APPROACHES TO CHARACTERIZING THE DEUTERIUM-HYDROGEN RATIO IN EARTH'S PRIMITIVE MANTLE

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ABSTRACT

We measured the δD of glassy conclusions in olivine crystals in basalt samples from the Hawaii Scientific Drilling Project with the intention of sampling primordial water from Earth's mantle. The δD values we obtained (after correction for background water) of -119‰ to 40‰, however, suggest that we are actually sampling the upper mantle, which contains surface water recycled by tectonic processing.

1 Research Objective

The source(s) of Earth's water, and the mechanism(s) for its delivery, are the subject of much debate. Here we outline the problem, and motivate the work carried out in this project.

1.1 Potential sources of Earth's water

The two end-member models of how Earth acquired its water are wet accretion and dry accretion. In the wet accretion model, the gas and dust of the solar nebula contained water, and as they accreted into planetary embryos and, eventually, the inner planets of the solar system, that water remained. In the dry accretion model, it was too hot in the inner accretion disk for hydrous minerals to form (< 3-5 AU), so the inner planets accreted with little or no water, and the bulk of Earth's water was delivered after formation. There are problems with both models.

The main difficulty with the wet accretion model has already been mentioned – the high temperature in the inner accretion disk. Proponents of this model (e.g. Drake 2005) suggest that significant amounts of water (up to three Earth oceans) could have been adsorbed onto rough dust grains in the disk, and that this water may have been at least partially retained during planet formation. Another challenge for this model is explaining how Earth could have retained its water during the Moon-forming event (an impact with a Mars-sized body). Drake points out that the Earth did not lose all its helium, which is more volatile than water, in this event; nonetheless, it is unclear that enough would have remained to account for Earth's current water content (3-10 Earth oceans by some estimates, e.g. Mottl et al 2007).

The main issue with the dry accretion model is determining the source or sources of the water that was eventually delivered to Earth. Comets are a possibility, as they are certainly wet and hit Earth with some regularity. The problem with comets as a source is that the deuterium to hydrogen ratio (D/H) of the water in the comets that have been measured is much higher than that of Earth's oceans (see Figure 1). So, if the comets we have measured are representative, and if the D/H of Earth's oceans is close to that of Earth's bulk primordial water, then comets could not have delivered all or even most of Earth's water[1]. However, there are reasons to believe that the existing D/H measurements may not be representative. First, all but three of the existing measurements are of Oort Cloud comets; the D/H of Jupiter family comets might be much lower – indeed, the D/H ratios of Jupiter family comets 45HMP and 103/P Hartley 2 are quite close to that of Earth's oceans. Second, all but two of the existing measurements are remote measurements of the gas subliming off the comet, which may have a different D/H from that of the frozen core [Brown et al 2012]. That said, the recent in-situ measurement of the D/H of the Jupiter family comet 67P/Churyumov-Gerasimenko by the Rosetta mission was extremely high, supporting the argument that bulk of Earth's water must come from some other source.

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[1] A similar argument against comet delivery can be made by comparing the Ar/H_2O ratios in comets and on Earth (Earth's is much lower). However, because this paper is focused on D/H, we do not develop this argument here.
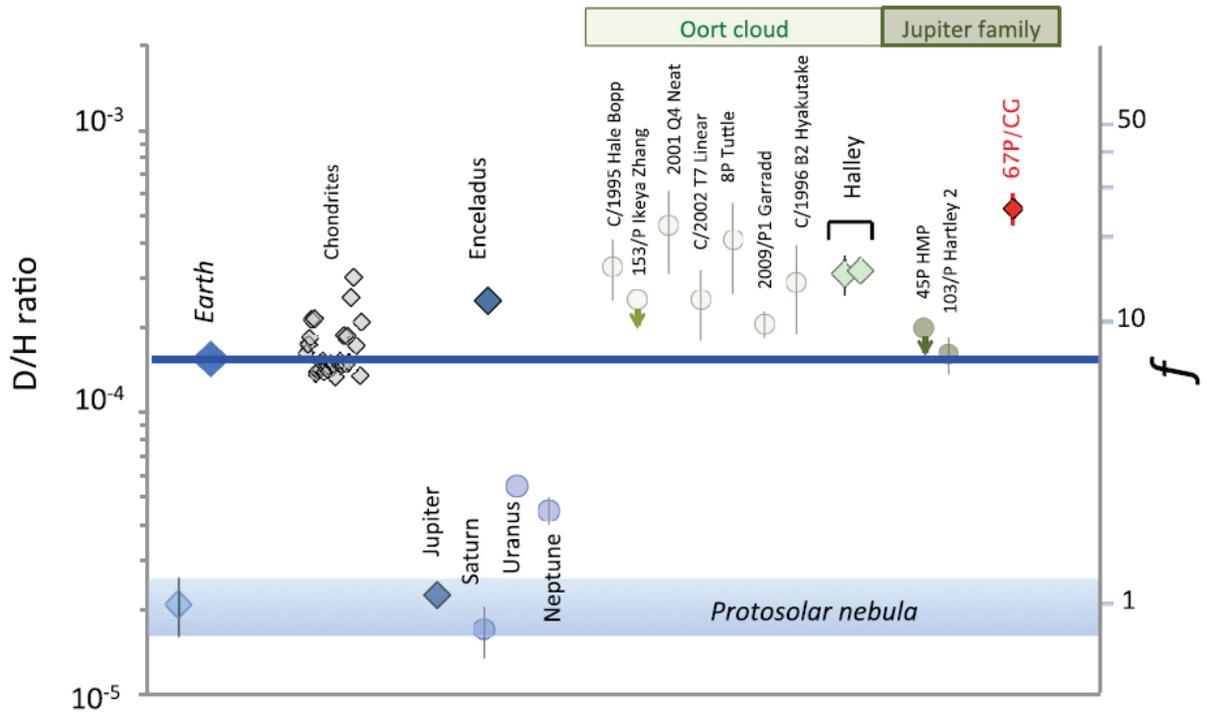
Figure 1. From Altwegg et al 2015. "D/H ratios in different objects of the solar system... Diamonds represent data obtained by means of in situ mass spectrometry measurements, and circles refer to data obtained with astronomical methods." [p 3. ibid] Note the red diamond labeled "67P/CG", which is the data point for comet 67P/Churyumov-Gerasimenko.

Asteroids are another potential source for Earth's water, and those sampled (via meteorites) have similar D/H ratios to that of Earth's oceans (see "Chondrites" in Figure 1). However, only the carbonaceous chondrites currently carry significant amounts of water, and they have other compositional issues. In particular, they have much lower $^{187}Os/^{188}Os$ levels than Earth's primitive upper mantle [Drake 2005][2]. However, it is possible that the currently anhydrous ordinary chondrites contained more hydrous minerals at the time of deposition (~4.5 billion years ago) and have since lost that water to thermal processing; however, if there had been large amounts of water, there would be evidence of that remaining in the minerals left behind. Another possibility is that the asteroid(s) that brought water to Earth had a significantly different composition to the ones we observe today.

