

Exploring Water in Shergottite Magmas Through Crystallization Experiments. C. L. Calvin¹ and M. J. Rutherford¹, ¹Brown University (324 Brook St, Box 1846, Providence, RI, 02912. Email: Christina_Calvin@brown.edu.)

Introduction: Evidence of water on Mars has been the subject of considerable study in recent years ranging from studies of surface morphology to analysis of weathering products. SNC meteorites provide a means to study hydration state of both the martian surface and mantle. For example, carbonates in ALH 84001 may suggest secondary, aqueous alteration at the martian surface [1]. Additional studies have found evidence for water in martian meteorites through H isotopes, Li and B concentrations, presence of possibly hydrated minerals such as apatite and amphibole [e.g. 2,3,4], and many other approaches. This study looks at lherzolic shergottite ALH 77005 and evaluates the evidence for and against the rock crystallizing from a hydrous magma. In addition, we synthesized the parental melt composition of ALH 77005 and performed crystallization experiments under both dry and water-bearing conditions to determine what the effect of water would be on the crystallization of this magma. We seek to answer the following questions: 1) Was the parental magma of ALH 77005 water-bearing and if so, how high was the concentration of water in this magma? 2) How does the liquid line of descent change with different water contents? and 3) What effect does a nominal amount of dissolved water have on the crystallization sequence and liquidus temperatures of this magma?

Methods: Two types of experiments were performed in this study along with analyses of thin sections. The first type of experiment rehomogenized melt inclusions in chips of ALH 77005. Melt inclusions were found in several different mineral phases that represent early to late stage crystallization. The second type of experiment was dry and anhydrous crystallization experiments from a synthesized ALH 77005 parental magma composition.

Rehomogenization Experiments. Experiments were performed in TZM pressure vessels. Samples were surrounded with graphite to fix the oxidation state of the experiment. The samples were brought to pressures of 800 or 1000 bars and temperatures of 1150, 1160, 1165, and 1185°C. Samples were run for durations ranging from 3 to 72 hours.

Crystallization Experiments. Crystallization experiments were performed on a synthesized parental melt composition that is equivalent to the glass composition in chromite-hosted melt inclusions identified in [5]. Aliquots of the synthesis were pressed into a pellet and placed in a platinum tube lined with graphite. The platinum tube was placed in a TZM pressure ves-

sel at pressures between 350 and 1800 bars. The sample was taken above the liquidus temperature, which was determined to be near 1185°C through the rehomogenization experiments of [5], and subsequently dropped in a series of time steps so that the sample was allowed to crystallize.

Water-bearing experiments were performed with both an inner and an outer capsule based on the COH buffer technique described by [6]. The inner capsule contained synthesized composition surrounded in graphite and enough oxalic acid ($H_2C_2O_4$) to saturate the melt with 1 wt % water. The outer capsule contained Ni-NiO. As with the anhydrous experiments, the samples were placed in TZM pressure vessels and taken above the liquidus before being lowered to a final temperature (1100 to 1175°C) where they were allowed to crystallize. The experiments were held at their final temperature for up to 30 hours and were immediately quenched upon completion of the experiment.

Results: Residual magmatic and mineral compositions were not significantly effected by the addition of water to crystallization experiments (Figure 1). However as shown in Figure 2, addition of water to the parental melt composition results in a lowering of the liquidus temperature during crystallization experiments.

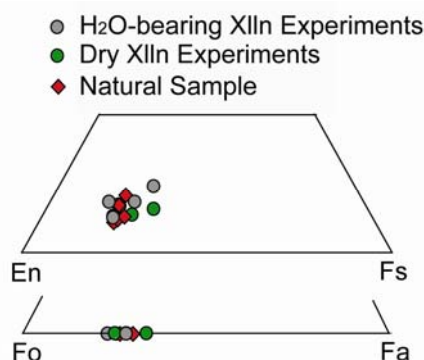


Figure 1. Olivine and pyroxene analyses from dry crystallization experiments compared with the natural sample.

Discussion: *Hydration state of ALH 77005.* We present three lines of evidence suggesting that ALH 77005 was a dry or nearly dry magma. First, neither our analysis nor any prior study of ALH 77005 has found evidence for hydrous minerals. This is a small but significant point. If phenocryst growth was below the surface, as suggested by the cumulate nature of this

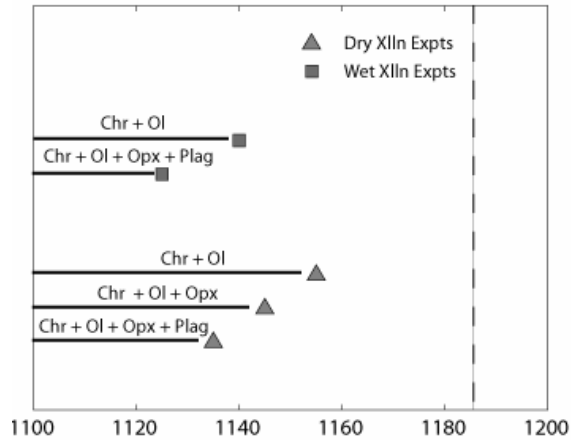


Figure 2. Appearance of various phases vs. temperature from both dry and water-bearing crystallization temperatures.

