Evidence for primordial water in Earth's deep mantle

Lydia J. Hallis[1,2*], Gary R. Huss[1,2], Kazuhide Nagashima[2], G. Jeffrey Taylor[1,2], Sæmundur A. Halldórsson[3**], David R. Hilton[3], Mike J. Mottl[5], and Karen J. Meech[1,4]

[1]NASA Astrobiology Institute, Institute for Astronomy, University of Hawai'i, 2680 Woodlawn Drive, Honolulu, Hawaii 96822-1839, USA.

[2]Hawai'i Institute of Geophysics and Planetology, Pacific Ocean Science and Technology (POST) Building, University of Hawai'i, 1680 East-West Road, Honolulu, HI 96822, USA.

[3] Scripps Institution of Oceanography, University California San Diego, 9500 Gilman Drive, La Jolla, California 92093-0244.

[4]Institute for Astronomy, University of Hawai'i, 2680 Woodlawn Drive, Honolulu, HI 96822, USA.

[5] Department of Oceanography, University of Hawai'i, Marine Sciences Building 304, 1000 Pope Road, Honolulu, HI 96822, USA

*Now at: School of Geological and Earth Sciences, University of Glasgow, Gregory Building, Lillybank Gardens, Glasgow, G12 8QQ, UK.

**Now at: Nordic Volcanological Center, Institute of Earth Sciences, University of Iceland, Askja, Sturlugata 7, 101 Reykjavík, Iceland.

Manuscript to be re-submitted to:

Science

Sept 2015

Total pages including abstract, text, references, table and figure caption: 13

Total words (abstract): 110

Total words (body text, references and figure caption): 2745

Total References: 40

The hydrogen-isotope (D/H) ratio of Earth can be used to constrain the origin of its water. However, the most accessible reservoir, Earth's oceans, may no longer represent the original (primordial) D/H ratio due to changes caused by water cycling between the surface and the interior. Thus, a reservoir completely isolated from surface processes is required to define Earth's original D/H signature. Here we present data from Baffin Island and Icelandic lavas, which suggest the deep mantle has a low D/H ratio (δD more negative than -218 ‰). Such strongly negative values indicate the existence of a component within Earth's interior that inherited its D/H ratio directly from the protosolar nebula.

Establishing Earth's initial D/H ratio is important for understanding the origin of our planet's water, as well as the dynamical processes that operated during planet formation in the Solar System. However, evolution of this ratio occurs over time due to surface and mantle processing. Collisions with hydrogen-bearing planetesimals or cometary material after Earth's accretion should have altered the D/H ratio of the planet's surface and upper mantle *(1)*. In addition, experimentally-based chemical models suggest an increase of the atmospheric D/H value by a factor of 2-9 since Earth's formation *(2)*. Preferential loss of the lighter hydrogen isotope from the upper atmosphere causes this increase, driven by thermal atmospheric escape or plasma interactions with the atmosphere. As atmospheric D/H is linked with that of ocean water and sediments, the D/H ratio of the mantle also increases with time via subduction and convective mixing. Only areas of the deep Earth that have not participated in this mixing process are likely to preserve Earth's initial D/H ratio.

Studies of the trace-element, radiogenic-isotope, and noble gas isotope characteristics of mid-ocean ridge basalts (MORB) and ocean-island basalts (OIB) reveal the existence of domains within Earth's mantle that have experienced distinct evolutionary histories *(3-4)*. Although alternative theories exist *(e.g., 5)*, most studies suggest high $^{3}He/^{4}He$ ratios in some OIB indicate the existence of relatively undegassed regions in the deep mantle compared to the upper mantle, which retain a greater

proportion of their primordial He *(6-7)*. Helium isotope ($^3He/^4He$) ratios over 30 times the present-day ratio of the Earth's atmosphere ($R_A = 1.38\times10^{-6}$) *(8)* can be found in volcanic rocks from oceanic islands, including Iceland and Hawaii *(9-12)*. Early Tertiary (60-Myr-old) lavas from Baffin Island and West Greenland, which represent volcanic rocks from the proto/early Iceland mantle plume, contain the highest recorded terrestrial $^3He/^4He$ ratios of up to 50 R_A *(6-7)*. These lavas also have Pb and Nd isotopic ratios consistent with primordial mantle ages (4.45-4.55 Ga) *(13)*, indicating the persistence of an ancient, isolated reservoir in the mantle. The undegassed and primitive nature *(14)* of this reservoir means it could preserve Earth's initial D/H ratio. This study targets mineral-hosted melt inclusions in these rocks in search of this primordial signal.