1.2   Earth's water

As discussed above, one of the key pieces of evidence in this debate is the D/H of Earth's water, as compared to the D/H of the various potential sources. However, a more useful comparison would be to the D/H of Earth's primordial water, that is, as it was when delivered to Earth. There are two interlocking

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[2] Because ^{187}Re decays to ^{187}Os with a half-life of ~40 billion years, the Re-Os system is useful for dating events (especially fractionation events, such as core formation or magma generation) in the history of the solar system [Shirey & Walker 1998]. Materials from the same reservoir (barring further fractionation) will follow the same evolution line. The formation of Earth's core would be expected to give primitive bulk silicate Earth a low $^{187}Os/^{188}Os$ relative to "solar" composition. If the upper mantle is a mix of primitive bulk silicate Earth and the material delivered in the late veneer, and if the late veneer was primarily delivered by carbonaceous chondrites, we would expect the $^{187}Os/^{188}Os$ for the upper mantle to be between that of the primitive bulk silicate Earth and the carbonaceous chondrites. Instead, it is higher than both.

approaches to determining this number. First, we can sample all of Earth's reservoirs of water to determine Earth's true current D/H, then use models of the various fractionating processes (e.g. thermal atmospheric escape) to work back to the primordial value. Second, we can search for a cache of primordial water still existing on/in Earth today, and sample that.

The Earth has several reservoirs of water (numbers given here are from Mottl et al 2007, p264). The D/H of Earth's oceans (aka VSMOW, for Vienna Standard Mean Ocean Water) is 155.76 x 10^{-6} (δD 0)[3]. The rest of the hydrosphere (e.g. ice, lakes, soils) has a lower D/H due to various fractionating processes (e.g. evaporation), bringing the total δD for the hydrosphere down to -6‰. The rocks and organic matter of the crust bring the δD of the exosphere down even further, to -17‰ (still very close to VSMOW). For the mantle, however, we don't even know the total amount of water stored there (estimates range from 200 to 2500 x 10^{18} kg, between ~0.1 and ~100 times the water of the exosphere). We do have some δD data for mid ocean ridge basalts which seem to sample the upper mantle (Hallis' (2014) survey of the literature suggests a range of +60‰ to -140‰); however, the water in these samples would include water brought into the mantle by the subduction of the ocean crust, so this reservoir is not primitive. So, it is useful to measure the D/H of other mantle samples for this reason alone – that is, to provide a more accurate estimate of the current D/H of Earth's water as a whole.

However, such an estimate is only meaningful with regard to the question of the origin of Earth's water if we understand the fractionating processes and the relationships between the various reservoirs. For example, consider the water cycle. The temperature of a gas is proportional to the average kinetic energy of its molecules. For a given kinetic energy, the velocity of a molecule is inversely proportional to its mass. So, on average, the lighter molecules (e.g. water with two hydrogen atoms) will be faster than the heavier molecules (e.g. water with one hydrogen atom and one deuterium atom). This fact drives several different fractionating processes.

When water evaporates, the isotopically light water is moving faster so can escape the liquid water more easily than the isotopically heavier water. So, isotopically light water is preferentially taken up from the oceans, producing water vapor which is rich in hydrogen (relative to deuterium). This is then carried inland as water vapor or condensed on particulates in the form of clouds. Condensation into rain droplets is the same process in the opposite direction, preferentially removing the heavier water from the clouds and sending it back down to the ground, where it ends up in ice or lakes. So, as the clouds move further away from their ocean origin, they get progressively enriched in hydrogen, as does the rain they produce. This results in far-inland water (e.g. mountain snow) being isotopically much lighter than ocean water. These processes produce two complementary reservoirs: inland water, which is isotopically light; and ocean water, which is isotopically heavy (at least, relative to the inland reservoir).

Some fractionating processes do not result in complementary reservoirs on Earth. Thermal escape is one example. The temperature of a gas is proportional to the average kinetic energy of its molecules. For a given kinetic energy, the velocity of a molecule is inversely proportional to its mass. So, on average, the lighter molecules (e.g. H2) will be faster than the heavier molecules (e.g. HD, D2), and thus more likely to reach escape velocity. The consequence for a planet's atmosphere is that it will tend to lose lighter molecules to space (aka Jeans escape). For this reason, the hydrogen in Earth's atmosphere has become

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[3] The deuterium/hydrogen ratio of water is often expressed as permille (‰) relative to the D/H of VSMOW. This is indicated with δD. So, δD_{sample} = [(D/H)$_{sample}$-(D/H)$_{VSMOW}$]/(D/H)$_{VSMOW}$ x 1000.

isotopically heavier over geologic time. Because the lighter gasses are lost, determining Earth's primordial D/H is not simply a matter of averaging existing reservoirs. Jeans escape is not the only culprit here. The Moon-forming impact discussed above can be thought of as driving a very high temperature thermal escape process, again resulting in an isotopically heavier atmosphere without a corresponding complementary reservoir. However, because mass-dependent fractionation is less effective at higher temperatures, the Moon-forming impact may not have had as great an effect on Earth's D/H as other processes.

To complicate matters, some of these reservoirs are further fractionated. For example, plate tectonics pulls the crust, including meteoritic (light) water, down into the upper mantle. This crustal material mixes with the rest of the upper mantle, and is eventually reintroduced to the crust as mid-ocean ridge basalts (MORBs). So, although we have a good estimate of D/H in MORBs based on a large number of measurements, it is difficult to back out the D/H values of the contributing reservoirs, and even harder to work back to the D/H of Earth's primordial water.

Intriguingly, there are reasons to think that the *lower* mantle might contain caches of water that has not participated in the geologic cycle, and is therefore primordial, or at least minimally fractionated or degassed. One argument is based on helium isotopes. Once outgassed, helium is quickly lost to space. So, because the only source of ^{3}He is primordial, whereas ^{4}He is formed through radiogenic processes, a high ^{3}He/^{4}He ratio is indicative of a primitive reservoir. Oceanic island basalts (OIBs) have ^{3}He/^{4}He ratios of ~40 x atmospheric, as compared to ~8 x atmospheric for MORBs. This suggests that the source of the mantle plumes that form OIBs, particularly those found in Iceland, Hawaii, Greenland and Baffin Island, is very primitive. A similar argument can be made using Ne isotopes [Mottl et al 2007].

For these reasons, in this study, we attempted to characterize the D/H of deep mantle sources by measuring the D/H of glassy inclusions in olivine crystals in samples from Hawai`i Scientific Drilling Project (HSDP2) [Garcia et al 2007].

2 Samples and Measurements

2.1 Ocean Island Basalts

Assuming that OIBs do in fact come from the lower mantle, we still have the challenges of a) identifying samples that retain water from the lower mantle, b) determining whether or not that water has been altered (e.g. contaminated or outgassed) in any way in the journey from the lower mantle to the laboratory and c) accurately measuring the D/H of the water.

As olivine crystals form, they sometimes trap small amounts of the surrounding melt. These glassy inclusions can contain measurable amounts of water. If the cooling happens quickly enough that the inclusions do not have enough time to degas, and if the olivine crystal retains its integrity, then the water in the inclusion should have the same D/H as the original melt. If the olivine formed in the deep mantle, then measuring the D/H of the water in the inclusion should give us one data point for the D/H of the deep mantle. This is a lot of "ifs".

2.2 My samples

The Hawai`i Scientific Drilling Project (HSDP2) has drilled ~3.1km into the island of Hawai`i, through the flank of the Mauna Loa volcano and into Mauna Kea [Garcia et al 2007]. This is the single deepest and most complete core from any oceanic island volcano. I focused on the submarine, pillow-lava-dominated

section, in particular the section that was quenched at depths of greater than ~2km below the current land surface, in the hopes that the quick quenching under pressure would prevent volatiles from being outgassed. I looked for volatiles trapped in glasses in unaltered olivine phenocrysts, which I analyzed with a Cameca ims 1280 ion microprobe to get D/H measurements.

