

SIMS ANALYSIS OF VOLATILES AND H ISOTOPE STUDIES OF THE NAKHLITES YAMATO 000593 (Y000593) AND NORTH WEST AFRICA 998 (NWA998); N.Z. Boctor¹, J. Wang¹, C.M.O.D'Alexander¹, E. Hauri¹, and A.J. Irving², ¹Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington, DC 20015; USA, ²University of Washington, Seattle, WA 98195, USA.

Introduction: Water and other volatiles play an important role in partial melting of mantle sources of primary magmas, and their eruption and crystallization history. Melt inclusions trapped in early crystallized minerals, e.g., olivine, preserve a range of compositional and isotopic variability, providing valuable information on their parent melt composition, pre-eruptive volatile abundances of magmas, and their degassing history [1,2]. The nakhlites are the least affected by shock metamorphism among the Martian meteorites. Their lack of pervasive alteration or shock melting suggest that their magmatic melt inclusions and nominally anhydrous minerals may provide clues to the volatiles abundances and H isotope signatures of their parental melts. Our initial study of H isotope signatures of clinopyroxene, melt inclusions, and some olivine in the nakhlites Gobernador Valadares and Nakhla showed that they contain an extraterrestrial H component [3]. In this investigation, we report the first SIMS analyses of the volatiles CO₂, F, S, and Cl in melt inclusions and nominally anhydrous minerals in the nakhlites Y000593 and NWA998. We also report the water abundances and H isotope signatures of these phases. Hydrogen isotope data determined for Lafayette, Nakhla, and Gobernador Valadares are also included.

Experimental: The abundances of H₂O, CO₂, F, S, and Cl were measured by a Cameca 6F ion microprobe using the techniques described by [1]. The major improvements these techniques provide over previous ion probe techniques are high quality vacuum and the use of a charge compensated Cs⁺ primary beam with collection of negatively charged secondary ions. Using these methods, routine detection limits measured on synthetic forsterite were H₂O 2-4 ppm, CO₂ <3 ppm, and F, Cl, and S <1 ppm [4]. Glass standards with appropriate concentration for all the analyzed volatile elements were used. SIMS operating conditions for H isotopic measurements were 15 Kv Cs⁺ primary beam of 2nA, 5Kv secondary accelerating voltage, a 50eV energy window, a mass resolution of 400 and an electron flood gun for charge compensation. Newly prepared polished thin sections of Y000593 and NWA998 were adequate for determining volatile abundances. We were unable to measure CO₂ abundances in the sections of other SNCs loaned to us, which previously have been multiply coated by carbon. We were unable to remove the carbon, which filled the cracks. Alternate thick sections of

these meteorites are being prepared without epoxy or carbon coats for volatile measurements.

Results: The volatile abundances and hydrogen isotope signatures of the melt inclusions, olivine, and clinopyroxene in Y000593 and NWA998 are given in Table 1 and 2, together with the δD values of the same phases in Lafayette, Nakhla, and Gobernador Valadares.

All the phases analyzed show an extraterrestrial H signature. Most of the melt inclusions show positive δD values, in general higher than those of their host olivines. Clinopyroxene is the most D enriched phase. The highest is in a pyroxene from Nakhla with a δD value of +1857‰. This value is much higher than the value report by [5] for Nakhla whole rock.

For volatiles other than water, CO₂ is most enriched in melt inclusions and least enriched in clinopyroxene. Olivine has higher CO₂ concentrations than clinopyroxene. Also it shows S concentrations much higher than the normal detection limit and is similar or higher than S concentrations in melt inclusions. Olivine also is enriched in Cl relative to the melt inclusions. The clinopyroxene and melt inclusions are enriched in F relative to olivine.