A range of D/H ratios are found on Earth. We compare the ratio of deuterium (^2H) to hydrogen (^1H) relative to Vienna Standard Mean Ocean Water (VSMOW, D/H = 1. 5576x10-4) using $\delta D=[((D/H)_{unknown}/(D/H)_{VSMOW})-1]\times1000$, in units of parts per thousand (per mil (‰)). The hydrological cycle fractionates hydrogen, creating glacial ice (standard Greenland Ice Sheet Precipitation δD = -190 ‰ *(15)*), ocean water (VSMOW δD = 0 ‰), and fresh water (δD = 0 to -300 ‰ *(16)*) reservoirs. Subduction provides a means to mix water back into the mantle, producing a variation in δD from -126 to +46 ‰ from slab dehydration and sediment recycling *(17-18)*. The MORB source appears to be better mixed, with a uniform δD of -60 ± 5 ‰ *(19)*.

We measured the D/H ratios of olivine-hosted glassy melt inclusions in two depleted picrite samples (basaltic rocks with abundant Mg-rich olivine) from Padloping Island, NW Baffin Island *(20)*, and in three picrite samples from Iceland's western and northern rift zones *(9,11)*. The high forsterite (Fo) contents of these olivines (Fo_{87-91}) suggest crystallization from primitive melts *(21)*. We monitored possible contamination from crustal materials, or meteoric water due to weathering, by measuring the oxygen isotope ratios of the samples *(21)*. One Icelandic sample shows slightly raised $\delta^{18}O$, indicative of

crustal contamination. All other samples fall within the range expected for uncontaminated mantle-derived samples.

Baffin Island melt inclusions are characterized by extremely low D/H ratios, from δD -97 to -218 ‰ (Table 1). Melt-inclusion dehydration, where H_2O preferentially diffuses faster than HDO through encapsulating olivine, accounts for the inverse correlation between δD and water content (Fig. 1A). The longer olivine grains are resident in hot melt prior to eruption then the stronger the effect of dehydration *(22)*. In addition to dehydration, melt-inclusion degassing can also raise D/H ratios and lower water contents. Melt inclusions may undergo degassing due to depressurization during eruption. We selected rapidly quenched sub-glacially (Iceland) and sub-aqueously (Baffin Island) erupted samples to mitigate the effects of degassing. However, two of the three Icelandic samples exhibit the high δD and low water contents indicative of this process. Revealingly, sample MID-1 is known to be one of the least degassed Icelandic basalts *(10)*, and contains melt inclusions with the lowest δD (-88 to -90 ‰) and highest H_2O contents (946-964 ppm) of the three Icelandic samples.

The wide spread in $\delta^{18}O$ values between samples (Table 1; Fig. 1B) supports a heterogeneous Baffin Island/Iceland plume with respect to $\delta^{18}O$ *(11,23-24)*. The Baffin Island melt inclusion $\delta^{18}O$ values (4.73-5.18 ‰) are similar to those of Baffin Island picrite matrix glasses (4.84-5.22 ‰) *(25)*. These values are lower than typical MORB $\delta^{18}O$ (5.5 ± 0.2 ‰ *(26)*), indicating a possible correlation between low D/H, low $^{18}O/^{16}O$, and high $^{3}He/^{4}He$ as an intrinsic property of the undegassed mantle.

Lithospheric slab dehydration during crustal subduction and deep recycling can produce low D/H ratios in glasses from plume-related localities *(17,27)*. Basaltic glasses from the Hawaiian Koolau volcano contain low δD values and similar water contents to the Baffin Island picrites *(27)* (Fig. 1a). However, the Koolau mantle source is thought to contain a substantial fraction of recycled upper oceanic crust and sediment *(27)*, and its distinct $\delta^{18}O$ (Fig. 1b) is attributed to an EM2 signature (sedimentary recycling). The Baffin Island and Iceland samples do not contain any evidence of a recycled slab component *(21)*,

hence their low δD values must be attributed to a different origin. The correlation between low D/H and high $^3He/^4He$ ratios in the Baffin Island/Iceland samples suggests they originate from a region isolated from mixing. Thus, our data support a heterogeneous mantle, which contains deep, primitive, undegassed regions that have never been involved in subduction-related mixing or recycling *(13)*.