I have a suite of HSDP2 samples, including six that are from high-olivine pillow-lava units for which ^{3}He/^{4}He has been measured by Kurz et al. (2004, see Table 1). Two of these units have samples with ^{3}He/^{4}He > 19 as measured by Kurz et al., whereas for the other four units, ^{3}He/^{4}He ranged between 12 and 15.

Table 1. Samples for which Kurz et al. (2004) have a relevant ^{3}He/^{4}He measurement (i.e. from the same sample or unit).

DEPTH (m)	UNIT	BOX	SAMPLE LABEL	^{3}He/^{4}He	^{3}He/^{4}He source
2045	283	694	SR747	23.2	another sample from same unit
2045	283	694	SR747	23.2	another sample from same unit
2130	284	726	SR0763	19.8	another sample from same unit
2130	284	726	SR0763	19.8	another sample from same unit
2730	316	940	SR891	14	this sample
2730	316	940	SR891	14	this sample
2825	326b (pillow)	978	R0913	14.9	from unit 327 (intrusive)
2825	326b (pillow)	978	R0913	14.9	from unit 327 (intrusive)
2825	326b (pillow)	978	R0913	14.9	from unit 327 (intrusive)
2825	326b (pillow)	978	R0913	14.9	from unit 327 (intrusive)
2930	335a	1016	SR0933	14.2	another sample from same unit
2930	335a	1016	SR0933	14.2	another sample from same unit

The procedure for processing our samples was as follows:

1. Samples were cut into 1.5mm slices. Slice 1 is labeled "A", slice 2 "B" etc.
2. Samples were polished on both sides, starting with dampened sandpaper (400 then 600 grit), then using diamond paste (15, 9, 6, and 3 μm). Samples were polished both by Minimet and by hand. Samples were frequently rinsed in water.
3. Samples were photographed using the microscope camera, and the images mosaicked together.
4. Samples were carbon-coated.
5. The SEM was used to identify inclusions, and to take photos (both on the scale of the inclusion and on the scale of the crystal). The approximate locations of the inclusions were noted on the mosaics. Inclusions were named by a) a number indicating which crystal-scale image they appear in, and b) a letter for each of the inclusions in a single image.
6. The samples were heated at 50°C degrees and at low pressure (~0.03 atmospheres) in a vacuum dessicator, for varying amounts of time (at least 48 hours per sample).
7. The samples were stored at low pressure (either in the SEM or in the dessicator).
8. The samples were probed using the electron microprobe.
9. Finally, the samples were probed using the ion microprobe. The isotopes measured were D, H and Si (to get the H abundance relative to the matrix element), using a Cs+ primary ion beam

and a mass resolving power of ~2000. Data was collected for 40 cycles. The beam was turned off for cycles 1-9 and 36-40, to measure the background count rates. Data for cycles 10 and 35 were discarded as potentially measuring the transient state as the beam is turned on (at 10) and off (at 35). Cycles 11-34 constituted the measurement. The background reduction strategy was:

    a. Raster 25 microns square.
    b. Deflection to focus everything generated across raster in the center.
    c. Mask with field aperture (5-7 microns)
    d. E-gate set at 70% of width and height, blocking a 50% frame.
10. Took data points in the center of the targeted inclusion and in the surrounding olivine.
11. Imaged drilled points in SEM.

Note that this approach is different from that in [Shaw et al 2008] and similar studies, where whole samples were crushed and searched for olivine crystals, which were then mounted and analyzed. Our approach is able to identify inclusions in ¼ - ½ of crystals, as opposed to 1/100 (informally reported in Shaw et al 2008); however, this difference may be due more to the sample sources than to the analysis technique.
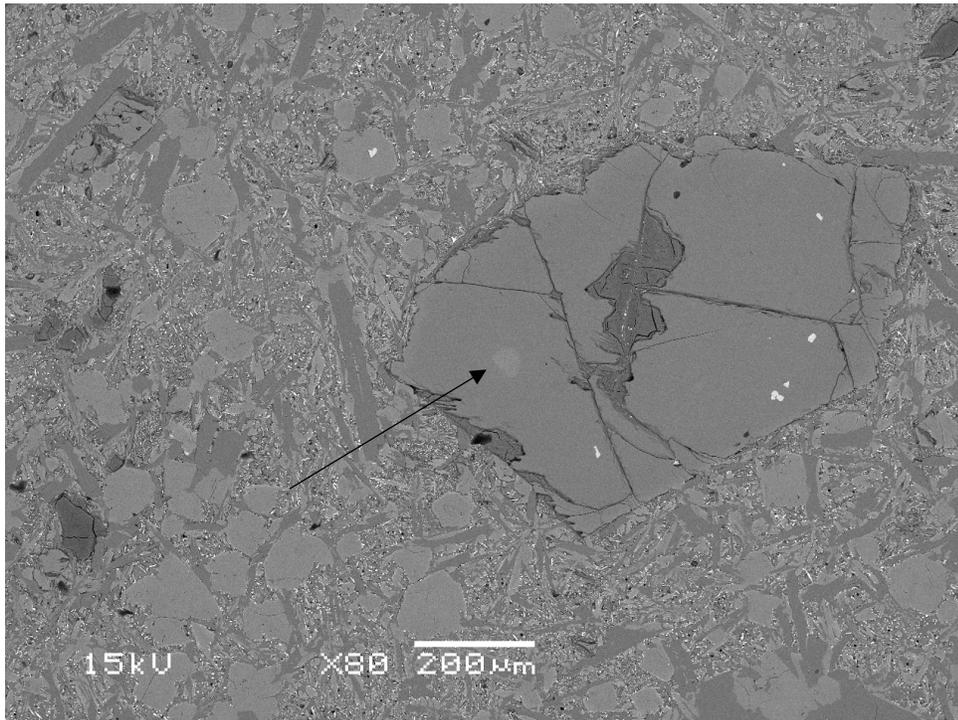

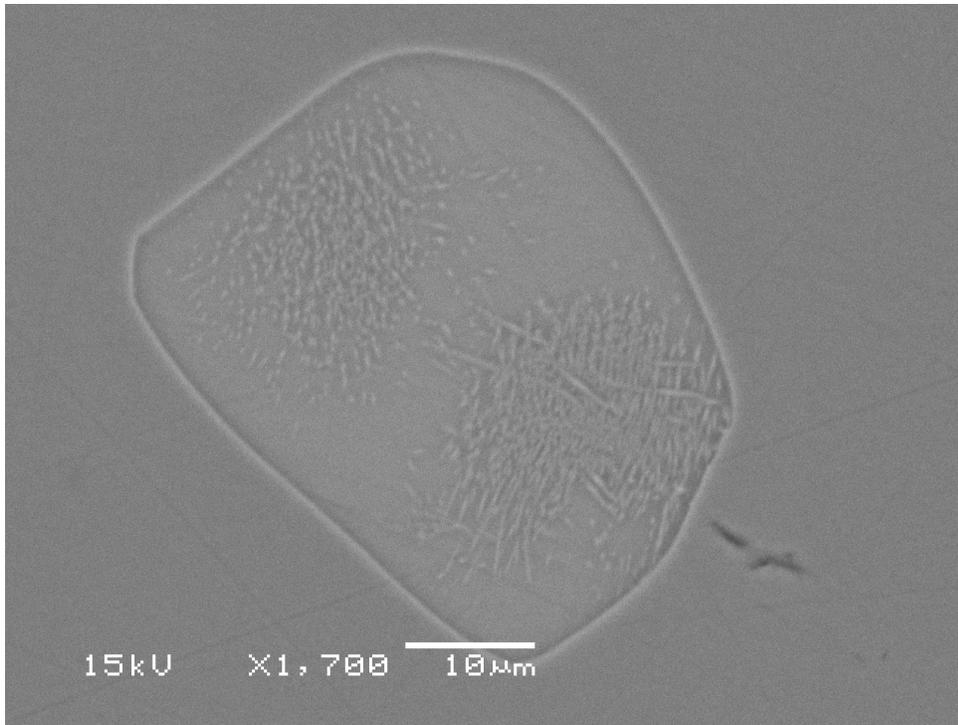*Figure 2. An olivine crystal, with a glassy inclusion indicated by the arrow.*

