WORKSHOP PROGRAM AND ABSTRACTS
WORKSHOP ON
WATER IN PLANETARY BASALTS

November 14–15, 2007
Houston, Texas

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Preface

This volume contains abstracts that have been accepted for presentation at the Workshop on Water in Planetary Basalts, November 14–15, 2007, Houston, Texas.

Administration and publications support for this meeting were provided by the staff of the Publications and Program Services Department at the Lunar and Planetary Institute.
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Wednesday, November 14, 2007

WELCOME
8:45 a.m. Berkners

8:45 a.m. Filiberto J. *
Welcome Address and Introduction

WATER IN PLANETARY BASALTS: AMOUNT
9:00 a.m. Berkners

Chairs: J. Filiberto
Q. Li

9:00 a.m. Righter K. * Moore G. M.
Stability of Hornblende and Biotite in Basic Planetary Magmas [#2017]

9:30 a.m. Treiman A. H. * [INVITED]
Volatile in Melt Inclusions: The Example of Kaersutite Versus Rhönite

10:00 a.m. Saal A. E. * Hauri E. H. LoCascio M. Van Orman J.
Rutherford M. J. Cooper R. F. [INVITED]
The Volatile Contents (CO₂, H₂O, F, S, Cl) of the Lunar Picritic Glasses [#2009]

10:30 a.m. BREAK

11:00 a.m. Peslier A. H
Water in Anhydrous Minerals of the Upper Mantle: A Review of Data of Natural Samples and Their Significance [#2003]

11:30 a.m. Boctor N. Z. * Alexander C. M. O’D. [INVITED]
Volatile Abundances and H Isotope Signature of Melt Inclusions and Nominally Anhydrous Minerals in Shergottites [#2004]

12:00 p.m. LUNCH

1:00 p.m. Calvin C. L. Rutherford M. J.
Exploring Water in Shergottite Magmas Through Crystallization Experiments [#2001]

1:30 p.m. Jones J. H. *
The Edge of Wetness: The Case for Dry Magmatism on Mars, II [#2006]

2:00 p.m. DISCUSSION

2:30 p.m. BREAK
Wednesday, November 14, 2007 (continued)

WATER IN SUBDUCTION ZONES
2:45 p.m. Berkners

Chair: E. H. Hauri


3:45 p.m. Draper D. S. * *Effect of Water on Crystallization of Mafic Arc High-Alumina Basalt from the South Sandwich Islands: Still No Liquidus Olivine [#2013]

4:15 p.m. DISCUSSION

5:00 p.m. RECEPTION
Thursday, November 15, 2007

**WATER IN THE MANTLE: EFFECTS ON MANTLE MELTING**

9:00 a.m. Berkners

**Chairs:** M. M. Hirschmann  
E. Medard

9:00 a.m. Dalton H. A.  Holloway J. R.  Sharp T. G.  Hervig R. L.  
*Investigation of the Effects of H₂O on Melting of a Primitive Martian Mantle Composition [#2012]*

9:30 a.m. Filiberto J.  Treiman A. H.  Kiefer W. S.  Li Q.  
*The Effect of Water on Liquidus Temperatures [#2010]*

10:00 a.m. Médard E.  Grove T. L.  
*Water in Basaltic Melts: Effect on Liquidus Temperatures, Olivine-Melt Thermometry and Mantle Melting [#2015]*

10:30 a.m. BREAK

11:00 a.m. Kiefer W. S.  Li Q.  Filiberto J. [INVITED]  
*Parameterizations of Magma Production in a Water-Undersaturated Martian Mantle: A Plea for Improved Experimental Petrology Constraints [#2016]*

11:30 a.m. Hirschmann M. M.  Aubaud C.  Withers T.  
*Hydrous Partial Melting of the Upper Mantle as Judged from Mineral/Melt Partition Coefficients [#2002]*

12:00 p.m. LUNCH

1:00 p.m. Grove T. L.  Médard E.  Till C. B. [INVITED]  
*The Role of H₂O on Mantle Melting in the Terrestrial Planets [#2007]*

1:30 p.m. Li Q.  Kiefer W. S.  
*The Effects of Water on Mantle Convection and Magma Production on Mars [#2011]*

2:00 p.m. Elkins-Tanton L. T.  
*Producing Volatile-rich Magmas Without Plate Tectonics: Upside-Down Melting [#2005]*

2:30 p.m. DISCUSSION
VOLATILE ABUNDANCES AND H ISOTOPE SIGNATURE OF MELT INCLUSIONS AND NOMINALLY ANHYDROUS MINERALS IN SHERGOTTITES; N.Z. Boctor1, C.M.O.D’Alexander1,  
1Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington, DC 20015, USA.

Introduction: Volatile elements are of great geochemical importance because they influence a wide range of geological processes. Water and other volatiles play a significant role in partial melting processes. Water degassing at shallow depths is the main source of energy for volcanic eruptions. Nominally anhydrous minerals contain trace or minor amounts of OH and constitute the main H reservoir in the Earth’s mantle and perhaps the Martian interior. Water in nominally anhydrous minerals has a profound effect on the rates of high-pressure phase transitions in planetary interiors. We studied the volatile abundances and H isotope signatures in nominally anhydrous minerals, glasses, and melt inclusions in the chassignites, nakhlites, and ALH 84001 [1, 2]. We are extending our investigation to the more challenging group of Martian meteorites, the shergottites [3], which unlike the nakhlites which are the least affected by impact metamorphism, show a wide range of shock effects from mild deformation to vitrification, shock melting, and high-pressure phase transitions [4].

Experimental: Small chips of Martian meteorites (EETA 79001, ALHA 77005, Shergotty, and Zagami) were mounted in indium metal to avoid contamination from epoxy and polished by alumina to avoid contamination from carbon-based abrasives.

The abundances of H2O, CO2, F, S, and Cl were measured with a Cameca 6F ion microprobe using the techniques described by [5]. A charge compensated Cs+ primary beam was used, and the negatively charged secondary ions were collected. Routine detection limits measured by this method measured on synthetic forsterite were H2O 2-4 ppm, CO2 <3 ppm, and F, Cl, and S <1 ppm. Glass standards with appropriate concentrations 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.

Results: Water abundance in cpx varies from one meteorite to another and ranges between 7 and 66 ppm for ALH 77005, 26 and 204 for EETA 79001. Zagami cpx has a higher water abundance (454 to 714 ppm). Shergotty cpx was highly fractured and unsuitable for analyses. Although additional analysis of cpx in other shergottites are needed, water abundances in the analyzed shergottites are lower than those in cpx from terrestrial mantle derived pyroxenes, which range between 130 and 970 ppm and also lower than the most primitive MORB (370 to 1220 ppm) [6]. Olivine in ALHA 77005 has water abundance of 14 to 205 ppm. The most hydrous naturally occurring mantle-derived olivine contains 240 ppm [7]. Water abundance in the melt inclusions in ALH 77005 ranges from 74 and 163 ppm, and △D for melt inclusions lies between +28 to +375‰. The △D for the host olivine ranges between ~47 to 746‰ with most of the olivine showing an extraterrestrial H signature.

Discussion. The low volatile abundance in nominally anhydrous minerals relative to terrestrial analogs suggests that either their parent melts degassed or volatiles were depleted in the source regions of magma generation. Devolatilization by impact would also lead to loss of volatiles, especially if partial melting occurs [8, 9]. Vesiculation of the feldspathic glass in ALHA 77005 and EETA 79001 suggest that volatile loss has occurred.

Although some of the melt inclusions and nominally anhydrous minerals show an extraterrestrial hydrogen signature, they generally show a modest D enrichment by Martian meteorite standards. The majority of Martian nominally anhydrous minerals with the exception of those who interacted with a Martian water reservoir that equilibrated with the Martian atmosphere also have low △D. If this low D/H signature is a primary magmatic signature and not due to terrestrial contamination, then the parent magma was D depleted. The low D/H ratio of the parent magma may be attributed to degassing, which decreases the △D values of the melt as a result of vapor-melt equilibrium isotope fractionation.

In the majority of meteorites we studied, there is no significant correlation between △D and H2O. Given the low water contents, contamination and devolatilization by impact may be complicating the interpretation of the H isotope data.

Exploring Water in Shergottite Magmas Through Crystallization Experiments. C. L. Calvin¹ and M. J. Rutherford¹, Brown 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 lherzolitic 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 vessel 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 (H₂C₂O₄) 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.

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
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$_2$O 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 metasomatizing agent.

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$_2$O. 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.

INVESTIGATION OF THE EFFECTS OF H₂O ON MELTING OF A PRIMITIVE MARTIAN MANTLE COMPOSITION. H. A. Dalton¹, J. R. Holloway², T. G. Sharp³, R. L. Hervig³. ¹Department of Earth Science, Rice University MS 126, PO Box 1892 Houston, Texas, 77251-1892 (heather.a.dalton@rice.edu), ²School of Earth and Space Exploration, Arizona State University Box 871404, Tempe, AZ 85287-1404.

Introduction: Many expressions of past liquid water on Mars have been observed from orbit, such as river channels, streamlined islands, and gullies on crater walls, and on the surface, such as layered rocks and sulfate deposits. Further evidence of Martian water is found in trace elements in the SNC meteorites [1, 2]. One of the sources of this water may be the mantle [3]. Many have performed experiments using hydrated terrestrial compositions [4], but few have utilized Martian compositions with small amounts of water. Recently, [5] have conducted experiments studying the effects of water on a modeled Martian mantle composition [6]. However, studies using moment of inertia data have shown that the Dreibus and Wänke modeled composition might not be correct [7, 8], and therefore, experimental results using that composition with water may not be relevant to Mars.

Primitive SNC meteorites may be good models of the Martian mantle. One such meteorite is Yamato 980459 (Y98), a porphyritic, olivine-phryic basaltic shergottite. It is composed of 48% pyroxene, 26% olivine, 25% mesostasis, and 1% other minerals and is the most primitive Martian meteorite collected thus far [9]. High-pressure experiments performed using an anhydrous Y98 synthetic composition have determined that a multiple saturation point of olivine and low-Ca orthopyroxene on the liquidus exists at 1.2 GPa and 1540°C, indicating that Y98 could be a primary melt of the Martian mantle and not a cumulate [10]. This project’s purpose was to perform melting experiments on a synthetic Y98 composition + 0.5 weight percent (wt%) H₂O to determine the effects of H₂O on the following: 1) phase equilibria; 2) melting temperature; 3) multiple saturation; and 4) possible fractionation and influence on liquid composition, and to determine how these differed from the anhydrous experiments.

Experimental Methods: A synthetic composition was created using an average of two reported compositions of Y98 [11, 12] with 0.5 wt% H₂O added (Table 1). Oxides and carbonates were ground together under ethyl alcohol using an agate mortar and pestle for 15 minutes, then left to dry. Two platinum crucibles containing the dry starting material powder were placed into a box furnace where the temperature was raised to 1000°C over three hours to eliminate any remaining volatiles, then removed and dry-ground with the mortar and pestle. The starting material was then placed into a one-atmosphere gas-mixing furnace at 1000°C with a CO/CO₂ ratio of 3/2 for two hours, removed from the furnace, quenched in water, and reground to ensure homogeneity. This was done twice with a resulting fO₂ of IW + 0.7 log units. After the material dried in a 100°C oven overnight, brucite (Mg(OH)₂) was added in place of a portion of the MgO in the starting material, resulting in 0.5 wt% H₂O in the composition. The method of [13] was used to control the oxygen fugacity. The starting material with a preset fO₂ was placed into a graphite capsule; the oxidation reaction of C from the graphite to form CO₂ affected the fO₂, keeping it at about IW + 0.7 log units.