Magma-ocean crystallization models *(28)*, and Nd isotopic evidence from some of Earth's oldest rocks *(29)*, indicate a small volume of late-solidifying dense cumulates developed during the first 30-75 million years of Earth history. High pressures near the base of Earth's magma ocean would cause magma to become denser than coexisting minerals, thus crystallization would proceed from the top downwards *(30).* Top down crystallization would trap volatile elements in cumulates at the deepest section of the mantle. Nd isotope data suggest such cumulates still exist, representing a hidden incompatible-element-enriched reservoir complementary to the depleted nature of most of Earth's mantle *(29,31)*. The depth of this enriched reservoir explains its absence in modern-day upper-mantle melts. However, deep plume melting can transfer melt from the core-mantle boundary to the surface *(32).* The olivine compositions of Baffin Island picrites, as well as other samples with high $^3He/^4He$ (e.g., basalts from Western Greenland and the Galapagos), suggest these lavas originated from a peridotite source ~20 % higher in Ni content than the modern depleted mantle source, apparently as a result of interaction with the Ni-rich core *(5)*. The noble gas composition of many OIB, including high proportions of solar Ne, suggests these plumes sample a volatile-rich reservoir *(33-34)*.

The lowest measured D/H value (δD = -218 ‰) provides an upper limit on the D/H of early Earth if the Baffin Island picrite melt inclusions sample a deep mantle reservoir with preserved primitive volatiles. One possibility is that this strongly negative δD was added to the Earth during initial accretion, via dust grains with adsorbed H_2O inherited directly from the protosolar nebula (-870‰) *(35)*. The temperature was high at Earth's orbital distance during the early solar system, but 1000-500 K would still allow adsorption of 25-300 % of Earth's ocean water onto fractal grains during Earth's accretion

(36). Solar wind hydrogen and additional accreting objects from the outer part of the inner solar system may also have mixed into the accreting planet *(34).* Experimentally-based atmospheric chemical models support protosolar nebula adsorption, as they suggest an initial δD between -500 and -889 ‰ for the Earth *(3)*.

The δD vs. H_2O (wt %) correlation for Baffin Island sample PI-19 (Fig. 1A) suggests a deep mantle source with a protosolar δD value of -870 ‰ would have a water content of 0.94 wt %. This value is higher than that calculated for typical bridgmanite (<220 ppm H_2O) *(37)*, although post-bridgmanite can contain more hydrogen *(38)*. In addition, isotopic ratios show that plume material is not typical of ambient mantle *(4-7)*, and primary Hawaiian magmas have been shown to contain 0.36-0.6 wt % water *(27)*. A 20/80% mixture of a protosolar-like deep mantle source (δD = -870 ‰, H_2O = 0.94 wt %) *(35)* and MORB (19, 37) reproduce the lowest measured Baffin Island δD values. This proportion is consistent with mantle Xe isotope anomalies, also estimated to reflect admixture with about 20 % of a solar Xe component *(33)*.

The similarity between the bulk chemical composition of the Earth and carbonaceous chondrites indicates that Earth accreted from building blocks similar to these meteorites *(39)*. An initial Earth δD value more negative than -218 ‰ is at the very lower end of the δD range for bulk-rock CM and CI chondrites (+338 to -227 ‰) *(40)*, while other carbonaceous chondrite groups have more positive bulk-rock δD (-48 to +763 ‰) *(40).* However, the δD range for water in CI and CM chondrites is low (-383 to -587 ‰) *(40)*, hinting that their parent bodies may have gained water via protosolar nebula adsorption. Recent reports of Earth-like δD in the Martian interior *(41)* also suggest protosolar nebula adsorption as a source for Martian water. Therefore, the adsorption mechanism could provide an important source of water in inner solar system terrestrial bodies.