Figure 3. The inclusion indicated in Figure 2. Note that there are no apparent cracks, but there is some crystallization. This would be considered a good inclusion to measure.
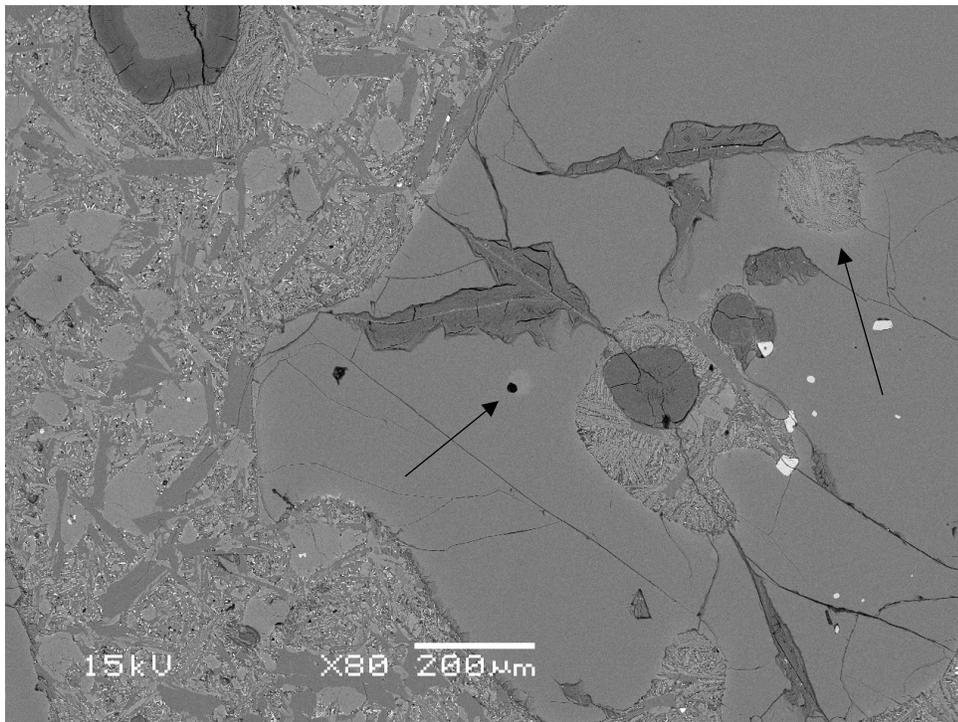

Figure 4. Another olivine crystal with multiple inclusions, indicated by arrows.
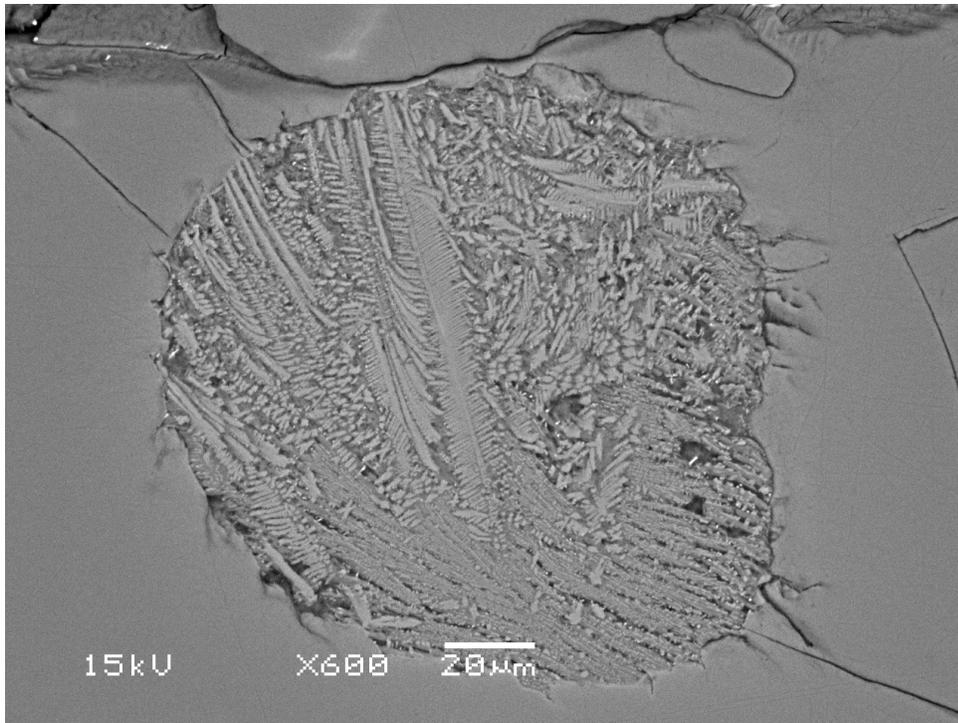
Figure 5. The larger of the two inclusions indicated by arrows in Figure 4. Note the high levels of crystallization and multiple impinging cracks. This would not be considered a target for measurement.
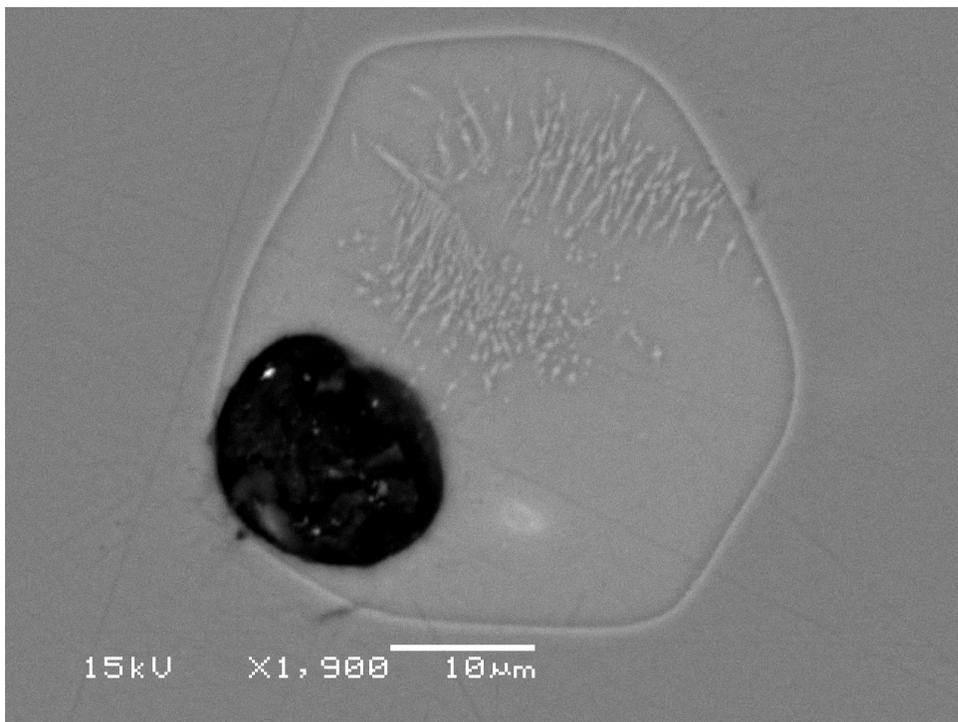

Figure 6. The smaller inclusion indicated by an arrow in Figure 4. Although there is little crystallization and no apparent impinging cracks, the black circle is a bubble, indicating outgassing. This would not be considered a good target for measurement, although we did attempt to probe several such inclusions.