rock, melt inclusions would be expected to behave as a closed system and build up P_{H_2O} during crystallization of daughter phases. Despite many detailed studies of this rock [e.g. 7,8,9,10], there are no reports of any hydrated phases in the ground mass or in highly crystallized melt inclusions (Figure 3). A second line of evidence comes from estimates of the oxidation state of ALH 77005 as presented by [11,12]. At QFM - 2 to QFM - 3, water would only be present in very low partial pressures ($P_{H_2O} < 0.1 P_{total}$) [6].

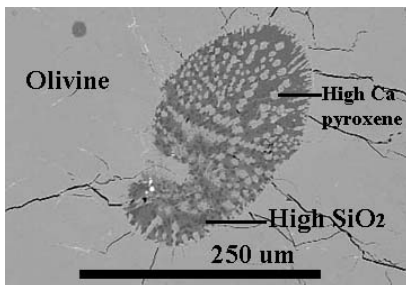


Figure 3. Highly-crystallized olivine-hosted melt inclusion in ALH 77005.

A third line of evidence comes from Cl and F analyses of rehomogenized melt inclusions. Cl strongly partitions into a water rich vapor or fluid phase [13,14]. We examined the Cl content of our rehomogenized melt inclusions and found that Cl increases by two orders of magnitude from the early crystallizing olivine (100 ppm) to the later crystallizing low-Ca pyroxene (10,000 ppm). Because Cl is consistently higher in the latest stage of crystallization and lowest in the earliest stages of crystallization, it suggests that the Cl content of these melt inclusions is magmatic rather than secondary. As such, two things

are indicated. 1) If there was H_2O in the melt inclusions Cl should have partitioned into the vapor phase generated during the experiment. As the Cl contents of the melt inclusions remain high, it is unlikely there was any water-bearing vapor generated during the experiment. 2) The increase in Cl has two likely origins. Cl could have increased during closed-system crystallization of the rock. The other alternative is that Cl was added through addition of new magma or through a metasomatising agent.

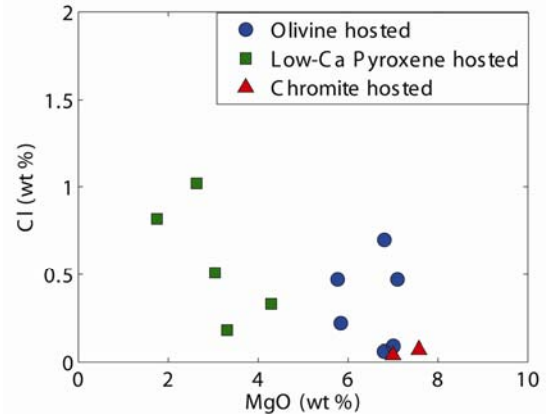


Figure 4. Chlorine contents from glasses in rehomogenized olivine, low-Ca pyroxene-hosted melt inclusions.

Effect of adding water to the parental melt of ALH 77005. By running both dry and water-bearing crystallization experiments, the effect of small additions of water is clear. The liquidus is lowered by as much as 20 °C with only 1 wt % H_2O . However, there is no significant difference between the compositions of minerals crystallized in the dry vs. the water-bearing experiments. Olivine and low-Ca pyroxene appear to have the same range of compositions that closely match the mineral compositions in the natural sample. In addition, the liquid lines of descent for these two types of experiments are almost identical and match that found by rehomogenizing melt inclusions.

References: [1] Romanek C. S. (1994) *Nature*, 372, 655-657. [2] Watson, L.L. et al. (1994) *Science*, 265, 86-90. [3] Lentz, R.C. et al. (2001) *GCA*, 65, 4551- 4565. [4] McCubbin, F. et al. (2006) *LPSC XXXVII*, Abstract #1098. [5] Calvin, C.L. and Rutherford, M.J. (submitted) [6] Eugster H. P. and Skippen G. B. (1967) In *Researches in Geochemistry*, Vol. 2 (ed. P. H. Abelson), 492-520. [7] Ikeda Y. (1994) *Proceedings of the NIPR Symposium on Antarctic Meteorites*, 9-29. [8] Ikeda Y. (1998) *Meteoritics and Planet. Sci.* 33, 803-812. [9] Lundberg L. et al. (1990) *GCA* 54, 2535-2547. [10] McSween H. Y., et al. (1979) *Science* 204, 1201-1203. [11] Wadhwa, M. (2001) *Science*, 291, 1527-1530. [12] Herd, C. D. K., et al. (2002). *GCA*, 66, 2025-2036. [13] Mathez, E. A. and Webster, J. D. 2005. *GCA* 69: 1275-1286. [14] Metrich, N. et al. 2001. *J. of Petr.* 42, 1471-1490.