References and notes:

1. O. Abramov, S. J. Mojzsis, Microbial habitability of the Hadean Earth during the late heavy bombardment. *Nature* **459**, 419-422 (2009).
2. H. Genda, M. Ikoma, Origin of the ocean on the Earth: Early evolution of water D/H in a hydrogen-rich atmosphere. *Icarus* **194**, 42-52 (2008).
3. A. W. Hofmann, Mantle geochemistry: The message from oceanic volcanism. *Nature* **385**, 219–229 (1997).
4. C. Herzberg, *et al.,* Nickel and helium evidence for melt above the core–mantle boundary. *Nature* **493**, 393-397 (2013).
5. H. M. Gonnermann, S. Mukhopadhyay, Preserving noble gases in a convecting mantle. *Nature* **459**, 560-563 (2009).
6. F. M. Stuart, S. Lass-Evans, J. G. Fitton, R. M. Ellam, High ^{3}He/^{4}He ratios in picritic basalts from Baffin Island and the role of a mixed reservoir in mantle plumes. *Nature* **424**, 57-59 (2003).
7. N. A. Starkey, *et al.,* Helium isotopes in early Iceland plume picrites: Constraints on the composition of high ^{3}He/^{4}He mantle. *Earth Planet. Sci. Lett.* **277**, 91–100 (2009).
8. J. Geiss, et al., The Apollo SWC experiment: Results, conclusions, consequences. *Space Sci. Rev.* **110**, 307-335 (2004).
9. D. R. Hilton, K. Grönvold, C. G. Macpherson, P. R. Castillo, Extreme ^{3}He/^{4}He ratios in northwest Iceland: Constraining the common component in mantle plumes. *Earth Planet. Sci. Lett.* **173**, 53–60 (1999).
10. E. Füri, *et al.,* Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: The role of He depletion, melt mixing, degassing fractionation and air interaction. *Geochim. Cosmochim. Acta* **74**, 3307–3332 (2010).

11. C. G. Macpherson, D. R. Hilton, J. M. D. Day, D. Lowry, K. Grönvold, High-$^{3}He/^{4}He$, depleted mantle and low-$\delta^{18}O$, recycled oceanic lithosphere in the source of central Iceland magmatism. *Earth Planet. Sci. Lett.* **233**, 411–427 (2005).

12. M. D. Kurz, W. J. Jenkins, S. R. Hart, Helium isotopic systematics of oceanic islands and mantle heterogeneity. *Nature* **297**, 43–47 (1982).

13. M. G. Jackson, *et al.,* Evidence for the survival of the oldest terrestrial mantle reservoir. *Nature* **466**, 853-856 (2010).

14. I. Robillard, D. Francis, J. N. Ludden, The relationship between E- and N-type magmas in the Baffin Bay Lavas. *Contrib. Mineral. Petrol.* **112**, 230–241 (1992).

15. J. Hoefs, *Stable Isotope Geochemistry (6th edition)*. Springer, Berlin (2009).

16. C. Lécuyer, P. Gillet, F. Robert, The hydrogen isotope composition of seawater and the global water cycle. *Chem. Geol.* **145**, 249–261 (1998).

17. A. M. Shaw, *et al,.* Long-term preservation of slab signatures in the mantle inferred from hydrogen isotopes. *Nature Geosci.* **5**, 224-228 (2012).

18. Q-K. Xia, *et al.,* Anomalously high δD values in the mantle. *Geophys. Res. Lett.* **29**, 2008.

19. M. Clog, C. Aubaud, P. Cartigny, L. Dosso, The hydrogen isotopic composition and water content of southern Pacific MORB: A reassessment of the D/H ratio of the depleted mantle reservoir. *Earth Planet. Sci. Lett.* **381**, 156-165 (2013).

20. D. Francis, The Baffin Bay lavas and the value of picrites as analogues of primary magmas. *Contrib. Mineral. Petrol.* **89**, 144-154 (1985).

21. Materials and Methods are available as Supplemetary materials on Science Online..

22. G. A. Gaetani, J. A. O'Leary, N. Shimizu, C. E. Bucholz, M. Newville, Rapid re-equilibration of H_2O and oxygen fugacity in olivine-hosted melt inclusions. *Geology* **40**, 915-918 (2012).