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Table 1: Composition of experimental starting material. The first column lists the oxides in the composition. The second and third columns are published Y98 meteorite composition values [8, 9]. The fourth column, the target composition, is an average of the two published compositions. The fifth column is the composition as it was weighed before mixing. The sixth column is the average of three experimental glass compositions from runs that produced only glass and quench. n.r. = not reported. n.m. = not measured. Because of the correction made by the electron microprobe to compensate for the compounds not measured, the compounds that were measured are slightly skewed to higher values from their actual composition.

The QuickPress non-end-loaded piston cylinder in the Depths of the Earth lab at Arizona State University was used to conduct high-pressure experiments. The
sample powder was placed into graphite inner capsules isolated from platinum outer capsules with pyrex powder. The assemblies also included a crushed aluminia rod, a Pyrex sleeve, and an NaCl sleeve. All of the runs included a Pyrex rod and an NaCl rod inside the furnace except for the 0.5-GPa runs, which used an MgO rod instead. Temperature was monitored using a C-type (W5Re/W25Re) thermocouple. Temperature and pressure ramps were done using the “hot piston out” method: ramping the pressure up to 10% above run pressure, ramping the temperature up to run temperature over about 45 minutes, and lowering the pressure to run pressure. The runs were performed at pressures of 0.5, 0.8, 1.2, 1.5, and 1.7 GPa, temperatures ranging between 1350°C and 1550°C, and durations of 30 to 90 minutes. The results of the experiments were analyzed using the JEOL JXA-8600 Superprobe at Arizona State University.

**Results:** Experimental results from this study and [10] are plotted in a phase diagram in Figure 1.

Figure 1: Phase diagram of Yamato 980459 + 0.5 wt% H2O. Points represent individual runs. Experimentally-determined liquidus, orthopyroxene-in, and olivine-out/pigeonite-in lines were constructed from these data (solid black lines). Ol = olivine, OPX = orthopyroxene, Pig = pigeonite. Liquidus, orthopyroxene-in, and olivine-out lines from the anhydrous experiments are represented with dashed black lines. The assemblages for the anhydrous experiments are represented with numbers: (1) is melt; (2) is olivine + melt; (3) is olivine + orthopyroxene + melt, and (4) is orthopyroxene + melt [10].

**Discussion:** The liquidus has decreased in temperature, up to 75°C, and decreased slightly in slope from the anhydrous experiments, suggesting that melt generation temperatures of this composition would be cooler. The lines are currently drawn so there is a multiple saturation point on the liquidus at 1.3 GPa and 1480°C. This point is defined by the intersection of the four reaction lines and is not well-constrained by the data present: it could be higher, lower, or the same pressure as its equivalent in the anhydrous experiments. As drawn, the point is 0.1 GPa higher than the anhydrous experiments and 60°C lower. The multiple saturation point for 0.5 wt% H2O could be at a higher pressure, indicating that a Y-980459-type melt with a small amount of H2O could form deeper within the Martian mantle than an anhydrous melt, and would not require such extremely high temperatures. At higher pressures, pigeonite is introduced where previously only orthopyroxene had formed. As currently drawn, the olivine-out line corresponds with the pigeonite-in line.

These experiments show that depth of melting determines the composition of the resulting partial melt: lower pressures result in higher melt silica contents, while higher pressures result in lower melt silica contents. Additionally, a Yamato 980459-type melt containing 0.5 wt% H2O could possibly form deeper within the Martian mantle, as evidenced by the possible higher pressures at which the multiple saturation point could exist. However, the exact pressure of the multiple saturation point in the hydrous system needs to be verified with further experiments. If the depth of origin of Yamato 980459 is represented by the multiple saturation pressure and represents the thickness of the Martian lithosphere [10], the existence of 0.5 wt% H2O in the mantle could suggest that the lithosphere is thicker than if the mantle source was anhydrous.

EFFECT OF WATER ON CRYSTALLIZATION OF MAFIC ARC HIGH-ALUMINA BASALT FROM THE SOUTH SANDWICH ISLANDS: STILL NO LIQUIDUS OLIVINE. David S. Draper, Institute of Meteoritics, 1 University of New Mexico MSC03-2050, Albuquerque NM 87131. david@draper.name

Introduction: During the late 1980s and early 1990s, a consensus view emerged from ongoing debate regarding whether island-arc tholeiites were derived from melting the subducted slab or the overlying mantle wedge. Trace-element, isotopic, and petrologic data have been cited to infer that most arc basalts originate in the mantle wedge and that wedge melting is either caused or facilitated by fluxing from fluids derived from devolatilization of the upper reaches of the subducting slab. Alumina-rich arc tholeiites (termed HAB for high-alumina basalt), the dominant lithology in most such settings, are thus held to be differentiates of more primitive, magnesian parents such as volumetrically less extensive high-magnesia basalts (HMB), and the more evolved lithologies such as andesites and dacites are, in turn, likely to be differentiates of HAB. Only in specialized settings is significant slab melting thought to occur, and then mostly to produce comparatively uncommon compositions such as the so-called adakites (magnesian andesites).

Yet one important feature of arc HAB phase equilibria that is not compatible with this model remains unaccounted for. Under anhydrous conditions, a typical primitive arc HAB, SSS.1.4 from the South Sandwich Islands in the Scotia arc (red star on Fig. 1), is not saturated with olivine at any pressure; instead, its liquidus phases are plagioclase, clinopyroxene, and garnet at increasingly elevated pressures; olivine does not appear until ~100°C beneath the liquidus [1]. But SSS.1.4 is not far in composition from some liquids coexisting with olivine ± clinopyroxene formed in melting experiments on arc HMB by [2], who argued (p. 16) that liquidus plagioclase was not expected for those HMB-derived melts because, in a clinopyroxene-olivine-plagioclase-quartz projection, those liquid compositions plot along “an extrapolated intermediate pressure Plg-Ol-Cpx cotectic while SSS.1.4 plots comfortably in the plagioclase field.” The question then becomes, if HABs like SSS.1.4 are indeed the product of olivine-dominated fractionation from more primitive precursors, why would the parental melts to SSS.1.4 fractionate to that cotectic and then jump across it into the plagioclase field, rather than following it down-temperature?

Two possible explanations for these anhydrous results are that SSS.1.4 suffered plagioclase accumulation in a process like that described by Crawford et al [3], or that SSS.1.4 liquid could be in reaction relationship with olivine. Draper and Johnston [4] tested the latter notion experimentally under anhydrous conditions, finding that such a process is feasible only for a few, comparatively Ca-poor arc HABs and does not account for typical HAB like SSS.1.4. They also calculated that plagioclase accumulation is unlikely to account for the nearly aphyric SSS.1.4 lava, and concluded that the most likely explanation was that if the parent magma to SSS.1.4 were hydrous, small amounts of water could expand the primary phase volume of olivine at the expense of that for plagioclase, removing the final hurdle for deriving SSS.1.4 from mantle-wedge-derived magnesian parental magmas. In this contribution, this process was tested experimentally by performing near-liquidus experiments on SSS.1.4 with several percent water added. Surprisingly, however, results thus far show that olivine is still not a near-liquidus phase for SSS.1.4 at 2-3 wt% H₂O, and probably even at 5 wt% H₂O.

Experiments: The experiments reported here were performed at ~2-3 and ~5 wt% H₂O under com-
paratively oxidized conditions relevant to arc magmatism. Powdered SSS.1.4 (a split from the original starting material of Johnston [1]) was run in sealed AuPd capsules with powdered oxalic acid dihydrate (OAD) as the fluid source in a piston-cylinder device at 0.5 to 1.0 GPa, 1075-1250°C for 4-21 hr. OAD breaks down at run conditions to a 50:50 molar mixture of H₂O and CO₂ (29 and 71% by weight, respectively); solubility of CO₂ at these conditions is less than 200-300 ppm [5], thus OAD provides a very convenient means for controlling water content and the added CO₂ should have virtually no effect on phase relations. Sample capsules were in turn sealed into outer AuPd capsules containing an oxygen buffer assemblage consisting of nickel + nickel oxide (NNO) or fayalite + quartz + magnetite (FMQ). These two buffers are < 0.5 log units apart at the conditions of these experiments and are appropriate for the higher oxygen fugacities held to be prevalent in arc basaltic magmatism. At these fugacities iron loss to the AuPd capsules is minimized [6]. Thus far approximately 10 experiments at ~2-3 wt% H₂O have been completed, with four at ~5 wt% H₂O.

Results: Fig. 2 summarizes the phase relations thus far determined. On the right are curves showing the anhydrous relations found by Johnston [1], showing the liquidus at ~1275°C at 1.0 GPa with a broad field of plagioclase crystallization; olivine forms ~100° beneath the liquidus at pressures below ~0.8 GPa. On the left, results from ~10 experiments at 2-3 wt% H₂O are illustrated by the grey field boundaries, and the 4 runs at ~5 wt% are shown by the symbols keyed to the legend. At 2-3 wt% H₂O the liquidus is depressed ~50°, and olivine again does not appear un-
til ~100° cooler at 0.5 GPa (beneath symbol legend). The primary phase volume for plagioclase has indeed contracted, but not enough for olivine to assume the liquidus. The four experiments at ~5 wt%, two above the liquidus and two below, imply the liquidus under these conditions is depressed ~175°. Neither subliquidus run contains olivine; the liquidus phase at ~0.8 GPa is either plagioclase or orthopyroxene, and at ~1.0 GPa is either plagioclase or clinopyroxene. Additional coverage will reveal more detail, but the clear result is that olivine does not assume the liquidus of HAB at ~2-3 wt% water; at 5 wt%, it could do so only at pressures less than 0.8 GPa.

Implications: The conflict described above between anhydrous results on arc HAB and HMB remains unresolved: primitive HAB SSS.1.4 still does not show liquidus olivine even with several percent water in the system, unless it does so at very low pressure and high water contents. With respect to the options listed earlier, could those processes act under hydrous conditions? Clearly plagioclase accumulation is unlikely in hydrous basalts, but it is possible that water-bearing liquids derived from mafic-phase fractionation of a parental HMB could enter into olivine-liquid reaction. A water bearing study similar to the earlier anhydrous work [4] would be required to make such a determination.


Figure 2 P-T summary diagram comparing anhydrous results on SSS.1.4 with water-bearing results at NNO (~FMQ) reported here. Liquidus depression is ~50 and ~175°C at ~2-3 and ~5 wt% H₂O, respectively. Olivine occurs at 0.5 GPa, 1140°C (~100°C below liquidus) with ~2-3 wt%, does not appear in the two subliquidus runs at ~5 wt% H₂O. L, gl, glass; sp, spinel; cpx, clinopyroxene; Plag, pl, plagioclase; Ol, olivine; opx, orthopyroxene.
PRODUCING VOLATILE-RICH MAGMAS WITHOUT PLATE TECTONICS: UPSIDE-DOWN MELTING. L. T. Elkins-Tanton, Massachusetts Institute of Technology, Cambridge, MA, ltelkins@mit.edu.

Introduction: On Earth magmatism occurs on continents in the absence of subduction, often producing volatile-rich magmas such as those in the Leucite Hills, the Sierra Nevada, and Peru’s Altiplano. The primary hypothesis to explain this volcanism is delamination, foundering of the lower lithosphere into the mantle [e.g., 1]. The numerical experiments presented here are scaled to the Earth, but this process is a strong candidate for magmatism on one-plate planets such as Mars and Venus [2, 3].