2.3 Problems with the sample handling methodology

Our results, below, suggest that this process does not effectively allow us to identify unaltered inclusions, nor to prevent contamination of the samples (potential problems with the samples themselves are considered in the Discussion section below).

First, the act of slicing the sample reduces the contextual information to two dimensions. That is, we can see cracks (which could allow the introduction of outside water) in the olivine crystal that impact the inclusion if they either go through the inclusion or touch the inclusion boundary in the cut plane. However, a crack that does not appear to intersect the inclusion in the cut plane may still intersect it at depth (i.e. inside the slice) or height (i.e. in the cut away material). So, an inclusion that appears intact may in fact be compromised.

Second, polishing with water both increases the risk of contamination, and could increase the background level, if our heating stage (#6, above) was insufficient.

3 Results

In this section, we present the results from this study, as well as those from a study that used an improved version of our procedure [Hallis 2014].

3.1 My results

We had issues with high water content, whether due to sample preparation or to the alteration history of the samples themselves, throughout this project. We refined the probe protocol over many sessions. Here we present the data from the final two samples (11253B and 933D2), for which our protocol was reasonably stable.

Table 2. Data for sample 11253B. Note that measurement sites are identified by the olivine crystal in which the inclusion of interest is embedded. So, inclusions 8a and 8b are in the same olivine crystal.

11253B	D/H		δD		H/^{30}Si		ppm water	
In and around Inclusion 8a								
Inclusion 8a Glass (failed measurement)								
Olivine 1	0.0001148	± 0.0000061	-263	± 39	0.17900	± 0.00011	1308	± 327
Olivine 2	0.0001243	± 0.0000063	-202	± 40	0.17426	± 0.00011	1274	± 318
In and around Inclusion 8b								
Inclusion 8b Glass	0.0001338	± 0.0000054	-141	± 35	0.61879	± 0.00029	4523	± 1131
Olivine	0.0001187	± 0.0000062	-238	± 40	0.17205	± 0.00011	1258	± 314
In and around Inclusion 4b								
Inclusion 4b Glass	0.0001389	± 0.0000054	-108	± 35	0.56113	± 0.00025	4102	± 1025
Olivine	0.0001195	± 0.0000061	-233	± 39	0.16118	± 0.00010	1178	± 295
In and around Inclusion 13								
Inclusion 13 Glass	0.0001483	± 0.0000054	-48	± 35	0.58206	± 0.00026	4255	± 1064
Olivine	0.0001184	± 0.0000060	-240	± 39	0.18285	± 0.00011	1337	± 334
In and around Inclusion 25								
Inclusion 25 Glass	0.0001330	± 0.0000054	-146	± 35	0.61063	± 0.00028	4464	± 1116
Olivine	0.0001212	± 0.0000062	-222	± 40	0.16292	± 0.00011	1191	± 298
Basalt near Inclusion 25	0.0001293	± 0.0000063	-170	± 41	0.17834	± 0.00012	1304	± 326
Average Glass	0.0001385	± 0.0000141	-111	± 90	0.59315	± 0.05306	4336	± 388
Average Olivine	0.0001195	± 0.0000063	-233	± 41	0.17204	± 0.01724	1258	± 126
Average Basalt	0.0001293	± 0.0000063	-170	± 41	0.17834	± 0.00012	1304	± 326

Table 3. Data for sample 933D2.

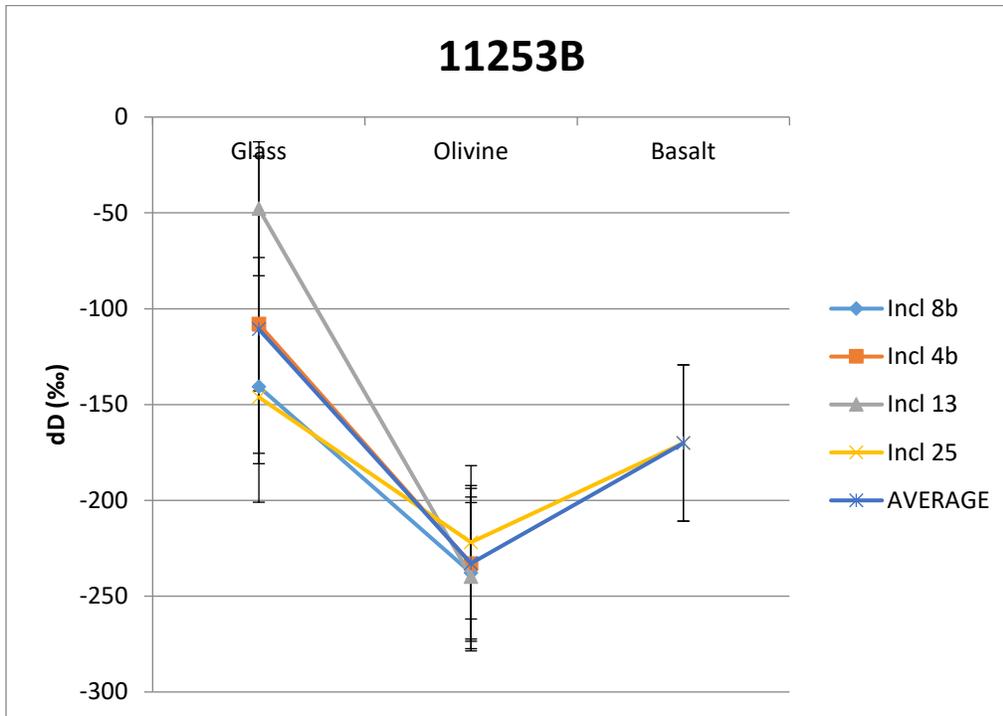| 933D2							
	D/H		δD		H/^{30}Si		ppm water	
In and around Inclusion 7							
Inclusion 7 Glass	0.0001501	± 0.0000054	-37	± 34	0.64711	± 0.00026	4730	± 1183
Olivine	0.0001408	± 0.0000059	-96	± 38	0.24092	± 0.00013	1761	± 440
In and around Inclusion 9							
Inclusion 9 Glass	0.0001460	± 0.0000054	-63	± 35	0.57636	± 0.00025	4213	± 1053
Olivine	0.0001418	± 0.0000059	-90	± 38	0.24818	± 0.00013	1814	± 454
Basalt near Inclusion 9	0.0001476	± 0.0000054	-52	± 35	0.64382	± 0.00029	4706	± 1177
In and around Inclusion 13							
Inclusion 13 Glass	0.0001450	± 0.0000053	-69	± 34	0.71268	± 0.00029	5210	± 1302
Olivine	0.0001341	± 0.0000059	-139	± 38	0.22694	± 0.00012	1659	± 415
In and around Inclusion 15							
Inclusions 15 Glass	0.0001469	± 0.0000054	-57	± 34	0.68758	± 0.00029	5026	± 1257
Olivine	0.0001430	± 0.0000060	-82	± 38	0.22908	± 0.00013	1675	± 419
In and around Inclusion 18							
Inclusion 18 Glass	0.0001510	± 0.0000054	-31	± 35	0.63991	± 0.00027	4678	± 1169
Olivine	0.0001321	± 0.0000060	-152	± 39	0.21177	± 0.00012	1548	± 387
Basalt near Inclusion 18	0.0001479	± 0.0000054	-51	± 34	0.89584	± 0.00040	6548	± 1637
Average Glass	**0.0001478**	**± 0.0000052**	**-51**	**± 34**	**0.65273**	**± 0.10410**	**4771**	**± 761**
Average Olivine	**0.0001383**	**± 0.0000099**	**-112**	**± 63**	**0.23138**	**± 0.02797**	**1691**	**± 204**
Average Basalt	**0.0001477**	**± 0.0000004**	**-52**	**± 2**	**0.76983**	**± 0.35640**	**5627**	**± 2605**

