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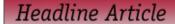
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Primeval Water in the Earth

--- Hydrogen isotopes in lavas derived from the deep mantle suggest the presence of a component inside the Earth that came directly from the primordial solar nebula.

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Lava flows derived from a mantle plume rising from deep in

Earth's mantle contain information about the chemical and isotopic composition of the earliest material to accrete as Earth was being assembled from dust and planetesimals. Lydia Hallis (University of Hawai'i, now at the University of Glasgow) and colleagues in the Hawai'i Institute of Geophysics and Planetology and the Institute for Astronomy, and at Scripps Institute of Oceanography (San Diego, California) measured the ratio of deuterium to hydrogen (expressed in delta notation as δD) in melt inclusions trapped in olivine phenocrysts in lava flows from Baffin Island, Canada. These rocks are notable for their high helium-3/helium-4 ratios, a marker for the presence of a primordial component. Baffin Island lavas derive from melting of a plume of deep mantle that rose from as deep as the boundary with the metallic core inside Earth. Hallis and coworkers found that the δD in the trapped melts were lower than measured previously for samples from the deep mantle, suggesting that the earliest Earth-forming projectiles contained a component derived from the protosolar nebula, the cloud of gas and dust from which the planets formed.

Reference:

- Hallis, L. J., Huss, G. R., Nagashima, K., Taylor, G. J., Halldórsson, S. A., Hilton, D. R., Mottl, M. J., and Meech, K. J. (2015) Evidence for Primordial Water in Earth's Deep Mantle, *Science*, v. 350, p. 795-797, doi: 10.1126/science.aac4834. [abstract]
- **PSRDpresents:** Primeval Water in the Earth--Short Slide Summary (with accompanying notes).

How and Where Did Earth Acquire Its Water?

The pale blue dot we live on gets much of its color from the oceans that cover 70% of its surface. The planet also has water in its atmosphere, flowing through permeable rocks, and steaming from volcanoes. A large supply of water, more than is on the surface, resides in the **mantle**, dissolved as H_2O , OH, or H in minerals. Where did all this water come from? Or, even more important, what does the distribution of water tell us about how the Earth formed?



While not as water rich as an icy satellite of Jupiter, Earth has plenty of water. It is contained not only in its oceans, but also in its interior, as shown when water steams off erupting lava, as here on Kilauea volcano, Hawai'i.

USGS Hawaiian Volcano Observatory.

hvo.wr.usgs.gov

These are deceptively tricky questions. One way of addressing them is to measure the **isotopic** composition of **hydrogen** in the Earth. Hydrogen has two major isotopes, one with an atomic weight of 1 (H, hydrogen, just a proton in its nucleus) and the other with an atomic weight of 2 (D, **deuterium**, with a proton and a neutron in its nucleus). The relative amounts of the two isotopes is expressed as the D/H ratio. Geochemists often use an alternative form to express the ratio, called delta D, or δD . This is the D/H ratio in a sample divided by the ratio in a terrestrial standard, minus 1, with the whole thing multiplied by 1000 to express things in parts per thousand. The terrestrial standard is called the Vienna standard mean ocean water, or VSMOW for short. In equation form, $\delta D = [(D/H)_{sample}/(D/H)_{vsmow} - 1] \times 1000$. If a sample has D/H the same as ocean water, δD is zero. If the sample has D/H larger than the value in VSMOW, δD is positive; a sample with D/H lower than SMOW has a negative value for δD .

Likely Solar System materials to accrete to the growing Earth during planet construction include comets and asteroids, or at least planetesimals like them. Comets from the Oort cloud in the outer Solar System have δD larger than +800. Comets from the Jupiter region have δD in the -300 to +300 range. **Carbonaceous chondrites** (which come from carbon- and water-rich asteroids in the outer asteroid belt) contain water with low δD values between -380 to -590. The protosolar **nebula**, the cloud of gas and dust from which the Solar System formed is estimated to have had a δD of -870.

With such large variations in δD , it would seem easy to determine where most of Earth's water came from. Unfortunately (or fortunately if you like the richness resulting from complications), Earth processes its water in ways that change its isotopic composition. A particularly important one is the preferential loss of hydrogen compared to deuterium from the upper atmosphere. Hidenori Genda and Masahiro Ikoma (Tokyo Institute of Technology) showed in 2008 that D/H might have increased by as much as a factor of 9 since the Earth formed. In turn, this changes D/H in water in the oceans and sediments. As the ocean floor is dragged into the mantle as one plate slides beneath another, the D/H in the mantle also changes. So, how do we figure out what Earth's D/H was in the first place? The answer lies in the deep mantle.