Here loss of the lower lithosphere is hypothesized to occur in a ductile manner [e.g., 4-11]. This mechanism requires no specific structural weakness beyond a dense region in the lithosphere that is gravitationally unstable with respect to the underlying mantle and that possesses a rheology conducive to flow [11,12].

In a lithosphere lying within the eclogite stability field but itself gravitationally stable, intruding melts may freeze as eclogites and thus create a dense lower-lithospheric region. Melt intrusion and freezing may occur in an arc setting [13], or above a mantle upwelling [12]. Density contrasts of as little as 1% are fully sufficient to drive gravitational instabilities.

Traditionally magmatism associated with instabilities has been attributed to return flow of the asthenosphere, but as numerical experiments demonstrate there is a second, possibly more important process to create melt. The sinking lithospheric material may heat conductively as it sinks and can cross its solidus and produce magma as described in more detail below. Because melting in instabilities occurs as they sink, we have termed this novel melting mechanism “upside-down melting.”

Numerical Experiments: A critical aspect of these models is the assertion that lithosphere available for delamination may contain volatiles and other incompatible elements; some hydrous phase stability regions are shown in Fig. 1 with typical starting conditions for an experiment. The experiments were conducted using the axisymmetric two-dimensional finite-element numerical code ConMan [14]; details are presented in Elkins-Tanton [2].

Adiabatic melting in the upper mantle adjacent to the instability: A gravitational instability forms when a vertical perturbation in a boundary grows through lateral flow, causing the instability to enlarge. The growing instability begins to sink into the underlying mantle material as a drip, exactly analogous to but reversed in the sense of growth from an ascending plume head. If at the time when the instability accelerates downward lateral flow cannot replenish material at the base of the instability fast enough, the material joining the instability separates at its edges from the laterally adjacent lithosphere. The result is an annulus of thinned lithosphere, centered on the instability (Fig. 2). Asthenospheric material can be drawn upward into this relatively shallow annulus by convection currents initiated by the moving instability, during which process the asthenosphere may melt adiabatically, depending upon the solidus and temperature of the asthenosphere and the height of the topography in the annulus. No dome forms in the lower lithosphere during ductile delamination.

Producing volatile-rich magmas without plate tectonics: The lower lithosphere involved in flow may contain 0.1 to 0.2 mass% of water if only the nominally anhydrous minerals are present [e.g., 15], and up to several weight percent of water if phlogopite or am-
The sinking lower lithosphere may devolatilize as it sinks just as descending lithosphere in a subduction zone devolatilizes as temperature and pressure increase. The initial temperature, the conductive temperature increase, and pressure change of the material at the center of each drip can be calculated from numerical experiment results, and are given in Fig. 3. Material that sinks relatively slowly heats conductively to higher temperatures while at lower pressures; material that sinks quickly retains its initial temperature to greater depths. These two generalized paths result in different predictions: the drips that sink slowly cross solidi in pressure-temperature space as they heat, and can move into regions where damp peridotite will melt while dry peridotite will not (Fig. 3B). The drips that sink quickly can descend into a region where free hydrous fluid exists. These latter drips therefore may release volatiles into the surrounding mantle without necessarily melting themselves (Fig. 3C).

This process has the potential to create primitive hydrous basaltic magmas with high alkali contents and lithospheric trace element signatures, typical of small-volume continental magmas worldwide (see references for Fig. 3 and in [10]). The pressures and temperatures of origin for a number of these hydrous, potassic magmas are shown in Fig. 3C, and they lie within the pressure and temperature parameter ranges predicted for melting from volatile-bearing sinking material. These magmas are compositionally distinct from the relatively dry adiabatic melts that result at mid-ocean ridges, and which the dry adiabatic melting created by the movement of the sinking instability would more closely resemble.

Conclusions: As it sinks material in instabilities may devolatilize (as a descending slab in a subduction zone does), may itself melt (“upside-down melting”), or may carry volatiles to depth, depending upon their rate of fall. Volatiles released into the mantle may be stabilized in solid phases or may trigger melting, even in cases where no dry adiabatic melting is triggered by convection around the sinking instability. In the upper mantle, where descending slabs are forced to move at plate rates and therefore devolatilize more completely, instabilities are able in some cases able to sink sufficiently fast that their volatiles are carried to depth and enrich the mantle. Volatiles carried to depth in this manner may be a primary means of creating mantle heterogeneity and of volatile recycling.

THE EFFECT OF WATER ON LIQUIDUS TEMPERATURES. J. Filiberto¹, A.H. Treiman¹, W.S. Kiefer¹, and Q Li¹, ¹Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX, 77058, Filiberto@lpi.usra.edu.

Introduction: Water is important to petrogenesis of basalts and enormous effort has been spent investigating the solubility limits of water in terrestrial basalts (e.g. [1]). Extensive crystallization experiments have also investigated the effect of water on the formation history and crystallization of basalts in terrestrial hot spot magmatism (e.g. [2-4]) and subduction zones (e.g. [5]).

In terrestrial systems water contents range from nearly anhydrous to water saturated; however planetary basalts do not necessarily have the same range in water contents. On Earth, basalts and evolved rocks with large amounts of water (1 wt% and higher) occur most often in subduction zones (e.g. [5]) and in evolved systems (i.e. rhyolites and granites [6]). Subduction zones, as they occur on Earth, have not been found on Mars. Therefore, it is reasonable to focus on the water contents found in terrestrial hotspot magmatism for comparison. Basalts in terrestrial hotspots are at the lower range of water contents found on Earth (~0.50 wt% H₂O in a tholeiite; [7]). Thus it is more reasonable to investigate the effects of small amounts of water planetary basalts genesis.

However, there is little agreement on the exact abundance and effect of water in Martian and other planetary, basalts. The presence of nominally hydrous minerals in the SNC meteorites continues to fuel debate regarding how much water is in Martian basalts, and therefore the Martian mantle. Proposals for water contents in Martian basalts range from high pre-eruptive water contents (2-5 wt%; [8-10]) to very low water contents (0 to 100’s of ppm: e.g., [11-13]). Experiments have been conducted on Martian basalts with water contents ranging from nearly anhydrous (e.g. [14, 15]) to water saturated (e.g. [16]), examining the effects on liquidus temperatures. This experimental work has then been used to develop theoretical (geophysical and thermodynamic) models to make predictions about the Martian mantle. These models are only robust if they are based on sufficient data. Currently limited knowledge of the effects of small amounts of water on crystallization of silicate melts makes it difficult to constrain these models at low H₂O contents. Not surprisingly this causes little agreement about the scale of the effect of water in planetary basaltic systems.

Previous Studies: Recently experiments conducted on terrestrial MORBs (mid-ocean ridge basalts) show that thermodynamic computer models, such as “MELTS”, do not accurately predict hydrous experimental phase relations [17, 18]. These works investigated the effect of small amounts of water on the liquidus temperature and on the composition of the first formed olivine. These experiments were conducted on terrestrial MORB compositions at rather low pressures and temperatures (100-500 MPa; 940-1220°C;) and showed that the effect of small amounts of water (<1 wt%) is strongly non-linear [19]. However, these experiments were conducted under relatively low pressure and may not be applicable to planetary basalt formation processes. Therefore, better models of planetary basaltic systems based on higher pressure experiments are needed.

Hydrous and anhydrous experiments have also been conducted on Martian basalts at pressures and temperatures relevant to the Martian mantle. [20] conducted liquidus-phase relations on the Gusev basalt Humphrey with ~0.8 wt% water which can be compared with the anhydrous work of [14] to show that 0.8 wt% lowers the liquids ~50 degrees (Figure 1).

![Figure 1](image-url)

Figure 1. Experimentally determined phase relations for the Humphrey composition anhydrous (solid line) [14] compared with hydrous (~0.8 wt% H₂O) experiments [20] emphasizing the effect of water on liquidus depression.

Hydrous and anhydrous experiments on Yamato 980459 (Y98) have also been conducted, but vary greatly in liquidus depression per water content from those of the Humphrey experiments [15, 21-23]. Addition of 0.5% water depresses the Y98 liquidus by ~50°C (comparable to the depression for the Humphrey composition with ~0.8% H₂O); addition of 2% H₂O depresses the Y98 liquidus by ~250°C. In a different set of experiments, addition of 0.8 – 1% H₂O depressed the Y98 liquidus by approximately 100°C. The sources of these discrepancies are not clear – one can-
not separate effects of water content, experimental procedures, and starting composition.

Similar studies to the MORB studies have not been conducted on Martian basalts to investigate whether composition can have an effect on the effect of water on liquidus temperatures. There are a number of models on the effect of water on the liquidus temperature for terrestrial basalts [24-27]; however, many of these are based on experiments on water-saturated basalts. In an attempt to solve these problems compositionally, various experimental data, from terrestrial and Martian basalts, has been combined to produce a new model of liquidus depression for water-undersaturated basalts.

Model: Hydrous and anhydrous experimental results have been combined from varying pressures, temperatures, water contents, and starting compositions with attention paid to the reliability of the data. Results have only been included in cases where hydrous and hydrous experiments have been conducted over similar pressures and temperatures in order to calculate delta T directly from the experiments, reducing the uncertainty from previous models. Also to reduce uncertainty in the model, only experiments which reported water analysis have been included. In addition, only experiments on natural compositions have been included.

Figure 2 shows the liquidus depression (delta T) per wt% water from these calculations. It is clear from this figure that the effect of water in the Yamato 980459 differs significantly from that of other Martian basalts and terrestrial basalts; however the Yamato data sets do not have accurate water contents available and therefore can be excluded from this study.

If the Y98 data is excluded the scatter in the data diminishes and this new model is consistent with previous models [24, 26] for water contents under 1 wt% but varies greatly at higher water contents. The regression line is a reasonable fit ($r^2 = 0.85$) considering the variability in pressure, temperature, experimental technique, and composition of all of the data. The equation $y=42.17x^{0.64}$ provides an empirical formula for predicting the liquidus depression (Delta T) for planetary basalts.

Conclusion: Experimental work has been combined from different pressures, temperatures, and compositions providing a new regression equation to predict the effect of water on liquidus depression (from 0-7 wt% water) on planetary basalts. However, many variables still remain elusive, i.e., pressure, temperature, and starting composition. These variables are currently being explored using this same data set.

THE ROLE OF H₂O ON MANTLE MELTING IN THE TERRESTRIAL PLANETS. T. L. Grove, E. Médard and C. B. Till, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA (tlgrove@mit.edu; emedard@mit.edu; ctill@mit.edu).

Introduction: Recent laboratory studies of the melting behavior of Martian and Earth mantle peridotite compositions have redefined our understanding of hydrous melting. Studies by Grove et al. [1] and Médard and Grove [2] have revisited the melting equilibria and the stability of hydrous phases on the solidus of mantle materials.