Figure 7. δD measurements for glassy inclusions ("Glass"), the surrounding olivine crystal ("Olivine") and the basaltic material surrounding the olivine ("Basalt"), for sample 11253B.
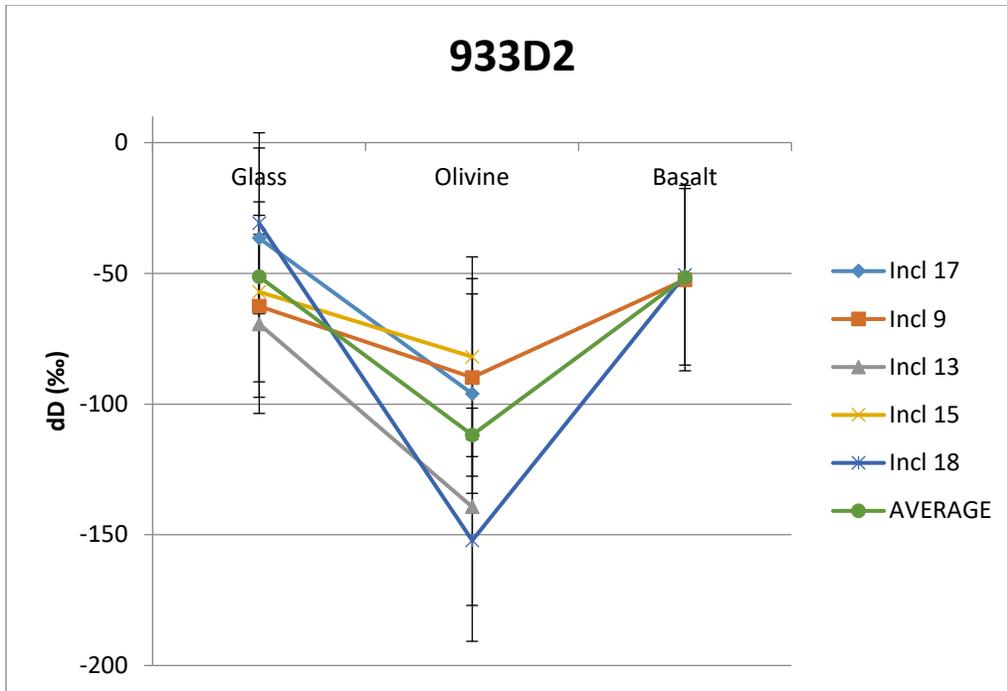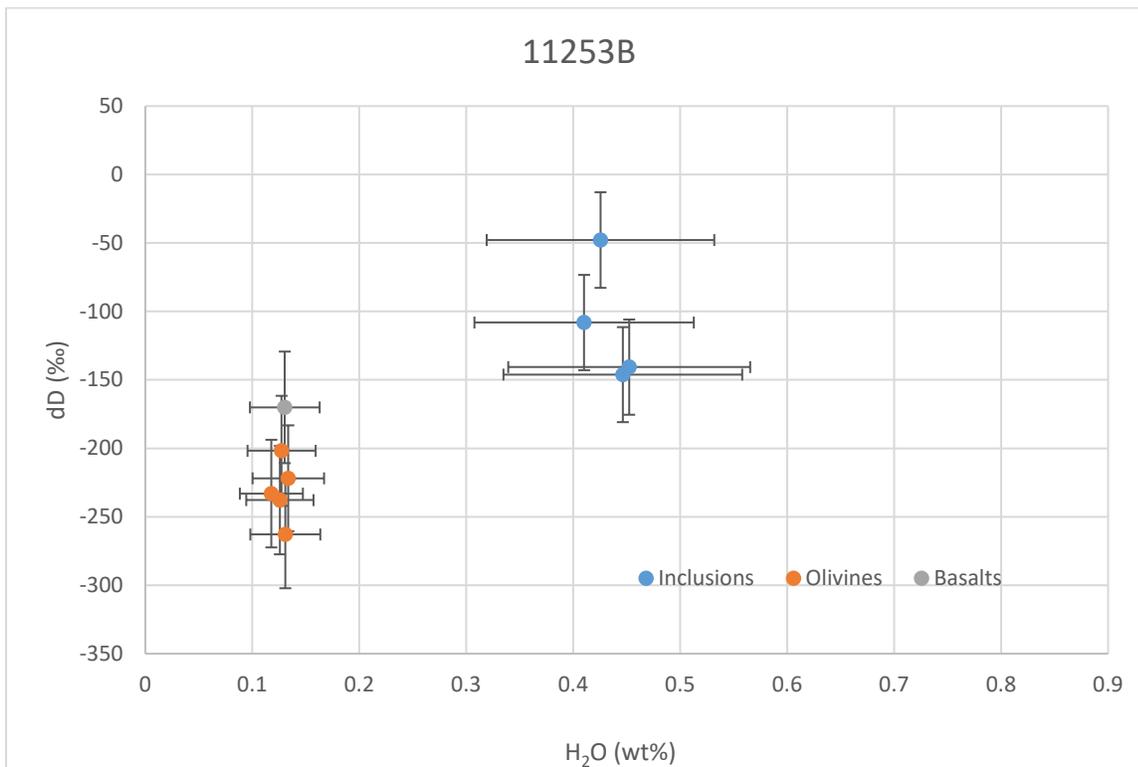
Figure 8. δD measurements for glassy inclusions ("Glass"), the surrounding olivine crystal ("Olivine") and the basaltic material surrounding the olivine ("Basalt"), for sample 933D2.

