WATER IN THE MARTIAN MANTLE: CLUES FROM LIGHT LITHOPHILE ELEMENTS IN MARTIAN METEORITES. R.C.F. Lentz\textsuperscript{1}, J.G. Ryan\textsuperscript{2}, L.R. Riciputi\textsuperscript{3}, and H.Y. McSween, Jr.\textsuperscript{1}, \textsuperscript{1}Department of Geological Sciences, University of Tennessee, Knoxville, TN 37996-1410 (rlentz@utk.edu); \textsuperscript{2}Department of Geology, University of South Florida, Tampa, FL 33620-5201; \textsuperscript{3}Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

**Introduction:** The global volatile inventory and outgassing history of Mars are controversial issues. Previous estimates have been made of past martian water volumes based on surface feature morphologies, atmospheric gas abundances, and volumetric estimates of volcanic material \cite{1}. More directly, water contents have been measured in the martian meteorites, but those are on the order of 130-350 ppm \cite{1}, too low it seems to be the source for all the water that once flowed on the martian surface. However, some terrestrial rocks with measurably low water contents have other compositional evidence, such as magmatic inclusions, which point to volatile-rich parent magmas \cite{2,3}. Kaersutitic amphiboles were found in some martian meteorite pyroxene cores, originally prompting suggestions of significant water pressures, but there have since been conflicting interpretations of the water contents of the parent magmas at depth \cite{1,4-6}.

We have examined a different aspect of the geochemical system to look for evidence of magmatic water in the martian meteorites. Lithium, beryllium, and boron have proven useful in terrestrial studies of water in subduction zone magmas \cite{e.g. 7}. The key to their usefulness is the differences in their solubility in hydrothermal fluids: Be is insoluble, B is highly soluble in fluids $>$200° C \cite{8}, and Li is highly soluble in fluids $>$350° \cite{9}. In addition, Li, Be, and B exhibit varying incompatibilities in pyroxene and plagioclase, and using SIMS, it is possible to examine these elements in the individual minerals of the SNC meteorites, helping us to learn more about these magmatic systems.

**Methods:** To date, we have measured 5-6 pyroxene grains (cores and rims) and 6-7 plagioclase (or maskelynite) grains each in thin sections of Nakhla, Lafayette, and Shergotty, with analysis of Zagami planned. Li, Be, B and several other trace elements were measured on the Cameca 4f ion microprobe at the Oak Ridge National Laboratory. The data were calibrated with natural and glass standards. To combat the potential problem of B contamination, all samples were soaked in a 1% mannitol solution for $>$2 hrs and rinsed with B-free distilled water prior to gold-coating, per a method developed by R. Hervig (pers. comm.). In addition, each sample spot was sputtered for $\sim$15 minutes (while measuring other incompatible elements) before B, Li, and Be were measured.

**Results and Interpretations:** Overall our SIMS data appear well-behaved, with most trace elements displaying expected incompatible element trends. Four data points measured on nakhlite plagioclase grains were discarded due to apparent contamination from surrounding matrix material (the beam spot exceeded the grain boundaries).

Two important points emerge from examination of the behavior of B and Be in nakhlite and Shergotty pyroxenes and plagioclase: martian mantle contents of B and Be appear to be quite different from terrestrial contents, and a significant fraction of water was probably lost from the Shergotty parent magma.

Firstly, based on K\textsubscript{d} values of B and Be, the pyroxene B/Be ratio should approximate the magmatic ratio of those elements (K\textsubscript{d} ratio $=$ 0.09/0.08 $= 1.1$). Our data show that the martian magmatic values are all extremely high when compared with terrestrial basalt values. For example, a typical MORB will have a pyroxene B/Be value around 1-5 \cite{10}, whereas Shergotty average pyroxene values are 110 for rims and 757 for cores, while nakhlite ratios range from 109-188. High B/Be values may be explained in two ways: low degrees of mantle melting \cite{10}, or a very different starting mantle composition. The former explanation seems unlikely since the very high values in the martian rocks would require extremely low degrees of melting, given a terrestrial starting composition. This runs contrary to expected degrees of melting for shergottites and nakhlites.

Before resorting to the second alternative, we should evaluate whether the data are reliable. Be seems the most suspect with some unexpectedly low pyroxene contents (0.002-0.048 ppm). While this might be attributable to measurement difficulties, when we compare relative Be contents in plagioclase and pyroxene, the ratios match what we might expect, given what we know about the order of phase crystallization in these rocks. In Shergotty, most of the pyroxene rims grew concurrently with plagioclase ($\sim$equilibrium), so we would expect the plagioclase:pyroxene ratio to match that of their respective K\textsubscript{d}’s (Be pl:px K\textsubscript{d} ratio $=$ 0.27/0.08 $= 3.8$). In fact, the average Shergotty Be pl:px-rims ratio is a good match: 2.8. Deviations from this equilibrium ratio do arise
between Shergotty pyroxene cores and plagioclase (average Be pl:px-cores ratio ~ 11). This suggests there was more Be available to the plagioclase than there had been for the pyroxene cores. This is probably due to evolution of the magma concentrating Be in the later magma stages, as befits an incompatible element. We see this effect even more dramatically in the nakhlites (average Be pl:px ratio ~ 40-360), where plagioclase grew as a very late stage mesostasis phase after significant magma evolution. Because our Be data behave in these predictable ways, we believe the data are acceptable, and we therefore conclude that martian mantle contents for Be and B are likely quite different from terrestrial mantle contents.

The other important factor of the Be and B data is the role of water in the parent magmas. In the nakhlites, Be and B behave simply as incompatible elements, gradually increasing from pyroxene cores to rims (Fig. 1a) and, as mentioned above, increasing significantly by the time plagioclase crystallizes. This suggests there has been no loss of B during crystallization.

Shergotty data are quite different. Be increases from pyroxene cores to rims, as mentioned above, but B does the opposite (Fig. 1a): it drops by more than half from ~4.9 ppm to ~2.1 ppm. There is also a comparable drop in Li from pyroxene cores to rims (Fig. 1b), from ~5.1 ppm to ~2.5 ppm. The fact that B and Li, but not Be, were highly depleted between core and rim growth suggests the loss of a hot, aqueous fluid from the magma.

Previous studies [11,12] have suggested the shergottite compositional change from Mg-rich pyroxene cores to Fe-rich rims was concurrent with eruption of the magma body or its injection as a shallow sill. With magma ascent comes an accompanying drop in confining pressure, causing any volatiles in a magma to exsolve. The low pressures on Mars should accentuate this effect [1]. If the parent magma of Shergotty did have a significant water content, this mechanism could well explain the significant loss of B and Li recorded by the minerals in Shergotty. The pyroxene cores grew at depth, in equilibrium with a pressurized magma. During ascent, exsolution prompted the separation of a volatile-rich component from the main magma body, leaving a B- and Li-depleted magma to continue crystallizing pyroxene rims and plagioclase.


Figure 1: Behavior of B, Be, and Li in pyroxene cores and rims in the nakhlites and Shergotty. Thin dark arrows denote trends from cores to rims. Grey arrows (inset boxes) show general trends expected for pyroxene crystallization and loss of hot aqueous fluids. Note that the Shergotty data roughly mimic the loss of magmatic water trends, while nakhlite data follow simple pyroxene crystallization trends.