![Figure 1. Comparison of water saturated phase relations between Earth (grey lines) and Martian (black lines) mantle compositions, after [2].](image)

The phase relations for the Earth and Martian mantle compositions are compared in Figure 1. In both cases the peridotite solidus at 3 GPa is ~800 °C, which is 200 °C lower than previously accepted values. At 3.0 GPa, the dry solidus for Earth or Martian mantle compositions is ~1400 °C [3, 4]. Addition of H₂O to planetary mantles can thus decrease melting temperatures by as much as 600 °C relative to dry melting. This will have important consequences for planetary differentiation. At pressures above 0.5 GPa, amphibole is present on the vapor-saturated solidus and remains stable to ~2 GPa. At pressures greater than 2.4 GPa chlorite becomes a stable phase on the solidus and it remains stable until ~3.6 GPa. Therefore, melting at 2.4 to 3.6 GPa occurs in the presence of chlorite, which contains ~12 wt. % H₂O. On the Earth, chlorite could transport large amounts of H₂O into the descending mantle wedge in subduction zones. On Mars, chlorite may be stored in the martian lithosphere. Chlorite may be the ultimate source of H₂O for terrestrial subduction zone magmatism. The stability of chlorite on the peridotite solidus may resolve the long-standing puzzle of how H₂O can be transported to a sufficient depth in the mantle wedge so that it can participate in melting to generate hydrous arc magmas.

Melting Earth’s Mantle: In light of these new insights into the chemical processes that lead to melt generation in subduction zones, we can focus on the influence of mantle dynamics and physical processes on melting. Variations in mantle permeability near the base of the wedge, above the subducted slab may exercise important controls on the access of fluids and/or melts to the overlying wedge. The presence of chlorite in the wedge may also influence rheological properties and seismicity in the vicinity of the slab - wedge interface. Advancing our understanding of the thermal structure in the convecting mantle is crucial because it influences melting in the wedge. Improved knowledge of rheology and permeability will help us to develop more robust models of mantle flow and temperature distribution in the mantle wedge. By combining evidence from petrology, geochemistry and geophysics the mysteries that attend the generation of melt in the mantle wedge can be resolved.

Water incorporation during accretion: Recent evidence from Ceres, a small proto-planet orbiting in the asteroid belt, indicates that large water-rich planetary bodies were in existence during the early evolution of the Solar System [5]. The formation of water-rich versus dry bodies is likely a complex function of initial amount of water in the planetesimals, timing of accretion, and concentration of short-lived radioactive isotopes [6]. The existence of water-rich planetesimals and small-protoplanets in the inner Solar System allows reexamination of the hypotheses for the incorporation of H₂O into planets.

Water and early melting on Mars: By combining hydrous phase relations and thermal models of planetary evolution we can gain some insight into the role played by H₂O during accretion. There are two main reason to focus on Mars: (1) Mars accreted from a chondritic mix richer in volatile elements than for other terrestrial planets [7]. (2) The size of Mars is almost identical to the typical size of a proto-planet just before the giant impact stage [8], suggesting that Mars may have escaped the formation of a planet-scale magma ocean that obliterated most of the signature of early accretion and differentiation processes on Earth.

We propose that an early hydrous melting event occurred during the accretion process. This melting
event profoundly differentiated the Martian mantle and removed H$_2$O from the planet’s interior. Water has a strong effect on melting temperatures and mantle viscosity, and the presence of water will accelerate the differentiation process, in agreement with the evidence that Mars differentiated into atmosphere, mantle and core at a very early stage [9].

Dehydration in the deeper parts of the planet would lead to flux melting in the shallower parts. Dehydration and degassing occur when the planet reached about 70% of its final radius (30% of its final mass). Figure from [2].

The innermost part of the planet would remain undegassed during accretion, and contains H$_2$O stored in buried hydrous silicates. A feature of all thermal models of planetary evolution is that the inside of the planet heats up only after or during the latest stages of accretion, as a result of core formation and heating by long-lived radioactive isotopes [11]. Large amounts of H$_2$O could thus be transferred into “nominally anhydrous silicates” in the deep mantle, and might even be incorporated into the core [12].

**References:**
GIANT IMPACTS, LATE VENEERS, AND THE GRADUAL HYDRATION OF THE EARTH’S MANTLE BY SUBDUCTION. E. H. Hauri¹, A. M. Shaw² and A. E. Saal³, DTM, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington DC 20015, ²Department of Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, ³Department of Geological Sciences, Brown University, 324 Brook Street, Providence, RI 02912

Introduction: The likelihood of one or more giant impact events occurring during the accretion of the Earth is very high [1,2], and some of these late-stage events could have imparted enough energy to completely melt the silicate portion of the proto-Earth [3,4]. Despite the uncertain nature and composition of the terrestrial atmosphere immediately after such impacts, it seems inescapable that the Earth’s mantle suffered a catastrophic loss of volatiles (including H₂O, CO₂ and noble gases) within the first 100 Ma of the planet’s history.

For these volatile species, the subsequent evolution of the Earth’s mantle has thus been characterized by a gradual re-hydration from without, via the subduction of oceanic lithosphere altered by water from an exosphere whose existence has been dated to 4.4 Ga [5,6]. The estimated composition of this exosphere shows many similarities to a mass-fractionated proto-atmosphere mixed with volatiles released during impact degassing of a chondritic late veneer.

Initial Accretion: Based on the geochemistry of ordinary and enstatite chondrites, formation of planetesimals and planetary embryos in the terrestrial planet region likely took place in a region of the primordial disk that was depleted in volatile elements. This initial zonation resulted in a proto-Earth that was depleted in the most volatile elements, with a thin tenous atmosphere.

Giants Impacts: Numerical simulations of planetary accretion indicate a very high likelihood of at least one (more likely several) giant impact events involving planetary embryos of ≥ 0.1 Me [2]. Another common feature of these simulations is the occurrence of collisions with sufficiently high angular momentum to satisfy the requirements of the present Earth-Moon system.

Giant impacts can further deplete the proto-Earth in highly volatile elements via three mechanisms. Impact erosion takes place due to violent ground motions that push the atmosphere to escape velocities [7]. Thermal escape of hydrogen and helium will be driven by solar activity and heat generated from magma ocean events triggered by giant impacts. Finally, hydrodynamic escape of heavier gases is accomplished via collisions with thermally-escaping H and He. Such a process is required from the relative abundances and isotopic compositions of terrestrial noble gases.

Magma Ocean Formation: Scaling laws derived from collisional modelling indicate that giant impacts will result in widespread melting of the proto-Earth [4, 8]. Though these melting events almost certainly happened on the growing Earth, the extent of melting is highly uncertain; melting of the upper mantle seems very plausible, but melting of the lower mantle requires sufficient heat to melt Mg-silicate perovskite. Better estimates of the extent of melting are hampered by a lack of appropriate collision modelling and disparities in the experimentally-determined melting point of Mg-perovskite [9,10].

Late Volatile Veneer: Highly siderophile element abundances in the Earth’s mantle appear to require the addition of a carbonaceous chondrite late veneer with a mass of 0.7% of the Earth’s mantle. The associated volatile budget contains 2 oceans of water and sufficient C, S and Cl to make up the present-day volatile abundances of the atmosphere and mantle. Stable isotope similarities of this chondritic late veneer and the Earth’s volatile budget provide support for the addition of this late veneer after solidification of the magma ocean, although some fraction of a mass-fractionated primordial atmosphere is also required.

Hydration of Earth’s Mantle: Due to impact degassing, it is likely that much of the Earth’s volatile budget was present at the surface, with an ocean volume ~2X higher than today. Forward modelling of the evolution of volatiles in the Earth’s interior via subduction hydration of an initially dry mantle, with an emphasis on H₂O, matches the present-day concentrations estimated from reservoir balance and mantle volatile estimates for H₂O, CO₂, S and Cl. Mantle convection is characterized by an initially high mantle viscosity, with gradual growth of a low-viscosity upper mantle due to the introduction of water at subduction zones. Today the Earth’s mantle may be characterized by a wet low-viscosity upper mantle and a dry, stiff lower mantle, though details of this scenario await proper numerical modelling.

Hydrous partial melting of the upper mantle as judged from mineral/melt partition coefficients.

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It has been known for more than 10 years that nominally anhydrous minerals may incite small amounts of melting in Earth’s mantle. In recent years, there has been a great increase in experimental data on the H$_2$O storage capacity of nominally anhydrous minerals. Yet, disagreement among models for the locus of dehydration melting in the upper mantle is growing rather than narrowing. Models span the gamut from requiring small amounts of hydrous melt throughout the upper mantle, to hydrous melting in a global low velocity zone layer at depths of ~80-200 km, to melting only beneath ridges and oceanic island in a restricted interval a few 10s of km beneath the locus of dry melting. These disagreements persist because direct experimental investigations of the influence of small amounts of H$_2$O on mantle melting are not feasible, and consequently understanding comes from parameterization of indirect experimental constraints.

One key constraint on the possible locus of hydrous melting in the upper mantle is the range of feasible concentrations of H$_2$O in near-solidus hydrous melts. For a mantle with a fixed amount of H$_2$O, $c_{H_2O}^{mantle}$, the maximum H$_2$O concentration of an incipient partial melt is given by $c_{H_2O}^{mantle} / D_{H_2O}^{peridotite/melt}$, where $D_{H_2O}^{peridotite/melt}$ is the equilibrium bulk partition coefficient between the peridotite mineral residue and the partial melt. Experimental determinations of $D_{H_2O}^{mineral/melt}$ for upper mantle minerals have been made feasible by new low-blank ion probe measurements. Although thermodynamic calculations of $D_{H_2O}^{olivine/melt}$ predict that it should depend on both pressure and H$_2$O concentration, such dependences are not apparent in the experimental data. Values for $D_{H_2O}^{garnet/melt}$ span a wide range, and are apparently controlled by the concentration of minor elements in garnet, notably TiO$_2$. Finally, values for $D_{H_2O}^{pyroxene/melt}$ depend strongly on the concentration of Al in pyroxene, and in particular on the abundance of tetrahedral Al in pyroxene.

Combining experimental constraints on $D_{H_2O}^{peridotite/melt}$ with the modal proportions and compositions of minerals near the peridotite solidus, it is possible to estimate the H$_2$O concentration of incipient partial melts. For mantle with 100 ppm H$_2$O, such partial melts have 1.2 wt. % H$_2$O at 3 GPa and 2.3 wt.% at 7 GPa. Such modest concentrations of H$_2$O provide only small stabilization of melt relative to a dry peridotite system, thereby supporting the inference that dehydration partial melting of normal mantle is feasible only near where the dry peridotite solidus is approached, meaning immediately below the locus of dry melting beneath ridges and mantle plumes.
**Introduction**: The issue of whether martian magmas are wet or dry is an important one. The answer to this basic question has profound consequences for how we think about Mars as a planet. Several lines of evidence have been presented that collectively suggest that shergottite parent magmas were once wet. These include: (i) phase equilibria studies that indicate that the Shergotty parent magma required ~2 wt.% water in order to be co-saturated with both pigeonite and augite [1], (ii) reverse zoning of light lithophile elements (Li and B) in shergottite pyroxenes, suggesting the exsolution and removal of an aqueous fluid [1], and (iii) measurement of D/H ratios in SNC minerals that are much lower than atmospheric, suggesting that there may be juvenile (primordial) mantle water [2].

Below I will review the evidence for the diametrically opposite case, that shergottite magmas were effectively dry (<< 1 wt.% H2O).

**The Martian Mantle.** Initially, it was believed that the Martian mantle was much like that of the Earth, producing basalts that are rather oxidized (~IW+3) compared to those from the Moon or the asteroid belt [3]. Consequently, it has also been assumed that magmas from the Martian mantle are similar to those on Earth, which have water as a significant component of their volatile inventory. But this view does not take into account the difference in tectonic styles between the two planets.

Reactions with Fe metal are likely to have dehydrated the early mantles of Earth and Mars. There is general agreement that there is no clear-cut evidence for terrestrial juvenile water and that the water in terrestrial basalts likely originates from water emplaced in the mantle by subducting slabs [4]. The fact that Mars does not have subduction-driven plate tectonics means that there is no obvious mechanism for hydrating the Martian mantle after core formation.