Discussion: It can be argued that the fractionated H isotope signature of clinopyroxenes implies that they crystallized from melts with high D/H ratios. The low δD values of most of the melt inclusions and their host olivines seem to preclude this explanation. The highest D enriched clinopyroxene in Nakhla (+1857‰) suggests partial equilibration with a fractionated Martian water reservoir. The δD range observed in the clinopyroxene may then represent mixing of a fractionated Martian H component with a low D magmatic component or a terrestrial contaminant. Our volatile abundance study is at an early stage, but the results provide interesting clues. The volatile abundances are lower than those found in typical terrestrial basalts. The abundances of the volatiles will depend on their concentrations in the source regions, the degree of melting, and the crystallization and the degassing history of the magma. CO₂ solubility varies considerably with pressure [6]. Sulfur solubility increases with increase of the Fe content of the melt and will vary with fO₂.

The large variation in CO₂ concentrations in each meteorite suggests entrapment at a wide range of

pressures. The higher contents of S and Cl in olivine relative to melt inclusions and pyroxene and the anomalously high CO₂ in olivine suggest that these enrichments are generated by either incipient secondary alteration or, possibly, surface contamination associated with polishing.

Most of the inclusions show low water contents and by Martian meteorite standards modest D enrichments. The hydrogen isotopes potentially offer clues to why the water contents of the melt inclusions are so low; degassing reduces the δD value of a magma due to vapor-melt equilibrium isotope fractionations, while diffusive loss of H from the melt inclusion through the host mineral increases the δD value of the inclusion. Both such effects are recorded in melt inclusions from Kilauea lavas [1]. However, there is no significant correlation between δD and H₂O. Given the low water contents in the inclusions, contamination may be complicating the interpretation of the δD values. The dual depletion of S and water in the melt inclusions and clinopyroxene suggest that S may also have been depleted during shallow degassing.

Water loss by degassing was proposed [7,8] to explain the low concentration of water in Martian meteorites. Despite the ambiguity of the δD values, our data on volatile abundances in Y000593 and NWA998 support this hypothesis. Our data also demonstrate that shallow degassing of S may have occurred.

References: [1] E. Hauri (2002) Chem. Geol., 183, 115-141. [2] G.A. Gaetani and E.B. Watson (2002) Chem. Geol., 183, 25-41. [3] N.Z. Boctor et al. (2002) Meteoritics and Planet. Sci. 37, A19. [4] K. Kouga et al. (2003) Geochemistry, Geophysics, Geosystems, 4, 1-20. [5] L.A. Leshin (1996) Geochim. Cosmochim. Acta, 60, 2635-2650. [6] I.M. Stolper and J.R. Holloway (1988) Earth Planet. Sci. Lett., 87, 397-408. [7] H.Y. McSween and R.P. Harvey (1993) Science, 259, 1890-1892. [8] H.Y. McSween et al. (2001) Nature, 409, 487-490.

Table 1. SIMS analyses of volatiles and H isotope signatures of melt inclusions and nominally anhydrous minerals in Y000593 and NWA998.

Sample	H ₂ O (ppm)	CO ₂ (ppm)	F (ppm)	S (ppm)	Cl (ppm)
Y000593					
Melt Incl.	17-221	5-294	28-63	0- 3.1	0-1.6
Olivine	350- 460	41-79	2.5-5.2	2.0-3.0	0-2.2
CPX	13-14	2.5-3.4	37-42	0-0.60	<1
NWA998					
Melt Incl.	64-229	23-90	4.3-101	0- 1.0	<1
Olivine	101- 177	18-28	3.3-4.0	1.9-5.6	0-2.6
CPX	25-42	3.8-30	85-115	0-1.1	<1

Table 2. SIMS analyses of H isotope signatures of melt inclusions and nominally anhydrous minerals in nakhlites.

Sample	δD (‰)
Y000593	
Melt Incl.	+147 to +379
Olivine	-367 to +187
CPX	+526 to +750
NWA998	
Melt Incl.	+35 to +70
Olivine	-377 to +136
CPX	+161 to +495
Lafayette	
Melt Incl.	-15 to +298
Nakhla*	
Melt Incl.	+0.5 to +218**
Olivine	-93 to +210
CPX	+151 to +1857
Governador	
Valadares*	
Melt Incl.	-92 to +361
Olivine	-18 to +33
CPX	+142 to +874

*Ranges determined from the data of [3] and new data acquired during this investigation.

**A high δD value of +1048 was found in one glassy melt inclusion in clinopyroxene.