23. A. A. Gurenko, M. Chaussidon, Oxygen isotope variations in primitive tholeiites of Iceland: Evidence from a SIMS study of glass inclusions, olivine phenocrysts and pillow rim glasses. *Earth Planet. Sci. Lett.* **205**, 63-79 (2002).

24. M. E. Hartley, T. Thordarson, J. G. Fitton, EIMF, Oxygen isotopes in melt inclusions and glasses from the Askja volcanic system, North Iceland. *Geochim. Cosmochim. Acta* **123**, 55–73 (2013).

25. A. J. R. Kent, *et al.,* Mantle heterogeneity during the formation of the North Atlantic Igneous Province: Constraints from trace element and Sr-Nd-Os-O isotope systematics of Baffin Island picrites. *Geochem. Geophys. Geosyst.* **5**, 11 (2004). doi:10.1029/2004GC000743.

26. J. M. Eiler, Oxygen isotope variation of basaltic lavas and rocks. *Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry* **43**, 319-364 (2001).

27. E. Hauri, SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in Hawaiian melt inclusions. *Chem. Geol.* **183**, 115–141 (2002).

28. L. T. Elkins-Tanton, Linked magma ocean solidification and atmospheric growth for Earth and Mars. *Earth Planet. Sci. Lett.* **271**, 181–191 (2008).

29. M. Boyet, R. W. Carlson, ^{142}Nd evidence for early (94.53 Ga) global differentiation of the silicate Earth. *Science* **309**, 576-581 (2005).

30. L. T. Elkins-Tanton, Formation of early water oceans on rocky planets. *Astrophys. Space Sci.* DOI 10.1007/s10509-010-0535-3 (2011).

31. S. Labrosse, J. W. Hernlund, N. Coltice, A crystallizing dense magma ocean at the base of the Earth's mantle. *Nature* **450**, 866-869 (2007).

32. D. V. Helmberger, L. Wen, X. Ding, Seismic evidence that the source of the Iceland hotspot lies at the core-mantle boundary. *Nature* **396**, 251-255 (1998).

33. G. Holland, C. J. Ballentine, Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* **441**, 186-191 (2006).

34. M. Trieloff, J. Kunz, D. A. Clague, D. Harrison, C. J. Allègre, The Nature of Pristine Noble Gases in Mantle Plumes. *Science* **288**, 1036-1038 (2000).

35. K. D. McKeegan, L. A. Leshin, Stable isotope variations in extraterrestrial materials. *Rev. Min. Geochem.* **43**, 279-318 (2001).

36. M. J. Drake, Origin of water in the terrestrial planets. Met. Planet. Sci. 40, 519-527 (2005).

37. W. R. Panero, J. S. Pigott, D. M. Reaman, J. E. Kabbes, Z. Liu, Dry (Mg,Fe)SiO_3 perovskite in the Earth's lower mantle. *J. Geophys. Res. Solid Earth* **120**, 894–908 (2015).

38. S. Akber-Knutson, G. Steinle-Neumann, P. D. Asimow, Effect of Al on the sharpness of the MgSiO3 perovskite to post-perovskite phase transition. *Geophys. Res. Lett.* **32**, L14303 (2005).

39. B. Marty, The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth Planet. Sci. Lett.* **313-314**, 56-66 (2012).

40. C. M. O'D. Alexander, et al., The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. Science 337, 721-723 (2012).

41. L. J. Hallis, G. J. Taylor, K. Nagashima, G. R. Huss, Magmatic water in the Martian meteorite Nakhla. Earth Planet. Sci. Lett. 359-360, 84-92 (2012).

42. A. K. Pedersen, L. M. Larsen, P. Riisager, K. S. Dueholm, in *The North Atlantic Igneous Province Stratigraphy, Tectonic, Volcanic and Magmatic Processes.* D. W. Jolley, B. R. Bell, Eds. *Geol. Soc. Lond. Spec. Publ.* **197**, 157–181 (2002).

43. D. B. Clarke, B. G. J. Upton, Tertiary basalts of Baffin Island: Field relations and tectonic setting. *Can. J. Earth Sci.* **8**, 248-258 (1971).