Also, it now appears that the Martian mantle is not as oxidized as was originally thought. Those shergottites that appear to be least affected by crustal contamination are also rather reduced (~IW to IW+1 [5]), about the fo2 expected for basalts with shergottite FeO contents (~18 wt.%) that have come from a source region that once equilibrated with Fe metal [6].

Another consideration is that the shergottites come from depleted source regions [e.g., 5]. QUE94201, for example, has an initial ɛ(^143Nd) of ~+50, five times larger than that of the depleted, terrestrial MORB mantle. To the extent that water acts as an incompatible element during basalt petrogenesis, the removal of basalt that depleted the martian mantle in incompatible elements represented a second chance at dehydration if reactions with metal were not sufficient to do the job.

In fact, because the shergottite source regions have not remained closed systems, there was a third chance at dehydration. Sm-Nd evidence indicates that melts were lost from the shergottite source regions shortly before shergottite petrogenesis. These missing melts should also have carried away any remaining water.

In summary, there is no compelling reason to believe that the Martian mantle should contain a significant amount of water or that basalts coming from that mantle should either.

**Water Contents of SNC Meteorites.** Regardless of these theoretical considerations, it is important to determine how much water is actually in SNC meteorites. For Shergotty and Zagami (meteorite falls whose original water contents have been estimated by phase equilibria [1]) clearly indigenous water (i.e., released above 350°C is 150-200 ppm [7]). This is in contrast to the estimates of ~2 wt.% by [1]. If Shergotty and Zagami originally contained 2 wt.% water, then their dehydration is required to be ≥99% efficient. For Chassigny, another fall, indigenous water is somewhat higher — ~350 ppm [7], but still very low.

**Mineralogy of SNC Meteorites.** The mineralogy of the SNC meteorites is consistent with these low water contents. Phosphates in SNC’s are either merrillite [Ca3(PO4)2] or chlorapatite [Ca5(PO4)3Cl], not hydroxy-apatite. Zagami chlorapatite, for example, only contains about 1000 ppm water [8]. Chlorapatite is the least stable form of apatite. For chlorapatite to form in preference to hydroxy-apatite, the activity of water must be very low.

The water content of SNC amphiboles is also low [8]. The argument has been made that significant water may have been liberated from these amphiboles by the shock events that ejected the SNC’s from Mars [1]. However, this seems unlikely. The martian amphiboles discovered thus far are kaersutites with high TiO2 contents. They are probably best thought of as oxy-amphiboles and necessarily so for Ti charge balance [9]. The SNC amphiboles probably have always had low hydroxyl contents, regardless of how much or how little water was lost due to shock.

**Shergotty Phase Equilibria.** Experimental studies on a reconstructed Shergotty inter-cumulus liquid (SIL) indicate that this composition has only pigeonite on its liquidus at one bar [10]. Therefore, the SIL is
not multiply saturated with pigeonite and augite at low pressure [10], even though petrographic observation of Shergotty requires it to be [3]. Addition of an augite component to the SIL composition produces multiple saturation at one bar and ~1150°C. Alternatively, addition of ~2 wt.% water to the SIL composition produces multiple pyroxene saturation at ~500 bar and ~1120°C [1]. McSween et al. [1] concluded, therefore, that significant water was necessary to produce the observed phase assemblages of Shergotty and Zagami.

This conclusion seems unlikely. First, both Shergotty and Zagami are exceedingly dry. Secondly, the one-bar anhydrous experiments that were fortified with augite reproduce the core pyroxene compositions of Shergotty and Zagami better than the hydrous experiments do. Third, the anhydrous experiments of [3] closely bracket the natural pyroxene compositions. Fourth, the anhydrous experiments of [3] and the anhydrous augite-fortified experiment (Sy-24) of [10] give nearly identical results. For major elements, the Sy-24 glass [10] and the average of Sh-7 and Sh-18 of [3] agree to within 10%. The temperature of the Sy-24 experiment was 1150°C and the average of the Sh-7 and Sh-18 run temperatures is 1148°C. This agreement between two very different experimental regimes is impressive. I conclude that the derivation of the SIL composition by Hale et al. [11] either systematically excluded an augite component or overestimated a pigeonite component. Therefore, the experiments on natural materials, where no compositional reconstruction is necessary [3], are to be preferred.

This conclusion has been argued against on the basis that the experiments of [3] were short and may not have approached equilibrium. However, the experimental pyroxene compositions of [3] change continuously with temperature and bracket the compositions of natural pyroxene cores. This observation implies that equilibrium was closely approached.

**Exsolution of Aqueous Phase: Li and B.** Of the various evidences for wet shergottites, the reverse zoning of the light-lithophile-elements (LLE) is perhaps the most interesting and compelling [1]. However, at least one experimental study failed to demonstrate that B prefers aqueous fluid over basaltic liquid [12]. Another study [13] found that the pyroxenes in NWA480 were unzoned in Li but were strongly zoned in 67Li. This is an area where more data and experiments would be welcome.

**Exsolution of Aqueous Phase: Halogens.** The Cl/Br ratios of SNC meteorites are remarkably close to that of Cl chondrites [14,15]. The Cl/Br ratio of Nakhla is quite a bit lower than Cl but this rock has experienced hydrothermal alteration, a process that could fractionate halogens. In fact, the experimental data of [16] suggest that the exsolution and loss of an aqueous fluid will fractionate Cl and Br. In their experiments at 900°C and 2 kbar, Ke(Cl/Br) for aqueous fluid/silicate melt is ~0.5. Therefore, the observation that Shergotty has a Cl/Br ratio that is both -chondritic and similar to other shergottites suggests that halogen fractionation did not occur. This may also suggest that no fluid phase was lost from the Shergotty parent magma.

**Recapitulation.** Taken as a whole, the evidence that SNC meteorites in general, and the shergottites in particular, were ever wet is not compelling. Certainly the water is not there today. If it was lost as a condensed aqueous fluid, it did not fractionate halogens much. If it was lost as steam from a magma chamber, then the loss process is required to be highly efficient. [Actually, both loss mechanisms are required to be efficient.] A more plausible explanation is that the water was never there.

**Juvenile Water on Mars?** In light of the foregoing discussion, is there juvenile water on Mars? Yes, there probably is such water, but not much of it. Combined H and C isotopic data can be used to identify martian volatile element reservoirs. The only SNC to have both isotopically light H and C is Chassigny [7], and these are properties attributed to the martian mantle [17]. Indigenous water in Chassigny is about 350 ppm and has a 67D of ~50 ‰. Because of the complex petrogenesis of Chassigny, translating this amount of magmatic water into source region concentrations is difficult. If Chassigny is 90% anhydrous cumulate of a 5% partial melt, then the martian mantle contained about 175 ppm water. To better constrain this concentration, better models both for the petrogenesis of Chassigny and the siting of Chassigny water would be required.

**References:**

Parameterizations of Magma Production in a Water-Undersaturated Martian Mantle: A Plea for Improved Experimental Petrology Constraints, Walter S. Kiefer, Qingsong Li, and Justin Filiberto, Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058, kiefer@lpi.usra.edu, http://www.lpi.usra.edu/science/kiefer/home.html

Introduction

Numerical simulations of magma production rates due to adiabatic decompression melting in a convecting mantle have been used to help constrain our knowledge of both the present-day mantle structure on Mars [1-5] and the long-term thermal evolution [6-9]. Many of these studies [4, 6-9] assume that the martian mantle solidus can be approximated by some version of the terrestrial mantle solidus [e.g., 10, 11]. Moreover, most of these studies have assumed either that the martian mantle is dry or that the water abundance does not affect the solidus temperature [1, 2, 4-9].

Both assumptions exert an important control on the magnitude of the predicted magma production rate. The martian mantle is thought to differ from the terrestrial mantle in several important ways. In particular, the martian mantle is thought to be enriched in Na and K relative to Earth. Mars also likely has a somewhat lower magnesium number than Earth [12, 13]. Both of these compositional effects act to lower the martian solidus relative to Earth [10]. In addition, up to several hundred ppm water might be present in the martian mantle [e.g., 14]. Our numerical simulations show that taken together, these two effects can alter the magma production rate by an order of magnitude [3]. Thus, it is essential to anchor our models as much as possible in Mars-specific experimental results.

Parameterization of Wet Melting on Mars

In our on-going numerical simulations of water-undersaturated melting on Mars [3], we are using the work of Katz et al. [15] to parameterize the effects of water on the solidus temperature and the production of melt as a function of temperature above the solidus. The Katz model has 3 essential components: a parameterization of the dry solidus as a function of pressure, a parameterization of the depression of the solidus due to the addition of water, and a parameterization of the melt production as a function of super-solidus temperature. Figure 1 compares the Katz et al. dry solidus with the nominally anhydrous Mars mantle compositions of Bertka and Holloway [12] and of Agee and Draper [13, 16]. The two sets of experimental results are for similar compositions, although they differ slightly in magnesium number (75 vs. 80). The results in Figure 1 and in [17] suggest that the Katz et al. [15] parameterization is an excellent starting point for magma production on Mars with small amounts of mantle water.

Figure 1. Constraints on the martian mantle solidus. The solid line is the dry solidus from the Katz et al. [15] parameterization. The symbols are experimental melting results for Mars analog compositions. Open triangles are sub-solidus, squares are experiments in which melt might be present, and filled triangles are above the solidus. Results for 0.5-3 GPa are from Bertka and Holloway [12]. Results for 5-7 GPa are from Agee and Draper [13, 16].

Issues for Further Study

Additional experimental petrology constraints will contribute to more realistic
predictions of the magma production rate and hence to improved models of the martian interior.

(1) Improved Constraints on the Martian Dry Solidus Between 2 and 7 GPa

The solidus in Figure 1 is only weakly constrained between 2 and 7 GPa. The martian lithosphere is relatively thick and most present-day melt generation likely occurs in this pressure range [2], although it is possible that some occurs at lower pressure [18]. It would therefore be very useful to have tighter experimental constraints on the dry solidus in this pressure interval, using the same starting composition at all pressures (recall that Fig. 1 includes results for two somewhat different compositions). Good experimental constraints on melting at lower pressure are also important, both to provide context for the higher P results and because early Mars had a thinner lithosphere [19], allowing melting at lower pressure.

(2) Improved Constraints on the Melt Fraction as a Function of Temperature Above the Solidus

Most of the experimental constraints used in the Katz model on the degree of melting above the solidus are at pressures of 3 GPa or lower, although a more limited set of experiments are available at 4-7 GPa [15]. Because of the importance of high pressure melting on present-day Mars, additional experimental constraints at high pressure would be a valuable addition to the model.

(3) Improved Constraints on the Depth of Melting for Martian Magmas

At present, our primary constraint on the thickness of the martian lithosphere comes from gravity models, which constrain the lithosphere’s thickness on length scales longer than 1000 km [e.g., 19]. Recently, multiple saturation pressures have been determined both for the shergottite Yamato 980459 [18] and for basalts in Gusev crater [20, 21]. Although multiple saturation pressures do not define a precise melting depth, they do appear to provide information about the average pressure of melt extraction from the mantle [22] and thus may serve as a useful additional constraint on mantle models. We plan to explore this in our on-going numerical modeling [3]. A useful experimental goal is to define an MSP for other martian mantle compositions whenever possible.

(4) What is the Role of Aluminum in Controlling the Solidus Temperature?