Sampling the Deep Mantle

Many lavas erupting on volcanic oceanic islands have the interesting characteristic that they contain a high ratio of helium-3 (³He) to helium-4 (⁴He). They do not contain much of either helium isotope, but the elevated ratio of ³He/⁴He ratio is informative. It indicates the presence of primordial helium in the regions of the mantle that give rise to oceanic island volcanoes. In contrast, abundant mid-ocean ridge **basalts** do not show such significant enrichments in ³He/⁴He, indicating (along with many other data) that ocean island and mid-ocean ridge **magmas** come from distinctly different geochemical reservoirs in the mantle.

One group of basalts from Baffin Island in the Canadian Arctic holds the current record for high ${}^{3}\text{He}/{}^{4}\text{He}$ with a ratio 50 times higher than in the Earth's atmosphere. These basalts are thus promising candidates for containing some primordial Earth stuff. It gets even better. In 2010, Matthew Jackson (Boston University) and colleagues showed through measurements of the isotopic compositions of lead (decay products from uranium and thorium) that the region of the mantle that melted to form the Baffin Island basalts formed between 4.45 and 4.55 billion years ago (see diagram below). This is ancient, basically dating from the time of Earth's accretion from countless planetesimals.

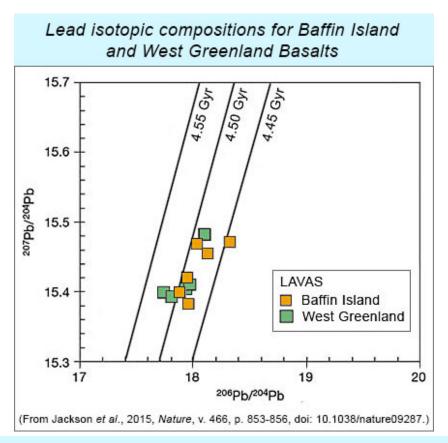
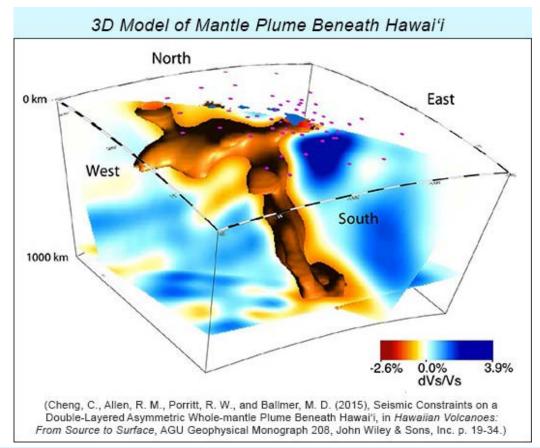


Diagram showing lead isotopic compositions for Baffin Island and West Greenland whole-rock samples. The isotopes ²⁰⁷Pb and ²⁰⁶Pb are changed by radioactive decay; ²⁰⁴Pb represents the initial lead abundance in a rock. Making judicious assumptions about the isotopic composition of the initial lead in the Solar System and that the Earth formed 4.55 billion years ago, all data should fall on a line (called the geochron) corresponding to their age of formation. The Baffin Island basalts fall between lines representing 4.55 and 4.45 billion years ago, indicating an ancient, primordial origin for their source region in the mantle. Combined with the ³He/⁴He data, the ancient mantle age makes the Baffin Island basalts excellent candidates for searching for Earth's most primordial water.

Baffin Island and other oceanic islands are thought to form when large plumes of solid mantle rock rises from deep in the mantle, probably near the boundary between the core and mantle. The plumes rise because of thermal variations, perhaps brought on by the primordial mantle regions having higher concentrations of heat-producing uranium and thorium. The slight temperature boost causes a region of the mantle to become more buoyant and to slowly rise. Surprising though it may seem, solids can move inside solids, especially if the solids are hot and at high pressure. The mantle is highly deformable, which enables the rigid tectonic plates to move on the more plastic substrate beneath them.



Plumes of mantle rock can rise slowly from the base of the mantle through temperature fluctuations that lead to portions becoming less dense than their surroundings. In this way, a plume carries a deep, ancient portion of the mantle upwards. Once the plume reaches relatively shallow levels (tens of kilometers deep), it begins to melt. The magmas migrate to the surface and erupt as lavas, producing ocean islands such as Hawai'i and Baffin Island. This illustration shows a 3D shear wave velocity model based on multiple geophysical datasets for the mantle plume beneath the Hawaiian islands. The plume is depicted as the irregularly-shaped low-velocity region (yellows to dark oranges).