44. M. Maisonneuve, Constraining the nature of E- and N-type components in the Baffin Island picrites using olivine-hosted melt inclusions. *MSc Thesis*, Department of Earth & Planetary Sciences McGill University, Montréal, Québec, Canada (2012). http://www.geotop.ca/upload/files/publications/memoire_maitrise/Maisonneuve%202013.pdf

45. I. Robillard, D. Francis, J. N. Ludden, The relationship between E- and N-type magmas in the Baffin Bay Lavas. *Contrib. Mineral. Petrol.* **112**, 230–241 (1992).

46. G. M. Yaxley, V. S. Kamenetsky, M. Kamenetsky, M. D. Norman, D. Francis, Origins of compositional heterogeneity in olivine-hosted melt inclusions from the Baffin Island picrites. *Contrib. Mineral. Petrol.* **148**, 426–442 (2004).

47. F. A. Darbyshire, R. S. White, K. F. Priestley, Structure of the crust and uppermost mantle of Iceland from a combined seismic and gravity study. *Earth Planet. Sci. Lett.* **181**, 409–428 (2000).

48. C. J. Wolfe, *et al.,* Mantle shear-wave velocity structure beneath the Hawaiian hot spot. *Science* **326**, 1388–1390 (2009).

49. I. T. Bjarnason, H. Schmeling, The lithosphere and asthenosphere of the Iceland hotspot from surface waves. *Geophys. J. Intern.* **178**, 394-418.

50. I. T. Bjarnason, An Iceland hotspot saga. *Jökull* 58, 3–16 (2008).

51. J. G. Schilling, P. S. Meyer, R. H. Kingsley, Evolution of the Iceland hotspot. *Nature* **296**, 313–320 (1982).

52. T. R. Elliot, C. J. Hawkesworth, K. Grönvold, Dynamic melting of the Iceland plume. *Nature* **351**, 201–206 (1991).

53. M. F. Thirlwall, M. A. M. Gee, R. N. Taylor, B. J. Murton, Mantle components in Iceland and adjacent ridges investigated using double-spike Pb isotope ratios. *Geochim. Cosmochim. Acta* **68**, 361–386 (2004).

54. H. Jóhannesson, K. Saemundsson, Geological map of Iceland: Iceland Institute of Natural History, scale 1:500,000 (1998).

55. C. J. Wolfe, I. T. Bjarnasson, J. C. VanDecar, S. C. Solomon, Seismic structure of the Iceland mantle plume. *Nature* **385,** 245–247 (1997).

56. D. Harrison, P. Burnard, G. Turner, Noble gas behaviour and composition in the mantle: constraints from the Iceland Plume. *Earth Planet. Sci. Lett.* **171**, 199–207 (1999).

57. S. Mukhopadhyay, Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. *Nature* **486**, 101–104 (2012).

58. N. Z. Boctor, C. M. O'D. Alexander, J. Wang, E. Hauri, The Sources of water in Martian meteorites: Clues from hydrogen isotopes. *Geochim. Cosmochim. Acta* **67**, 3971–3989 (2003).

59. L. J. Hallis, *et al.,* Hydrogen isotope analyses of alteration phases in the nakhlite martian meteorites. *Geochim. Cosmochim. Acta* **97**, 105–119 (2012).

60. T. Usui, C. M. O'D. Alexander, J. Wang, J. Simon, J. H. Jones, Origin of water and mantle–crust interactions on Mars inferred from hydrogen isotopes and volatile element abundances of olivine-hosted melt inclusions of primitive shergottites. *Earth Planet. Sci. Lett.* **357–358**, 119–129.

61. J. J. Barnes, *et al.,* Accurate and precise measurements of the D/H ratio and hydroxyl content in lunar apatites using NanoSIMS. *Chem. Geol.* **337–338**, 48–55 (2013).

62. E. Hauri, *et al.,* SIMS analysis of volatiles in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chem. Geol.* **183**, 99–114 (2002).

63. E. Hauri, *et al.,* Matrix effects in hydrogen isotope analysis of silicate glasses by SIMS. Chem. Geol. 235, 352–365 (2006).

64. F. M. McCubbin, A. Steele, E. H. Haurib, H. Nekvasilc, S. Yamashitad, R. J. Hemleya, Nominally hydrous magmatism on the Moon. *Proc. Natl. Acad. Sci.* **107**, 11223–11228 (2010).

