

ARGUMENTS IN SUPPORT OF A DRY MARTIAN MANTLE. J.H. Jones, KR, NASA/JSC, Houston, TX 77058 (john.h.jones@nasa.gov).

Introduction: The first order of business should probably be a definition of “dry.” Anecdotally, I have heard that Sean Soloman once said, “I don’t care what John Jones says, the martian mantle must have at least ten ppm water.” I regard ten ppm as “dry,” so clearly there is a difference between petrologically dry and geophysically dry. I have no reason to doubt that Sean is correct from a geophysical point of view. Therefore, I will only defend the notion that the martian mantle is petrologically dry. Ten ppm water is apparently sufficient to radically change the rheology of a peridotite mantle, but it cannot play more than a minor role in the melting and phase equilibria during basalt petrogenesis. It would be difficult to rule out that any nominally-anhydrous experiment actually contained ten ppm water.

I will discuss several strong arguments in favor of a dry martian mantle: (i) Dessiccation by reaction with Fe-Ni metal; (ii) Dessiccation by removal of water, as an incompatible element; (iii) Analysis of water in martian (SNC) meteorites; and (iv) Inference of mantle water concentrations from the analysis of primitive martian melt compositions.

Metal-Water Reactions: Most of us have experienced the tendency of metal to rust. In the subsolidus state, there is no reason to suspect that a primitive planetary mantle containing metal and a hydrous component will betray our personal experience. However, rather than reacting to form Fe_2O_3 , the likely reaction products are FeO and H_2 . Under the assumption that hydrogen will be mobile and escape, this reaction should continue until either the hydrous component or the metal is virtually extinct. Because we know that Mars has a metallic core, there must have been more metal than water in the early martian mantle. Therefore, the principle of Le Chatelier would predict that, if the reaction went to completion, that water would be mostly reacted away.

There is also a second means by which metal may dehydrate a planetary mantle. At high pressure (~50 kbar), metal may react with hydrous phases to produce iron hydride FeH_x and FeO. In this case, the hydrogen that is produced need not escape the system for the reaction to continue — as long as the water to metal ratio is low.

At this juncture it is probably wise to ask, “What is the probability that the martian mantle was ever in equilibrium with metal?” And the answer is “extremely high.”

The experiments of Stolper (1977) defined the redox conditions necessary for a basalt of eucritic composition to be in low-pressure equilibrium with iron metal. The strong depletion of siderophile elements in eucrites ensures that their source regions were once in equilibrium with metal. But the most important property of eucrites, in this regard, is that they have 18-20 wt.% FeO. These basalts become metal-saturated at about IW-1. Neglecting small differences in other elements, we infer that lunar and martian basalts also came from source regions that were in equilibrium with metal because they, too, have 18-20 wt.% FeO.

Therefore, the tie between experiments on eucrites and the FeO contents of SNC basalts virtually ensures that the martian mantle also began life in equilibrium with Fe-Ni metal, a known dessiccant.

Water as an Incompatible Element: In addition to dehydration by reaction with metal, there was also an early, ~4.5 b.y. depletion of incompatible elements in the martian mantle. There are at least two distinct martian mantles: the nakhlite source and the shergottite source. Both are depleted, but the shergottite mantle is the most depleted. The nakhlite mantle has a depletion factor about 2X lower than that of the terrestrial MORB mantle. The shergottite mantle is about three times more depleted than the nakhlite mantle. In short, these are serious depletions.

Water is notoriously incompatible during basalt petrogenesis. Therefore, basalt removal of incompatible elements is also a great dessiccant.

Additionally, in the case of the shergottites, there was a second depletion event just before the various shergottites were formed.

Therefore, in the case of the shergottites, there were three dehydration events before the final igneous events that produced the ~500-150 m.y. shergottites.

Water in Martian Meteorites: The nakhlites are not good candidates for inferring the water contents of martian basalts. They have been hydrothermally altered, subsolidus, and therefore their water contents are not representative of their parent melts. Previously, I have noted that enriched shergottites such as Shergotty and Zagami have ~150-200 ppm water; Chassigny has ~350 ppm water (Jones, 2004; Leshin et al., 1996). These are low enough to be considered petrologically dry. Further, if Chassigny is 90% cumulus olivine that crystallized from a melt that was produced by ~5% partial melting, this translates to a source region water content of ~175 ppm (Jones, 2004). The nakhlites, which are petrologically closely related to the chassign-

nites, are believed to have been produced by about 0.5% partial melting (Shih et al., 2005, 2010). If such small degrees of partial melting also pertain to Chassigny, then the estimate of water in the source is lowered to ~18 ppm.