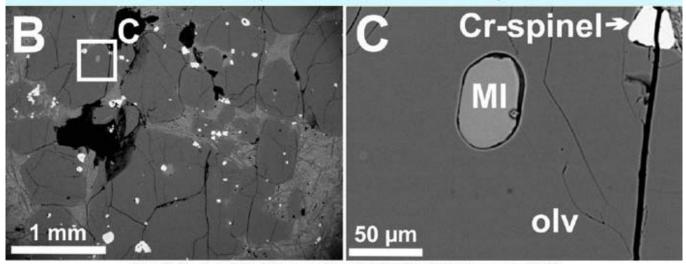
Plumes rise slowly. Once the pressure is low enough, in the range of 20,000 times atmospheric pressure (50 to 100 kilometers deep), the solid plume begins to melt. The magma migrates faster than the plume rises and erupts, allowing geologists to sample the deep mantle by collecting lava rocks formed from a plume that had risen and then melted.

Baffin Island would seem to be a great place to search for clues to the D/H in the ancient Earth. Lydia Hallis and her colleagues certainly thought so.

D/H in Baffin Island Samples

B affin Island and Greenland formed almost at the same time, the initial crust-building activity of what is known as the Iceland Plume. All three locations are good for probing the deep mantle, but the Baffin Island samples give the clearest picture, so I concentrate on those results. The samples have high ³He/⁴He (of course) and are picritic basalts. This means that the rocks contain a lot of large olivine crystals. Those olivine crystals are important because as they grow from the ascending magma, they tend to trap some of the surrounding magma. The trapped blebs are called melt inclusions. Many end up composed mostly of glass, basically frozen melt. The melt inclusions contain H₂O and OH dissolved in the trapped magma, allowing measurements of the D/H ratio. An example of a melt inclusion and its setting in one of the Baffin Island samples is shown in the images below.

Baffin Island Basalt Sample with Olivine-hosted Glassy Melt Inclusion

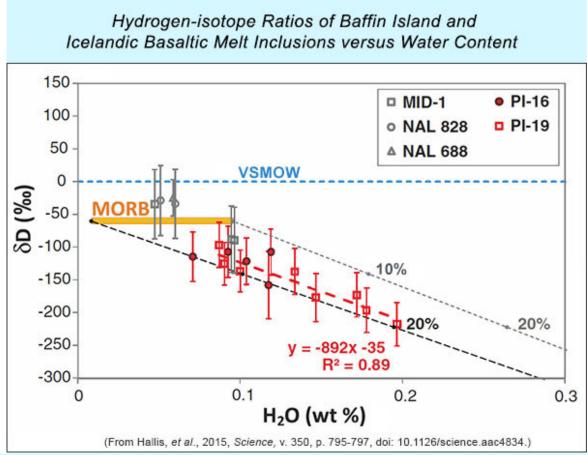


(From Hallis, et al., 2015, Science, v. 350, p. 795-797, doi: 10.1126/science.aac4834.)

Backscatter electron images of a Baffin Island sample analyzed by Hallis and colleagues. [LEFT] Olivine phenocrysts (dark grey) with box labeled C outlining an olivine-hosted glassy melt inclusion. [RIGHT] Area C at higher magnification shows melt inclusion (MI) in olivine (olv) with a nearby chromium spinel crystal (Cr-spinel).

To prove that nothing is simple, Lydia Hallis had to worry about loss of water from the melt inclusions and the accompanying change in the D/H ratio (because D moves slower that H). This was mitigated by studying samples that were erupted under water, which causes rapid cooling and minimizes water loss. It might seem ironic or even illogical that a water measurement is less compromised if a lava erupts under water. Why wouldn't water move into the sample? The answer is that the outer part of the flow quenches to glass and forms a barrier to water reactions.

Measurements were done using the University of Hawai'i Secondary Ion Mass Spectrometer. This laboratory, managed by Gary Huss and Kazu Nagashima, is state-of-the-art, but still required substantial development work by them and Lydia Hallis. In the diagram below, δD increases with decreasing H_2O , suggesting some water loss. Most important, the data show that the primordial water in the deep mantle probed by the Baffin Island magmas have a δD of -218 or lower. These are the lowest values measured for terrestrial samples and emphasize that the deep mantle source is distinct from other places in the mantle.