65. F. M. McCubbin, E. H. Hauri, S. M. Elardo, K. E. Vander Kaaden, J. Wang, C. K. Shearer Jr., Hydrous melting of the martian mantle produced both depleted and enriched shergottites. *Geology* **40**, 683–686 (2012).

66. I. C. W. Fitzsimons, B. Harte, R. M. Clark, SIMS stable isotope measurement: Counting statistics and analytical precision. *Mineralogic. Mag.* **64**, 59–83 (2000).

67. M. E. Hartley, T. Thordarson, C. Taylor, J. G. Fitton, EIMF, Evaluation of the effects of composition on instrumental mass fractionation during SIMS oxygen isotope analyses of glasses. *Chem. Geol.* **334**, 312–323 (2012).

68. J. M. Eiler, C. Graham, J. W. Valley, SIMS analysis of oxygen isotopes: Matrix effects in complex minerals and glasses. *Chem. Geol.* **138**, 221–244 (1997).

69. J. W. Valley, N. T. Kita, In situ oxygen isotope geochemistry by ion microprobe. Secondary Ion Mass Spectrometry in the Earth and Planetary Sciences*: Mineral. Assoc. Canada Short Course* **41**, 19–63 (2009).

70. N. T. Kita, T. Ushikubo, B. Fu, J. W. Valley, High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chem. Geol.* **264**, 43–57 (2009).

71. A. D. Brandon, D. W. Graham, T. Waight, B. Gautason, ^{186}Os and ^{187}Os enrichments and high ^{3}He/^{4}He sources in the Earth's mantle: Evidence from Icelandic picrites. Geochim. Cosmochim. Acta 71, 4570–4591 (2007).

72. V. Debaille, R. G. Trønnes, A. D. Brandon, T. E. Waight, D. W. Graham, C-T. A. Lee, Primitive off-rift basalts from Iceland and Jan Mayen: Os-isotopic evidence for a mantle source containing enriched subcontinental lithosphere. Geochim. Cosmochim. Acta 73, 3423-3449 (2009).

73. C. W. Dale, D. G. Pearson, N. A. Starkey, F. M. Stuart, R. M. Ellam, L. M. Larsen, J. G. Fitton, C. G. Macpherson, Osmium isotopes in Baffin Island and West Greenland picrites: Implications for the ^{187}Os/^{188}Os composition of the convecting mantle and the nature of high ^{3}He/^{4}He mantle. Earth Planet. Sci. Lett. 278, 267-277 (2009).

Acknowledgements This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement No. NNA09-DA77A, issued through the Office of Space Science. We would like to thank Prof. Don Francis for allocation of the Baffin Island picrite samples and Karl Grönvold for invaluable help in the field in Iceland. The data reported in this paper are tabulated in the Supplementary Material.

Author Contributions L. J. Hallis prepared samples, collected and processed data, and was the primary author of this manuscript. G. R. Huss and K. Nagashima managed the ion-microprobe, perfected hydrogen and oxygen isotope analytical methods, and assisted with data processing. S. A. Halldórsson and D. R. Hilton collected the Icelandic samples and provided Icelandic geological background. G. J Taylor assisted with the development of hydrogen isotope analytical methods and provided Solar System disk model chemistry information. K. Meech initiated this study and provided Solar System disk model chemistry information. All authors discussed the results and commented on the manuscript.

Author Information Correspondence and requests for materials should be addressed to L. J. Hallis (lydia.hallis@glasgow.ac.uk).

Table 1: **Water content, D/H ratio (δD) and $^{18}O/^{16}O$ ratio ($\delta^{18}O$) of Baffin Island and Icelandic samples.** Due to the small size of melt inclusions in the samples, it was mostly not possible to collect hydrogen and oxygen isotope data from the same inclusions. Therefore, oxygen isotope data is calculated based on the average value of melt inclusions (n=2-4) within the same olivine grain as that measured for D/H. Olivine oxygen data is also presented as an average (n=2-6). Scanning electron microscope images showing the location of each data point on the sample surfaces are available *(21)*.