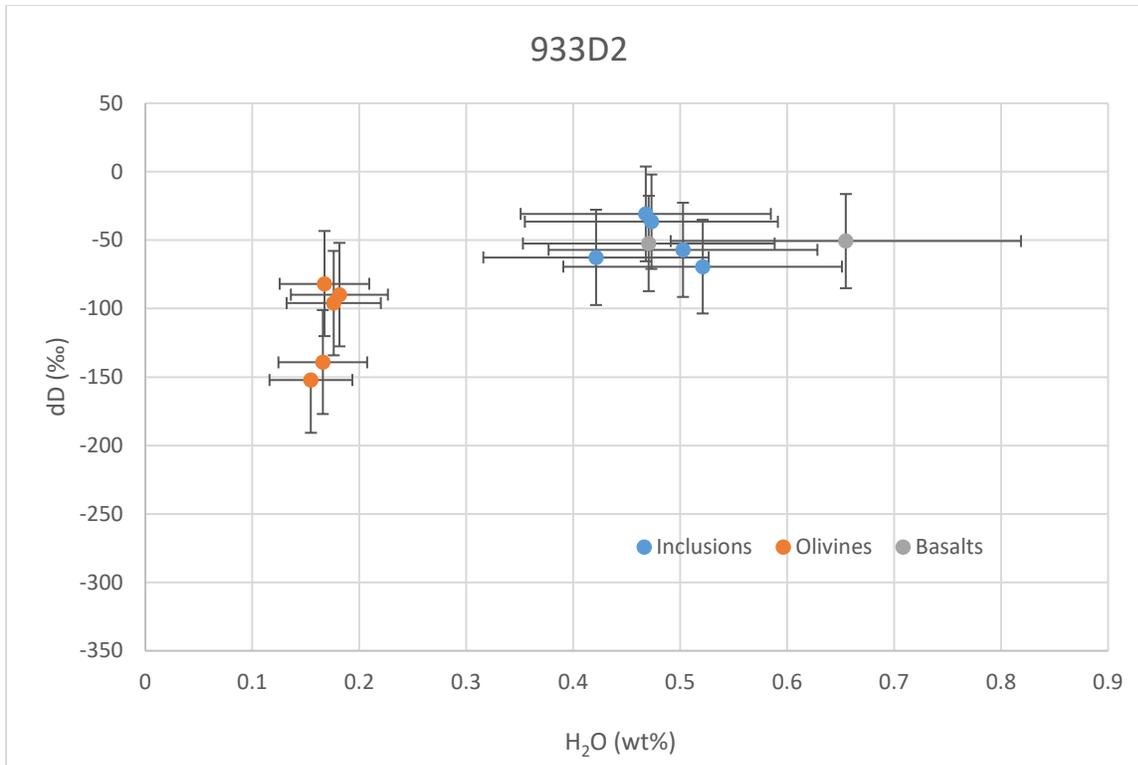*Figure 9. Water content (parts per million) vs. δD for sample 11253B.*

Figure 10. Water content (parts per million) vs. δD for sample 933D2.

3.2 Results from Hallis 2014

Hallis (2014) took essentially the same approach that we did, but with a different set of samples and a more refined methodology. Her targets were also glassy inclusions in olivine, but they were in two picrite samples from Baffin Island (the red data points in Figure 11) and three basalt samples from Iceland (the grey data points in Figure 11). Note that the Icelandic samples fall within the typical δD range for the upper mantle, whereas the Baffin Island samples have a significantly lower δD.
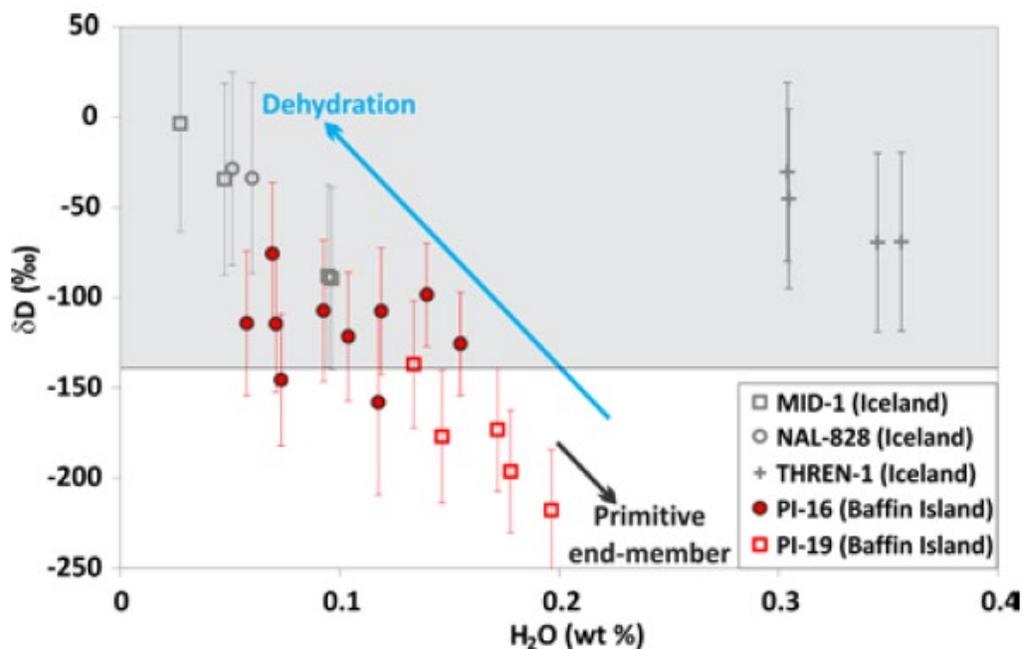
Figure 11. From Hallis 2014. "δD (‰) vs. H2O (wt %) plot, showing the inversely proportional relationship between the D/H ratio and water contents of measured Baffin Island and Icelandic olivine-bound melt inclusions. The high water content of inclusions within Icelandic basalt THREN-1 may indicate meteoric water infiltration. Alternatively, these inclusions could be the product of a comparatively water rich parental melt. 2σ uncertainties are shown for δD. The grey region represents the extent of δD range for the terrestrial upper mantle." [p.1, ibid]

4 Discussion

Here we point out some features in our results and those of Hallis, and put them in the context of the larger questions discussed in Section 1.

4.1 D/H

The measured δD for the inclusions in our samples ranged from -31‰ to -146‰, most within the 'typical' range for the upper mantle of +60‰ to -140‰ (based on MORB samples), and comparable to Hallis' results for the Iceland samples. We do not see the inverse correlation between water content and δD that her data shows, however. Hallis argues that this correlation is due to the partial degassing of inclusions during residence in the melt, a fractionation process in which the lighter isotope is preferentially lost.

One striking aspect of our results is the apparently high water level in our olivines (~1500ppm). Olivine is nominally anhydrous, and naturally-occurring olivine formed at low pressure normally contains less than 100ppm (~10ppm is a typical value). However, Smyth et al (2006) were able to produce olivine with much higher water content (up to 8900ppm) under the high pressure and temperature conditions of the upper mantle. Unfortunately, it is unclear whether the relatively high water levels we measured are due to such formation conditions (which would be interesting), due to post-formation contamination in the mantle, on the ocean floor, in the lab, or at some other point in its history, or due to problems in measurement.

However, with some reasonable assumptions, it might be possible to refine our results somewhat. First, Gary Huss has learned through experience that the background hydrogen in the ion probe is isotopically light, with δD of -400‰ to -500‰. Also, we learned the hard way that samples as thick as ours cannot be fully dried out (at least, not in the time frame of this study) by gentle heating at low pressure, as in the vacuum oven or sample airlock. So, it would be reasonable to assume that the measurements of olivine are dominated by background hydrogen, given the high water-content measurements and the very negative δD. The same may be true for the basalt, since the water contents are similar. The data for the inclusions is probably less affected, because of their higher intrinsic water content.