Water Content of Primitive Martian Melts:

There are two martian meteorites, in particular, that might be considered primitive: QUE 94201 (QUE) and Y980459 (Y98). QUE is isotopically primitive; it has an initial $\epsilon(^{143}\text{Nd})$ of ~+48. However, QUE is petrologically evolved. It contains no magnesian olivine and has a bulk Mg# of ~30.

Conversely, Y98 is slightly isotopically evolved, with an initial $\epsilon(^{143}\text{Nd})$ of ~+37, consistent with having assimilated an enriched component. The difference in $\epsilon(^{143}\text{Nd})$ between QUE and Y98 is nearly as large as the total range of that observed in terrestrial MORB's. But, petrologically, Y98 is very primitive, with mafic olivine on the liquidus (~1420°C at one bar) and a bulk Mg# of ~60.

In addition, Y98 has two other important petrologic aspects: (i) Using an olivine/liquid $K_D(\text{Fe}/\text{Mg})$ of ~0.35, the predicted composition of olivine in equilibrium with the composition of the bulk rock is ~0.86, which is in agreement with olivine cores in Y98 itself. This strongly suggests that Y98 is a true liquid composition. And (ii) Y98 cooled quickly. It has only olivine and pyroxene as silicate phenocrysts. The groundmass is glassy with dendritic quench crystals. There is no plagioclase or mesostasis. Consequently, for the purposes of this discussion, I will concentrate on Y98 as a primitive liquid from the shergottite mantle.

Melt inclusions in Y98 olivines. Like the Y98 groundmass, melt inclusions in Y98 are glassy, and also typically lack dendritic quench crystals. These aspects make them particularly amenable to ion probe analysis.

Usui et al. (2012) have reported ion probe analyses for several volatile elements in these inclusions: H_2O , CO_2 , F, Cl, and S; and several aspects of these analyses are of importance here. First, three of these inclusions have constant $\text{H}_2\text{O}/\text{CO}_2/\text{F}$ ratios, indicating that these olivine-hosted inclusions have remained closed systems, even with respect to hydrogen. Presumably, this is a consequence of the rapid cooling of Y98.

Second, the maximum CO_2 content of the Y98 melt inclusions (~1600 ppm) imply that these inclusions were trapped at pressures of ~ ≤ 3 kbar, based on CO_2 solubility in basaltic liquids.

Third, the water content of Y98 melt inclusions is ~ ≤ 250 ppm. Using electron microprobe analyses of these inclusions and comparing these analyses to those of the bulk rock, Usui et al. (2012) calculate that the

original water content of the Y98 parent liquid was 75-116 ppm. These abundances are consistent with those of bulk Shergotty and Zagami, considering that these latter shergottites are very evolved (Mg# ~40) compared to Y98.

Fourth, the δD of Y98 melt inclusions was found to be ~+300%, much like chondritic values. Therefore, the water in these inclusions can not have been much affected by interaction with the atmospheric/surficial reservoir, which has a δD of ~+5000%. But in actuality, even our value of +300% could merely be an upper limit to the true D/H ratio. For example, stepped thermal releases (200-1000°C) of a bulk sample of Chassigny gave δD of -50 to -100% (Leshin et al., 1996).

Water content of the Y98 mantle. Any calculation of the water concentration in the Y98 source region is, by definition, model dependent. However, Usui et al. (2012) reasonably assume that the bulk $^{12}\text{O}/^{16}\text{O}$ for Y98 is likely to be 0.01-0.001 — in other words, highly incompatible.

The degree of partial melting that produced Y98 is also unknown, but it is likely to have been quite high. However, assuming 20-40% partial melting, Usui et al. calculated a source water content of 15-50 ppm — petrologically dry and geophysically wet. And, although unlikely, if Y98 represents a 100% melt of the shergottite mantle, its bulk water content of 116 ppm places a rather low upper limit on permissible water in the Y98 source.

Contrasting Philosophies in Investigations of Martian Volatiles — Particularly Water. The approach of Usui et al. (2012) toward understanding martian volatile element inventories has been to find the most primitive martian basalt. We have had some success with this approach, but this was not a foregone conclusion. These are difficult analyses and we have, therefore, published much fewer data than we have collected. But a subset of our analyses appear to represent melt inclusions that have not become contaminated and that have retained the volatiles of our analytical suite in their primary ratios.

But it should be noted that there is a second, complementary approach that, in principle, requires nothing more than an electron microprobe — analyses of chlorapatites in evolved shergottites such as Shergotty, Zagami, or QUE (McCubbin et al., 2012). To the extent that apatite stoichiometry can be trusted, high-quality analyses of apatites would allow their water content to be determined by difference. But regardless, it is clear that depleted shergottites such as Y98 are much simpler to interpret petrologically than are the evolved shergottites. But ultimately, these two approaches should, in theory, come into agreement.