In addition to the differences in Na and Mg number noted earlier, another difference between Earth and Mars is the lower Al abundance in the martian mantle [12, 13]. Because Al is a refractory element, one might expect lowering the Al on Mars to lower the solidus, although we know of no specific experimental test of this.

THE EFFECTS OF WATER ON MANTLE CONVECTION AND Magma PRODUCTION ON MARS.
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Introduction: Even small amounts of water (<100 ppm) significantly affect the mantle’s viscosity and its solidus temperature. With an axi-symmetrical numerical model, we explore how water affects mantle convection and magma production on Mars. The results show that increasing mantle water content decreases the solidus and increases both melt fraction and melting volume, thus increasing the rate of magma production. In addition, increasing water content decreases viscosity and increases the convective vigor, resulting in a thinner near-surface boundary layer. This permits greater adiabatic decompression in the plume and enhances melt production. While thermal Rayleigh number (Ra), core-mantle boundary temperature ($T_c - m$) and water content all significantly affect magma production rate, increasing water content lowers the required Ra and $T_c - m$ to meet the observed present-day magma production rate on Mars.

Mantle Convection Model: Prior models of mantle plume volcanism on Mars include models in spherical axisymmetric geometry with both depth-dependent viscosity [1] and temperature-dependent viscosity [2, 3] and in Cartesian geometry with temperature-dependent viscosity [4]. Here, we extend these models to include the effects of both temperature-dependent and water-content-dependent rheology, using an Arrhenius form of the flow law [5, 6].

We use a finite element model to solve the partial differential equations for conservation of mass, momentum, and energy in spherical axisymmetric geometry [7]. The model domain is $1.0 \leq r \leq 2.0$ in the radial direction, and $0 \leq \theta \leq \pi/4$ in the lateral direction (Figure 1). It is meshed with $128 \times 128$ elements, with a typical resolution of 13 km. The model includes both internal radioactivity heating (4.1x10^{12} W/kg, [8]), which is partitioned between the mantle and the crust, and basal heating due to the heat flux out of the core. The surface and bottom boundaries are set with fixed temperature conditions and the side boundaries are thermally insulated. All four boundaries are free-slip. An initial temperature perturbation is applied, causing a plume to form at $\theta = 0$. Each model is run until a statistical steady state is reached. We have used physical constants as in [2].

Water Effects on Rheology and Melting: Most estimates of the present-day water content in the Martian mantle are a few hundred ppm or less [9-12]. This amount of water may significantly affect the mantle’s viscosity and solidus. The viscosity of olivine aggregates decreases roughly linearly with increasing water fugacity above a threshold fugacity [5, 6]. The translation from water fugacity to water content is temperature and pressure dependent [13]. As a first-order approximation, we assume that the viscosity of the Martian mantle decreases linearly with increasing water content if water content is larger than 5 ppm.

The recent water-saturated melting study of Médard and Grove [14] may be relevant to the early history of Mars but does not directly address melting at the low water contents that are thought to occur in the present-day mantle. We therefore apply the melting parameterizations of Katz et al. [15], which shows, for example, that 1000 ppm of water lowers the peridotite solidus by ~150 K. We assume that for a given amount of mantle water, the decrease in the solidus temperature is the same for the Mars mantle as it is for the terrestrial mantle composition. We also apply the melting fraction formula developed by Katz et al. [15]. Using the melting fraction equation, we calculate melting using the an approach similar to computational approach as in Kiefer [1].

Results: Besides water content, viscosity and Ra are functions of several poorly constrained variables, including grain size, activation volume and core-mantle boundary temperature. Thus we treat Ra as an independent variable from water content. To explore water effects on solidus, we set a reference case (Ra = 3.45x10^6, E = 160 kJ/mole, crustal heat fraction = 0.5). Here we fix the Ra and allow the water content change the solidus. As the water content increases from 5 ppm to 200 ppm, the solidus decreases by ~68 K. This causes increase of melt fraction [15] and melting volume in the plume head (Figure 1). Both effects cause the magma production rate to increase significantly (Figure 2).
Figure 1. Mantle melting of (a) dry, and (b) 200 ppm water. The white regions show the location of decompression melt. The color bar is saturated for T<0.5.

Figure 2. Magma production rates are plotted against water content. The volume-averaged thermal Ra is fixed at 3.45e6.

The magma production rate is a function of core-mantle boundary temperature, thermal Ra and water content. Increasing core-mantle boundary temperature, thermal Ra or water content all increase magma production rate. A range of combination of these three parameters may satisfy the observational magma production rate (Fig. 3). With fixed core-mantle boundary temperature, increasing water content decreases the required thermal Ra number for magma generation. Meanwhile, with fixed thermal Ra, increasing water content decreases the required core-mantle boundary temperature to meet the present-day magma production rate on Mars (Figure 3). Adding just a few hundred ppm water permits the martian mantle to be 100 K cooler than in the dry case and still satisfy the observed present-day volcanism rate.

**WATER IN BASALTIC MELTS: EFFECT ON LIQUIDUS TEMPERATURES, OLIVINE-MELT THERMOMETRY AND MANTLE MELTING.** E. Médard¹,² and T. L. Grove¹, ¹Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA (emedard@mit.edu; tlgrove@mit.edu), ²Institut für Mineralogie und Petrographie, ETH Zürich, 8092 Zürich, Switzerland

**Introduction:** We performed a series of high-pressure experiments and thermodynamic calculations to quantify the effect of water on the olivine liquidus of primitive basalts. The amount of water in the terrestrial planets is poorly known, but estimates as high as several hundreds of ppm have been proposed for Mars [1], and in terrestrial subduction zones [2] and subcontinental lithosphere. In the mantle, water will decrease melting temperatures [3,4] and broaden melting zones [5] during adiabatic decompression melting, increasing the proportion of low-degree melts in the melting column. Water also drastically changes the liquid line of descent of basaltic magmas: it is responsible for the calcalkaline vs tholeiitic differentiation trend [6].

However, quantitative estimates of the effect of water on basalt phase equilibria are scarce and often incompatible with each other. This is a consequence of the experimental difficulties inherent in carrying out hydrous experiments, including the ability to maintain a constant H₂O content, and to quench water-rich hydrous melts to analyzable glasses. The olivine-melt equilibrium is of critical importance for the understanding of magmatic processes: (1) since olivine is the low-pressure liquidus phase in mantle-derived magmas, thermometry based on the olivine-melt equilibrium provides the primary evidence for estimating melting temperatures in planetary mantles. (2) the effect of water on the olivine-melt equilibrium can also be used as a first approximation to parameterize hydrous melting models [7], olivine being the dominant phase in the upper mantles of the terrestrial planets.

**Experimental strategy:** Our experimental approach has been to measure the dry liquidus temperature, and liquidus temperatures for various amounts of added H₂O, on the same basaltic bulk composition. For each H₂O concentration, we then calculate the liquidus depression, ΔT, as the difference between the dry liquidus temperature at a given pressure and the liquidus temperature for the same melt composition with a known amount of H₂O added (Fig. 1). This method allows us to separate the effect of H₂O from other potential influences (e.g., melt composition, pressure). Most of the H₂O-bearing experiments were performed under water-saturated conditions and the water contents were analyzed using a variety of methods (SIMS, by-difference and oxygen analysis with electron microprobe). Further experimental and analytical details are given in [8].

![Fig. 1. Experimental determination of liquidus depression for tholeiitic basalts. For each experiment, the difference between the dry liquidus temperature and the experimental temperature is plotted as a function of H₂O concentration. Olivine-free and olivine-bearing experiments bracket the liquidus depression curve. The black curve is a thermodynamic model based on the data.](image)

**Liquidus depression:** The experimental data indicate a stronger effect of water at small water concentration, which progressively weakens at higher water concentration. The non-linear effect of H₂O indicates that incorporation of H₂O in silicate melts is non-ideal, and involves interaction between H₂O and other melt components. A non-ideal solution model that treats the effect of H₂O addition as a positive excess free energy can be fitted to the data to describe the effect of melting point lowering (Figure 1). Results from the thermodynamic model can be approximated by the purely empirical equation (H₂O in wt%):

\[
\Delta T (^\circ C) = 39.2 \cdot \left( C_{H_2O}^{melt} \right) - 2.84 \cdot \left( C_{H_2O}^{melt} \right)^2 + 0.0772 \cdot \left( C_{H_2O}^{melt} \right)^3
\]

Additional experiments on a alkali-rich olivine-leucitite, and comparison with other experimental data on MORB [9] indicate that there is no compositional dependence and that this equation is valid for any basaltic composition, within uncertainty. This equation
can be added to existing “dry” olivine-liquid geothermometers to calculate equilibrium temperatures for primitive, mantle derived basaltic magmas.

**Application to planetary basalts:** As an example, we performed calculations on two Martian basaltic compositions that have been argued to represent primary mantle melts: Adirondack-class basalts from Gusev Crater [10,11], and a primitive olivine-phryic “shergotite”, Yamato 980459 [12,13]. We use the dry olivine-liquid thermometer of [14] and our experimental determination of the effect of water. The amount of H$_2$O in primitive Martian basalts is unknown, but estimates vary between 0 and 1.8 wt% [1]. For Adirondack-class basalts, the dry liquidus temperature at 1.0 GPa (near the multiple saturation point) is 1355 °C. With 0.8 wt% H$_2$O, it decreases to 1325 °C and to 1290 °C with 1.8 wt% H$_2$O. This is in excellent agreement with [11] who experimentally determined a liquidus temperature of 1320 °C for ~0.8 wt% H$_2$O. Taking into account the compositional variability for Adirondack-class basalt, the dry liquidus temperature is 1360 ± 15 °C, with addition of 1.8 wt% H$_2$O causing a decrease in liquidus temperature of ~65 °C. For Yamato 980459, dry liquidus temperature near the multiple-saturation point (1.2 GPa) is 1480 ± 10 °C, and 1415 °C with 1.8 wt% H$_2$O. Even if Adirondack-class basalts were dry and shergotites contained a large amount of H$_2$O there is still a significant difference in liquidus temperature, indicating the existence of two different thermal regimes on Mars.

**Water and mantle melting:** Experimentally determined olivine-liquidus depression can also be used to parameterize water-undersaturated mantle melting. Fig. 2 shows an example using an approach similar to the one used by [7]. For a given bulk H$_2$O content in the mantle and a given melt fraction, we calculate the H$_2$O content in the melt using partition coefficients from [15]. Using a melt fraction / temperature relationship for dry melting [16], we can then calculate melt fraction / temperature relationships for water-undersaturated melting using our experimental calibration of liquidus depression. This model assumes that melt composition at a given melt fraction is only marginally affected by addition of H$_2$O, an assumption justified by the experimental data of [17]. Although the scarcity of experimental data on hydrous mantle melting makes ground-truthing difficult, this model is in general agreement with previous estimates (e.g., [4]). An important feature of the model is that water concentrations relevant for planetary mantles (hundreds of ppm) would only have a significant effect at low melt fractions (< 5 wt%), i.e. in the deeper part of melting columns in the case of adiabatic decompression melting.
WATER IN ANHYDROUS MINERALS OF THE UPPER MANTLE: A REVIEW OF DATA OF NATURAL SAMPLES AND THEIR SIGNIFICANCE

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To a depth of 410 km, the Earth's mantle is made of olivine, typically making up 55 to 95% in weight of the upper-mantle dominant rock-type, peridotite, and orthopyroxene, clinopyroxene and an accessory phase such as spinel and/or garnet. Although nominally anhydrous, these minerals (except spinel) can accommodate small amounts of water, characteristically <5 to 600 ppm H$_2$O in natural samples (Bell, 1992), as protons inserted in mineral defects and vacancies. These apparently trivial water contents actually have a disproportionate influence on many physical and chemical properties of peridotite, and therefore on that of the entire upper-mantle (Hirschmann et al., 2005). In particular, the presence of bound H in the structure of upper-mantle minerals can lower their viscosity (Hirth & Kohlstedt, 2004; Mackwell et al., 1985; Mei & Kohlstedt, 2000a; Mei & Kohlstedt, 2000b), enhance their radiative transfer (Hofmeister, 2004), attenuate passing seismic waves (Karato & Jung, 1998), increase their electrical conductivity (Hier-Majumder et al., 2005; Karato, 1990; Simpson & Tommasi, 2005), and of course lower their melting temperatures and affect the speciation of fluid or melt (Asimow & Langmuir, 2003; Green, 1973; Hirose & Kawamoto, 1995). As key processes of the Earth's dynamics find their origin in the upper-mantle, from plate tectonics to magma generation, it is therefore crucial to determine in what form and how much water is present in its prominent phases. A combination of our own data and that available in the literature aims at addressing 2 key questions regarding water in the deep Earth:

1) How representative is the water content measured in mantle samples from the real content at depth?