So, if we assume that all the water measured in the olivine is really contamination, we can correct the δD measurement for the inclusions using a simple mass balance subtraction. The results of this correction are given in Figure 12. Because there is *some* water in olivine, this is likely to be an overcorrection, with the true values lying somewhere between the original measurement and the corrected one.
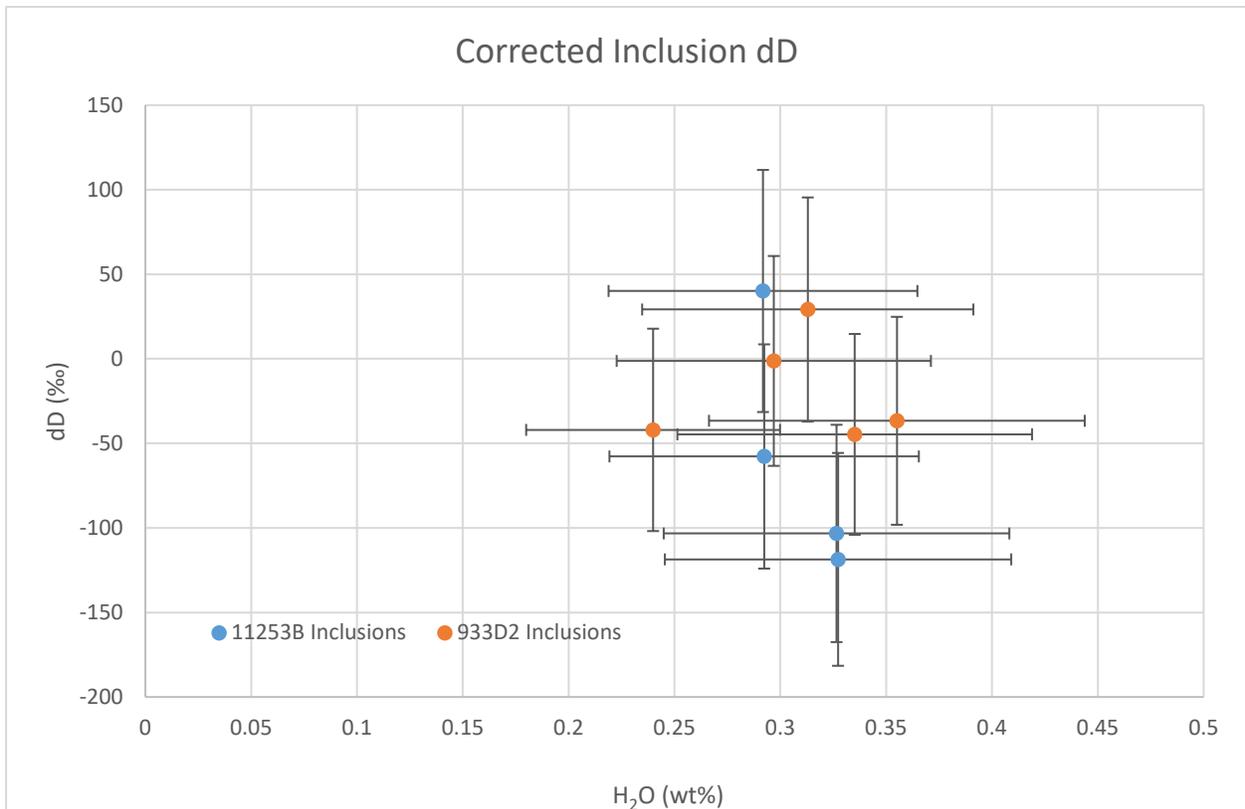

Figure 12. δD for inclusions in both samples, corrected as described in section 4.1.

The range of our corrected measurements is +40‰ to -119‰, which falls nicely in the range for the upper mantle (+60‰ to -140‰.) This would suggest that our samples, despite their promising source, do not contain primordial water, and are instead typical of the upper mantle, which includes surface water introduced by tectonic processing.

4.2 ^{3}He/^{4}He

In Section 1, we pointed out that OIBs have much higher ^{3}He/^{4}He ratios than MORBs. However, not all OIB sources have this characteristic - in fact, such OIBs are rare. The highest ^{3}He/^{4}He measured to date are up to ~50 times the atmospheric level (R_a), in samples from 60Myr old lavas in western Greenland and Baffin Island [Jackson et al 2010]. Samples from the H2DP2 have much more modest ^{3}He/^{4}He ratios, ranging from ~10-14.5 R_a, with brief excursions as high as 24.7 R_a [Kurz et al, 2004]. ^{3}He/^{4}He ratios are known for only one of the *samples* made available to us (SR891 at 14 R_a). Unfortunately, the glass inclusions in this sample were of poor quality, with high levels of crystallization, bubbles, and cracks. Table 1 gives the ^{3}He/^{4}He values for the *units* from which the other samples were taken; the value for unit 335a (sample SR933) is 14.2, and for 11253.2 is unknown.

We completed our analysis for two samples (SR933 and 11253.2)If we assume the ^{3}He/^{4}He ratios for these two samples were in the 10-15 R_a range, which is close to that of the MORBs, it is perhaps not surprising that our D/H ratios are also in the typical range for MORBs. That is, although *some* OIBs appear to sample the lower mantle and its (hopefully primordial) water, the ones we looked at probably do not.

However, Hallis' samples *were* from OIBs with high ^{3}He/^{4}He ratios, supporting her argument that they could contain primordial water.

4.3 Implications for the origins of Earth's water

Unfortunately, for the reasons described above, this project is unlikely to make a significant contribution to the debate over the origin of Earth's water. However, closely related work (e.g. Hallis et al 2012a, 2012b and 2014; Robinson 2014a, 2014b and 2014c) has produced results that any model of the early history of Earth must take into account.

Hallis' work with the OIBs of Baffin Island and western Greenland suggests that Earth's primordial water had a δD considerably lower than that of Earth's oceans. If her observed inverse relationship between hydration and δD holds true, the primordial δD could be considerably lower than her lowest measurement of -220‰.

Hallis also conducted a similar analysis on samples from the Martian meteorite Nakhla. Because Mars does not have tectonic processing, the water that was entrained in the magma that crystallized to form the crust should be primordial. Although Hallis found a wide range of δD values, the known differentiation and weathering processes that could have introduced atmospheric water would all have increased δD, so her lowest value (-111‰) should be an upper limit on the primordial Martian value.

Most analyses of lunar samples show a wide range of δD, with the lower end in the 'typical' range for Earth [Robinson et al 2014b]. However, Robinson did measure one sample with much lower values (-338‰ to -683‰). This sample did not appear to have been altered by metamorphism or solar wind implantation (the only likely processes that could have lowered the δD), suggesting that there is a primordial reservoir of water on the Moon with a relatively low δD. Such a reservoir could indicate the isotopic composition of the water of Earth at the time of the Moon-forming impact.

Taken together, these results suggest a relatively low value for the δD of Earth's primordial water. This presents a problem for models that call for a significant contribution by comets, *if* our current measurements of δD for comets prove representative. Even chondritic asteroids have a δD which is too

high – again, assuming our measurements are representative of chondrite composition at the time of delivery. This would seem to offer support for the models that lean towards wet accretion, although that end member still has the problems pointed out in Section 1.

5   Summary

Hoping to measure the δD of primordial Earth's water, and thus contribute to the debate on the origin of Earth's water, we measured the δD of glassy conclusions in olivine crystals in basalt samples that were quenched in deep ocean during the formation of Mauna Kea. However, our results (after correction for background water) give a δD typical of mid-ocean ridge basalts, suggesting that we are actually sampling the upper mantle, which contains surface water recycled by tectonic processing.

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