D/H ratios (expressed as δD) in Baffin Island (red circles and squares) and Iceland melt inclusions (grey symbols). VSMOW is Vienna standard mean ocean water. The data clearly show that the Baffin Island samples are distinctly different from Mid-Ocean Ridge Basalts (MORB, orange bar) and their deep origin suggests that the lowest δD value is indicative of the deep mantle. It appears that there was a component present in the early Earth that had low δD . The percentages along the dashed grey lines show how much of a primordial water component (δD of -870) could be present in the Baffin Island lavas, assuming mixing with mantle rock with δD like that in MORB.

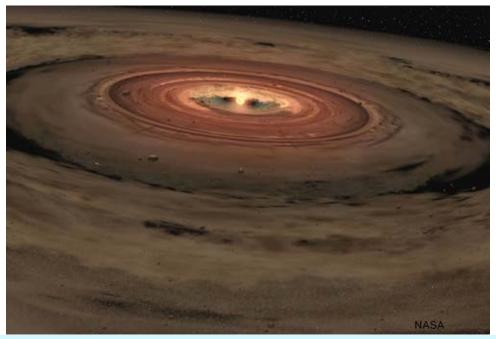
Accretion of the Earth

Earth and the other rocky planets did not form spontaneously with a uniform composition. Numerical models of planetary accretion show that formation of the Earth took tens of millions of years and involved substantial mixing of materials originally located from the inner Solar System (from the inner asteroid belt to Mercury) to the outer Solar System (beyond Jupiter's present orbit). As explained in PSRD article:

Making and Differentiating Planets, the consequence of the mixing is that the planets accreted heterogeneously. Water and other volatiles arrived in progressively larger amounts during assembly of the Earth. Nevertheless, some water could have arrived from the beginning, ending up in the deep mantle. The idea of heterogeneous accretion is also supported by the late accretion of tungsten isotopes (see PSRD article: Tungsten Isotopes, Formation of the Moon, and Lopsided Addition to Earth and Moon.

Hallis and coworkers suggest that the strongly negative δD materials were added to Earth early in its accretion (ending up deep inside the fully-constructed planet). These primitive materials might have been incorporated as dust grains into Earth or into planetesimals that accreted to Earth. Hallis points out that H_2O could have been adsorbed onto grains in the protosolar nebula. The early arrivals might also have been like the two most primitive types of carbonaceous chondrites (CI and CM). Water in these rocks have δD values of -380 to -590, and may themselves have adsorbed protosolar water. A complication with this idea is that analyses of bulk-rock CI and CM chondrites have much higher δD values, ranging from -227 to

+338. The bulk values include hydrogen and deuterium locked in organic molecules.



This artist's conception is based on astronomical observations of a disk surrounding a young star. The dust is in contact with hydrogen-rich gas that has an extremely low D/H ratio. Planets form by accretion of the dusty materials into larger and larger objects, with considerable mixing during planetary accretion.

The Baffin Island data point toward the materials arriving early in Earth's accretion having low δD . The data are consistent with materials arriving later in planet construction having higher δD , but perhaps more likely show the effects of the strong, global processing of water in the atmosphere-ocean-sedimentary cycle. Lydia Hallis notes that the upper reaches of Earth, including the upper mantle, reflect atmospheric-ocean interactions whereas the deep regions inside the Earth reflect its primordial composition. Ironically, Baffin Island is surrounded by ocean representing the shallow part of the water cycle, but its rocks record the isotopic composition of the deep mantle.

Additional Resources

Links open in a new window.

- Cheng, C., Allen, R. M., Porritt, R. W. and Ballmer, M. D. (2015) Seismic Constraints on a Double-Layered Asymmetric Whole-Mantle Plume Beneath Hawai'i, in *Hawaiian Volcanoes: From Source to Surface* (eds R. Carey, V. Cayol, M. Poland and D. Weis), John Wiley & Sons, Inc, Hoboken, NJ., p. 19-34, doi: 10.1002/9781118872079.ch2 [abstract]
- Genda, H. and Ikoma, B. (2008) Origin of the Ocean on the Earth: Early Evolution of Water D/H in a Hydrogen-rich Atmosphere, *Icarus*, v. 194, p. 42-52, doi: 10.1016/j.icarus.2007.09.007. [abstract]
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- Jackson, M. G., Carlson, R. W., Kurz, M. D., Kempton, P. D., Francis, D., and Blusztajn, J. (2010) Evidence for the Survival of the Oldest Terrestrial Mantle Reservoir, *Nature*, v. 466, p. 853-856, doi: 10.1038/nature09287. [abstract]
- Taylor, G. J. (2015) Tungsten Isotopes, Formation of the Moon, and Lopsided Addition to Earth and Moon, *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/June15/W-Earth-Moon.html
- Taylor, G. J. (2015) Making and Differentiating Planets, *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/July15/making-planets.html



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