Diffusion profiles of hydrogen across olivine grains from mantle xenoliths suggest that olivine can loose a significant portion of its water during transport of the xenolith to the surface (Demouchy et al, 2006; Peslier & Luhr, 2006). This phenomena is particularly heightened in xenoliths brought up by alkali basalts, but not too prominent in xenoliths brought up by kimberlites. This is likely the result of the higher temperatures and lower ascent rates of alkali basalts compared to kimberlites (Peslier et al, 2007). Pyroxenes, on the other hand, appear mostly immune to H loss during xenolith transport (Peslier et al., 2002).

Abyssal peridotites minerals have water contents 2 to 3 times lower than those from continental xenoliths, and lower than the water content of a typical N-MORB source calculated from water contents measured in MORB glasses (Peslier et al, 2007). The low water content of abyssal peridotites is likely the consequence of the slow adiabatic decompression of the oceanic mantle beneath ridges. Both melting (H is incompatible and goes into melt(s); Aubaud et al., 2007) and decreasing H solubility in mantle
minerals with lower pressures (review by Keppler & Bolfan-Casanova, 2006) combine to deprive abyssal peridotites minerals of their water.

Water contents measured in xenolithic olivines and in abyssal peridotites minerals should thus be used with caution to compare the water content of various upper-mantle settings and in assessing the water budget of the upper-mantle.

2) How much water is there in the Earth's mantle and does it vary between mantle settings?

Pyroxene water contents have similar ranges in cratonic mantle xenoliths, as represented by the southern African samples, than in those in off-cratonic settings, as represented by Western North American and Japanese samples of the lithospheric mantle beneath mobile belts. Our preliminary results suggest that beneath cratons, olivine and pyroxene water contents increase with increasing pressure and decreasing oxygen fugacity, up until about 4.5 GPa and 3.3 ΔFMQ beyond which water contents decrease, maybe in response to a change in water solubility in pyroxene (Mierdel et al., 2007) and/or a different fluid environment. Based on all data available, the water content of the continental lithospheric mantle ranges from 20 to 160 ppm H2O. This is similar to the range of water contents of 50-200 ppm for N-MORB source calculated from water analyzes of MORB glasses and melt inclusions (e.g. Dixon et al., 1988; Michael, 1988; Saal et al., 2002). Only mantle wedge environments may have low water contents in response to an oxidizing environment (Peslier et al, 2002), and the source mantle region of OIB have high water contents (several hundred ppm H2O; e.g. Moore & Schilling, 1973; Dixon et al., 2002; Asimow et al, 2004). Overall, water content variations in the upper-mantle appear larger vertically (change with depth) than laterally (various tectonic settings).

Moore J.G. and Schilling J-G. (1973) CMP 41, 105-008
STABILITY OF HORNBLENDE AND BIOTITE IN BASIC PLANETARY MAGMAS. K. Righter and G. M. Moore, 1NASA-JSC, Mailcode KT, 2101 NASA Parkway, Houston, TX 77058; kevin.righter-1@nasa.gov, 2Dept. of Geological Sciences, Arizona State University, Tempe, AZ 85287; gordon.moore@asu.edu.

Introduction: The addition of water to basic magma changes many of its properties and phase relations. With great interest in the planetary community about the role of water in the martian mantle and crust, hornblende and biotite stability are sometimes invoked to explain unusual features of martian magmatic meteorites [1,2]. The purpose of this paper is to present an overview of our knowledge of the stability of these phases in basic magmas, with an emphasis of the effect of a) bulk composition, b) fluid speciation and composition, and c) phase compositions.

Experimental studies and bulk composition effects:
Amphibole stability in basic magmas has been the focus of many experimental studies, with the most detailed constraints coming from relatively low pressure experiments (< 3 kb) with H2O-rich fluids [3, 4, 5]. These studies have shown that similar bulk compositions can have amphibole as the liquidus phase above 5 wt% water [3], whereas lower water content liquids will have orthopyroxene and plagioclase (Fig. 1). The stabilizing role of Na2O was identified by [5], and since most basic magmatic amphiboles are pargasitic, this seems reasonable. Amphibole stability may thus be controlled by the equilibrium:

5MgSiO3 + 2CaAl2Si2O8 + 0.5Na2O + H2O = 2NaCa2Mg5(AlSi3)Si4O22(OH)2 + 1.5 Al2O3 + 3SiO2

hornblende (edenite) plagioclase melt melt

This equilibrium has been used to explain the occurrence of hornblende-bearing and opx-plagioclase bearing andesites in the Mexican Volcanic Belt, where the rock bulk compositions are identical.

Biotite stability has also been the focus of experimental studies [6,7] but relatively fewer than available for amphibole. However, it is clear that > 5 wt% water is required before phlogopite is stable in a primitive potassium-rich basalt (minette; Fig. 2). Although this is well defined at low pressures in a water-saturated system, the required water contents are less clear in a C-H-O fluid [e.g., 7], since the fluid composition changes with pressure, CO2 fugacity (or H2O fugacity), and oxygen fugacity [7]. Similarly, these minette experiments have been used to explain the occurrence of phlogopite-bearing and olivine-augite bearing basic lavas in the Mexican Volcanic Belt, where the rock bulk compositions are identical.

Figure 1: Phase diagram for basaltic andesite at water saturated conditions and NNO+2 (from [3]). Phase boundary lines are phase-in lines plus liquid. Sub-horizontal dashed lines are isopleths of water concentration calculated from the residual glass compositions and the water solubility model of [8]. Small numbers next to data points in the plagioclase field give the anorthite content of the feldspars. Box represents the range of temperatures from pyroxene geothermometry for Colima lavas [9]. (Hbde hornblende, Opx orthopyroxene, Plag plagioclase, Aug augite). Note the shaded area represents the conditions of equilibrium for the Colima assemblage and the lined area that for the Mascota spessartite.

Figure 2: Phase diagram for minette at water saturated conditions, NNO+2 (from [6]). (Phlog phlogopite, oliv olivine, Magnt magnetite, Aug augite, apat apatite, liq liquid). Numbers next to data points represent calculated water contents of liquid according to the solubility model of [8].
However, the critical K2O content required to stabilize phlogopite over olivine is not well understood, and may be an issue for further investigation.

**Volatile compositional effects:**

Low pressure experiments in water-saturated conditions can define the stability field well, but natural systems have more complex fluid compositions that include C, H, and O. For example, a basalt at 3 kb water saturated will have similar amounts of water to a fluid saturated basalt in the C-H-O system at 15 kb (where both CO2 and H2O are the dominant volatiles) [10]. Although this is understood qualitatively for many kinds of applications, it is not well understood quantitatively for many specific natural examples. In addition, and perhaps of greater interest for martian magmas, the effect of chlorine could be large, and fluids in the H-C-O-Cl system are largely unexplored for basic magmas.

**Phase compositional effects:**

Hydrous phases such as amphibole and biotite can have hydroxy-, oxy-, fluor-, and chlor-components, which of course will have a large effect on the stability fields of these minerals. Additionally, cation composition is variable with (OH,O,F,Cl) content in both biotite [11] and amphiboles [12]. As a result, phases that are commonly thought to be “hydrous” can actually contain very little OH, such as the martian meteorite amphiboles and biotites which are nearly OH-free compared to other more hydrous meteoritic or terrestrial mantle amphiboles and biotites (Fig. 3). Another variable is the extent of ferrous vs. ferric iron in both biotite and amphibole. For phlogopitic biotites, it has been found at low pressures that the Fe3+/ΣFe is always greater in the liquid than in the phlogopite at natural fO2 [6]. However, for amphibole, there are some conditions where Fe3+/ΣFe is greater in the amphibole than in the liquid [14] This must be considered in any modeling or analysis of hydrous phases in planetary magmas [13].

**Implications for planetary magmas and future:**

Clearly, there are many variables (bulk, fluid and phase composition) that are yet to be quantified to fully understand the stability of hydrous phases. The stability of several other phases such as anthophyllite (Mg, Fe)2Si8O22(OH)2, or antigorite ((Mg, Fe)3Si2O5(OH)4) might be relevant, but bulk compositional constraints might predict much higher water contents and pressures than are reasonable.

**References:**

THE VOLATILE CONTENTS (CO$_2$, H$_2$O, F, S, Cl) OF THE LUNAR PICRITIC GLASSES. A. E. Saal$^1$, E. H. Hauri$^2$, M. LoCascio$^1$, J. Van Orman$^3$, M. J. Rutherford$^1$ and R. F. Cooper$^1$. $^1$Department of Geological Sciences, Brown University, 324 Brook St., Box 1846, Providence, RI, 02912. $^2$Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW Washington, DC 20015.$^3$Department of Geological Sciences Case Western Reserve University, Cleveland, OH 44106.

**Introduction:** Studies of volatile elements in magmatic systems have particular importance, because volatiles influence mantle melting, magma crystallization and volcanic eruption, and their abundances and spatial distribution provide important constraints on models for the thermal and chemical evolution of the Moon’s interior. The composition and origin of the lunar volatiles has been the subject of considerable interest and one of the most important unsolved questions regarding the formation of the Moon. The general consensus today is that the Moon formed and evolved through a single or series of catastrophic heating events[1] in which most of the highly volatile elements were either stripped or evaporated away. Hydrogen being the lightest element is thought to have been completely lost during this period[2]. Most of the geochemical inferences about the deepest section of the moon have been based on studies of the most primitive melts erupted on the Moon’s surface, the lunar volcanic glasses[3]. The assumption that lunar magmas are anhydrous is based on 1) the accepted model of lunar formation from a giant impact[1], which would cause the depletion in volatiles; and 2) the previously applied analytical techniques having high detection limits, which were not able to constrain the volatile contents (e.g. H$_2$O) of the picritic glasses[4]. However, there exists indirect evidence that volatile elements might have played a role in the generation of the lunar volcanic glasses. The association of a fire-fountain mechanism of eruption with condensation and enrichment of volatile elements on the surface of the lunar volcanic glasses suggests the existence of a deep mantle source comparatively enriched in volatiles. The implication that follows this view is that, contrary to prevailing ideas, the bulk Moon is not uniformly depleted in highly volatile elements.

In this abstract, using state-of-the-art analytical techniques, we report the magmatic volatile contents of individual lunar picritic glasses from the Apollo 15 and 17 landing sites.

