CNRS, F-91191 Gif sur Yvette, France.