Baffin Island picrites

sample and phase	H_2O (ppm)	δD (‰)	2σ (‰)	$\delta^{18}O$ (‰)	2σ (‰)
PI-16_area 4_melt inclusion 1	709	-115	38	5.18	0.25
PI-16_area 6_melt inclusion 1	926	-107	39	5.18	0.25
PI-16_area 7_melt inclusion 1	1189	-108	35	5.18	0.25
PI-16_area 8_melt inclusion 1	1039	-122	36	5.18	0.25
PI-16_area 9_melt inclusion 1	1175	-158	51	5.18	0.25
PI-16_area 9_melt inclusion 2	576	-114	40	5.18	0.25
PI-16_area 4_olivine 1	194			4.53	0.34
PI-16_area 6_olivine 1	413			4.53	0.34
PI-16_area 7_olivine 1	153			4.53	0.34
PI-16_area 8_olivine 1	200			4.53	0.34
PI-16_area 9_olivine 1	187			4.53	0.34
PI-19_area 1_melt inclusion 1	1337	-137	35	4.73	0.16
PI-19_area 1_melt inclusion 2	1465	-177	37	4.73	0.16
PI-19_area 2_melt inclusion 1	1719	-173	34	4.73	0.16
PI-19_area 2_melt inclusion 2	1964	-218	34	4.73	0.16
PI-19_area 3_melt inclusion 1	1779	-197	34	4.73	0.16
PI-19_area 6_melt inclusion 1	997	-137	32		
PI-19_area 7_melt inclusion 1	868	-97	34		
PI-19_area 8_melt inclusion 1	901	-126	32		
PI-19_area 1_olivine 1	557			4.38	0.25
PI-19_area 2_olivine 1	641			4.38	0.25
PI-19_area 2_olivine 2	712			4.38	0.25
PI-19_area 3_olivine 1	781			4.38	0.25
PI-19_area 8_olivine 1	187				
PI-19_area 8_olivine 2	190				

Icelandic basalts

MID-1_bullet 2_melt inclusion 1	946	-88	51	4.83	0.40
MID-1_bullet 2_melt inclusion 2	964	-90	50	4.83	0.40
MID-1_bullet 3_melt inclusion 1	474	-34	53	4.83	0.40
MID-1_bullet 2_olivine 1	157			2.43	0.46
MID-1_bullet 3_olivine 1	85			2.43	0.46
NAL828_bullet 5_melt inclusion 1	600	-34	53	6.54	0.48
NAL828_bullet 5_melt inclusion 2	510	-29	53	6.54	0.48
NAL828_bullet 5_olivine 1	100			5.36	0.46
NAL 688_bullet 13_melt inclusion 1	587	-25	28	5.89	0.35
NAL 688_bullet 13_olivine 1	36			5.72	0.56

Fig. 1: Hydrogen and oxygen isotope ratios. The hydrogen isotope ratios (δD) of Baffin Island and Icelandic basaltic melt inclusions vs. water content (A) and oxygen isotope ratios (B). Uncertainties are 2σ, except for (B) δD, where error bars represent the full range of the dataset. The δD vs. H_2O (A) data trendline gradient for sample PI-19 is shown by the red dashed line. Mixing lines between a protosolar-like deep mantle source (δD = -870 ‰, H_2O = 0.94 wt %) *(35)* and MORB *(19,37)* are shown by the black and grey dashed lines, which assume minimum and maximum MORB source region H_2O contents of 0.008 and 0.095 wt %, respectively *(37)*. Melt inclusion data from the Hawaiian Koolau volcano, which contains the lowest δD values of the Hawaiian plume *(27),* are represented by the green crosses and envelope in (A) and green cross in (B). Average melt inclusion δD values are shown on the δD vs. $\delta^{18}O$ plot (B). The coloured envelopes (B) indicate regions of crustal contamination, based on the $\delta^{18}O$ varitation of possible contaminants from the Icelandic crust (-7.5 to +1.65 ‰, green envelope) *(24)*, and hydtrothermally altered oceanic crust (+7 to +15 ‰, yellow envelope) *(26).* The δD variation of the envelopes is as reported for hydrothermally altered oceanic crust (-34 to 46 ‰) *(17-18)*.

Supplementary Materials

Materials and methods

Supplementary Text

Figures S1-S9

Tables S1-S3

References *41-72*