**Samples and Analytical Techniques:** We investigated three compositionally distinct glasses from two lunar samples: very-low-Ti and low-Ti glasses in sample 15427,41, and high-Ti glasses in sample 74220,864 from Apollo 15 and 17 landing sites respectively. The glassy spherules range in size from 100-300 µm for 74220,864 and from 200-400 µm with one outlier at 700 µm for 15427,41. Not all of the glass beads are completely glassy; some of them, usually the larger beads, show crystallization of either olivine (15427,41) or olivine and ilmenite (74220,864). The major, and average trace-element contents of the lunar volcanic glasses are consistent with previously reported data[3]. The abundances of volatiles dissolved in the interior of the lunar picritic glasses were measured by SIMS using a Cameca IMS6F and the Nanosims at DTM, CIW, employing methods recently developed for the microanalysis of trace amounts of H$_2$O, CO$_2$, F, S, Cl in glasses and nominally anhydrous minerals[5]. For the IMS 6F a typical 10-min SIMS measurement for volatile abundances is made on a singly polished specimen using a Cs+ primary beam (~14 nA accelerated to 10 kv) with collection of negatively charged secondary ions. We used a 10 µm primary beam rastered at 25µm, which results in a 35 µm crater. We pre-sputter for 3-5 min prior to analysis, during this time, we monitored secondary ion images of $^{12}$C, $^{17}$OH, $^{19}$F, $^{32}$S and $^{35}$Cl projected on the channel plate. This procedure helped avoid inclusions and cracks, which appear as bright features on the projected image (especially $^{12}$C image), and dendritic crystals (dark shapes on $^{32}$S image). After each beam spot was carefully examined a field aperture was inserted to permit transmission of ions only from the central 10 µm of the 35 µm crater (i.e., always 25 µm away from the crater edge) thus avoiding transmission of ions from the edge of the sputter crater and the surface of the sample. Counting times were 10 s for $^{12}$C and 5 s for all other elements. Pressure in the ion probe sample chamber was ~6x10$^{-10}$ torr during the analyses. The samples was placed in the ion probe sample chamber for ~12 h before analysis; this approach allowed the best detection limits for H$_2$O. Detection limits (~ 6 ppm H$_2$O and CO$_2$, ~0.09 ppm F, ~0.027 ppm S, ~0.03 ppm Cl by weight) were determined by the repeated analysis of synthetic forsterite (0.4 ppm H$_2$O as determined by FTIR) located on each sample mount. Calibrations for H$_2$O were verified for glasses and nominally anhydrous mineral standards prior to each analytical session; abundances for the other volatile elements (CO$_2$, F, S, Cl) were calculated from the calibrations performed on glass standards. SIMS calibrations are regressions of ion probe signals compared to known concentrations. The ion probe...
signal is normally taken as the intensity ratio of two elements, one being the element of interest and the other a matrix element common to many phases. In this study, standard volatile concentrations are plotted against measured volatile/30Si ratios. This provides a robust analysis, which is little influenced by primary beam fluctuations or by ionization efficiency changes owing to matrix effects[5]. The techniques for the Nanosim will be reported by Hauri in this abstract volume.

**Results:** All volcanic picritic glasses have CO₂ below or within the 2σ standard deviation of the detection limit for our runs (6 ppm CO₂) and will not be considered further. The volatile contents after background correction have the following ranges: 4-46 ppm (±2 ppm 2σ) for H₂O; 4-40 ppm (±0.2 ppm 2σ) for F; 115-576 ppm (±3 ppm 2σ) for S; and 0.06-2 ppm (±0.03 ppm 2σ) for Cl. Two outstanding features of the data is the significant correlation among H₂O, Cl, F, and S contents shown in Table 1, and the clear relationship between the volatile and the major and trace element contents for the four compositional subgroups (A, B, C, D) of Delano’s very-low-Ti glasses[6]. This relationship between volatile, major and trace elements support the hypothesis that there were significant differences in the initial volatile content, and/or the mechanism of degassing and eruption among these glasses was different. Most importantly, the correlations among the volatiles suggest that the measured H₂O content in the volcanic glasses is indigenous. These results suggest that H₂O cannot be produced by solar wind implantation of H⁺ followed by diffusion into the spherule, but rather indicate that all the volatiles represent indigenous contents that were affected by degassing processes subsequently to the fire-fountain style of eruption. To test this hypothesis we determined concentration profiles for the volatiles within a single selected glass bead to evaluate whether or not a concentration gradient exist in a single bead. Our data for the very-low-Ti glass define concentration profiles with decreasing volatile contents from the core to the rim of the glass bead. This is especially significant for H₂O, which decreases from ~ 30 ppm in the center to ~14 ppm in the margin of the bead, supporting the hypothesis of the indigenous origin of H₂O subsequently affected by degassing processes during melt decompression and eruption. Moreover, the volatile contents observed on a single glass bead reproduce essentially the same trends in a volatile-volatile plot as those defined by the volatile contents of all the very-low-Ti glasses. This observation supports the hypothesis that degassing has been the main process affecting the volatile contents of the lunar volcanic glasses. Finally, there seems to be a clear distinction between the S and F contents of the different groups of picritic glasses, consistent with their distinctive major and trace element compositions[3]. The very-low-Ti glasses range to the lowest F and S values, the high-Ti group is intermediate and the low-Ti glasses have the highest contents of these elements. Thus, the data suggests significant differences in either the volatile content of their mantle source material, and/or their mechanism of degassing and eruption.

Lunar magmas are generally believed to have been produced by melting of cumulates at depth [3]; however the source of the heat required for the generation of the primitive melts is not clear. The presence of volatiles in the lunar glasses, suggesting a non-trivial volatile content in their melt-source region, may provide a possible solution to this problem, as the presence of water in lowering the melting temperature of silicate rocks is well known. The possible origin of the volatiles will be discussed.

**Conclusions:** We reported new volatile contents (CO₂, H₂O, F, S, Cl) for the lunar picritic glasses, which by virtue of SIMS analysis provide improved detection limits by almost an order of magnitude. To our knowledge this is the first definitive confirmation of the presence of “magmatic” H₂O in primitive lunar basalts. Our results suggest that, contrary to the prevailing ideas, the bulk Moon is not uniformly depleted in highly volatile elements, and the presence of water in particular must be included to constrain models for the thermal and chemical evolution of the Moon’s interior.

**Table 1: Correlation matrix for volatiles contents in green glasses from Apollo 15 landing site.**

<table>
<thead>
<tr>
<th></th>
<th>H₂O ppm</th>
<th>F ppm</th>
<th>S ppm</th>
<th>Cl ppm</th>
</tr>
</thead>
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<td>H₂O ppm</td>
<td>1.0000</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>F ppm</td>
<td>0.9333</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S ppm</td>
<td>0.8845</td>
<td>0.8683</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>Cl ppm</td>
<td>0.9560</td>
<td>0.9797</td>
<td>0.8897</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

**References:**
FORMATION AND ASCENT OF H₂O-RICH MAFIC MAGMAS IN SUBDUCTION ZONES. Paul Wallace¹ Emily Johnson¹, Vlad Manea²³, Nathalie Vigouroux¹, and Hugo Delgado Granados¹, ¹University of Oregon, Department of Geological Sciences, Eugene, OR 97403-1272, ²Centro de Geociencias, UNAM, Juriquilla, Mexico, ³Caltech, Pasadena, CA, ⁴Simon Fraser Univ., Burnaby, British Columbia, Canada, ⁵Inst. de Geofísica, UNAM, Ciudad Universitaria, México.

Introduction: Mafic cinder cones are common in subduction-related volcanic arcs. Such cones exhibit a wide range of eruptive styles and are often violently explosive, but the mechanisms driving explosive cinder cone eruptions are still poorly understood, as is the nature of their underlying plumbing systems. Melt inclusions in olivine phenocrysts from tephra deposits can be used to determine the H₂O contents of mafic magmas erupted from cinder cones. Such data provide a record of ascent, degassing and crystallization processes beneath these cones and show evidence for temporal changes in plumbing systems that mirror changes in eruptive style and magma composition.

The H₂O data also provide information about magma generation in the underlying mantle wedge and dehydration in the subducted slab that ultimately drives subduction zone magmatism.

H₂O and magma ascent through the crust: We have analyzed major elements and volatiles in olivine-hosted melt inclusions from 14 cinder cones in the central and western Trans-Mexican Volcanic Belt (TMVB), including the historic eruptions of Paricutín and Jorullo. Melt inclusions from each cone have highly variable H₂O (typically <1 wt% to maximum values of 4 to 5.5 wt%) and CO₂ (<50 to 5000 ppm), corresponding to crystallization pressures of <100 bars to ~5 kb. This indicates that olivine crystallized from variably degassed melts over a range of depths extending from the mid-crust to very shallow levels. The highest CO₂ contents (≤5000 ppm) are found in potassic minettes and basanites from the western TMVB, whereas values ≤1500 ppm are typical of calc-alkaline basalts and basaltic andesites. Modeling of major element variations and comparison to phase equilibria demonstrate that olivine crystallization was driven by H₂O loss from melts during ascent. Olivine-melt geothermometry suggests temperatures of 1100-1200°C for these melts at depth. A puzzling feature of the melt inclusion data is that H₂O often decreases more rapidly with degassing than is predicted by degassing models. A likely explanation involves open-system degassing in which relatively CO₂-rich and H₂O-poor vapor fluxes upwards through the conduit from degassing magma at greater depths.

Slab dehydration and magma generation: Our data from these primitive basaltic cones (many contain Fo₈₇.₉₀ olivine) reveal the surprising result that H₂O contents are high (3.0-5.2 wt%) from the volcanic front to ~150 km behind the front. The high H₂O across the arc, combined with high S and Cl, suggest that flux of volatiles from the subducted plate has affected a broad region of the underlying mantle.

To understand the depths over which subducted slab components dehydrate beneath the arc, we have modeled the thermal structure of the mantle wedge and slab using a 2D numerical model. We then use phase equilibria to evaluate dehydration of subducted sediment, altered oceanic crust, and hydrated lithospheric mantle in the slab. An important constraint is that volcanism has migrated towards the trench over the last 3 Ma, suggesting an increase in slab dip angle. Thus our studied cones farthest from the trench are older than those closer to the trench, and their volatile contents likely reflect mantle hydration resulting from a different slab geometry than the present-day configuration.

For the present-day slab model (13 Ma oceanic crust at trench), maximum mantle wedge temperatures beneath the volcanic front (1200-1300°C) agree with petrological calculations. The model results predict dehydration of subducted sediment and altered oceanic crust mostly beneath the forearc, consistent with the relatively young and therefore hot nature of the subducted slab. Subducted lithospheric mantle, if hydrated, would undergo dehydration beneath the arc ~50 km behind the volcanic front. In addition, chlorite formed by hydration of the overlying mantle wedge would no longer be stable ~100 km behind the volcanic front. Thus the width and high magmatic H₂O in the Quaternary arc are due to both dehydration of subducted serpentinitized mantle and the stability of chlorite in the overlying mantle wedge.

For the 3 Ma slab model, subducted sediment and oceanic crust dehydrate largely beneath the wide forearc during near-horizontal subduction. The main source of H₂O to flux the wedge beneath the volcanic front at 2-3 Ma comes from chlorite breakdown and possibly dehydration of serpentinitized lithospheric mantle in the slab. Thus our results for both the present-day and 3 Ma slab configurations suggest important roles for both chlorite breakdown in the lower part of the mantle wedge and deserpentinization of the downgoing slab in magma generation beneath Mexico.