

Origin of planetary water by adsorption in the accretion disk

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Two main scenarios can account for the delivery of water to the inner planets: either the water originated outside of the inner solar system and was later delivered to the terrestrial planets or the source of water was local. A source for this 'endogenous' water could be represented by dust grains present in the accretion disk onto which water had been previously adsorbed [1].

Monte Carlo simulation of adsorption at nebular T, P and $f_{\text{H}_2\text{O}}$ onto spherical grains showed that this mechanism can store up to 3 times the Earth's oceans [2]. This model, however, did not take into account the specific surface interactions between water gas and the crystalline surface nor did it investigate rigorously the role of porosity.

To fill this gap, we are performing molecular dynamics simulations of the system water - olivine using the open source code LAMMPS [3]. The bulk olivine was modelled using periodic boundary conditions (PBC) and Buckingham potentials for the short-range interactions with a cut off distance of 10 Å for both short and long-range interactions. Long-range Coulombic interactions were calculated using the Ewald method. To allow for partially covalent bonds in the silica group and in water molecules we allowed for angle dependent forces by introducing angle interactions among triplet of atoms. The "virtual crystal" was then cleaved by removing the PBC in the positive z direction, thus creating a free surface. After the top layered relaxed we inserted water molecules and studied their trajectories. This simulation will allow construction of surface site adsorption probabilities at P, T condition of the nebula.

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Origin of water by inward migration of phyllosilicates or hydrous asteroids

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Hydrated minerals occur in accretionary rims around chondrules in CM chondrites [1]. The most abundant phase is Mg-rich serpentine, which occurs as small (~20 nm) crystals with cylindrical or fibrous morphologies [2]. Previous models of gas-grain kinetics suggest that these phyllosilicates did not form by gas-solid reactions in the solar nebula [3]. However, anhydrous minerals also occur in these chondrule rims. The hydrated and anhydrous regions are in direct contact with each other, suggesting that the rims formed by accreting material from multiple nebular reservoirs [2]. These results are consistent with a nebular origin for fine-grained phyllosilicates.

We have shown that shock waves in icy regions of the nebula produced conditions that allowed rapid mineral hydration [4,5]. The time scales for phyllosilicate formation are similar to the time it takes for a shocked system to cool from the temperature of phyllosilicate stability to that of water ice condensation. This scenario allows for simultaneous formation of chondrules and fine-grained accretionary rims.

Recent calculations show that these hydrous minerals could have been transported into the hotter regions of the nebula by gas drag and incorporated into the planetesimals which formed there [6]. The hydrated minerals were able to survive for long periods of time in this hot region due to the sluggish dehydration kinetics.

The total amount of water in the Earth's hydrosphere is $\sim 1.6 \times 10^{24}$ g. Delivery of this mass of water requires the Earth to have accreted $\sim 2.5 \times 10^{25}$ g of serpentine, which is $\sim 0.4\%$ of the total mass of the Earth. Thus, the delivery of hydrated material to the inner solar system need not be very efficient to supply all of the water present on Earth today.

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Oxygen isotopes and water in the inner solar system

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Bulk O-isotope compositions of the terrestrial planets (Earth, Moon, Mars) and their possible building blocks – different chondritic and achondritic planetesimals – are ¹⁶O-depleted relative to the postulated ¹⁶O-rich ($\delta^{17,18}\text{O} \sim -50\%$) initial composition of the protosolar molecular cloud or protoplanetary disk (Clayton, 2002; Yurimoto & Kuramoto, 2004; Young & Lyons, 2004; Krot et al., 2005) that may have been recorded by refractory inclusions and rare chondrules in primitive chondrites. According to these models, the UV photolysis of CO preferentially dissociates C¹⁷O and C¹⁸O in certain zones of the disk or molecular cloud. If this process occurs in the stability field of water ice, the released ¹⁷O and ¹⁸O are incorporated into water ice, while the residual CO gas becomes enriched in ¹⁶O. Subsequent enhancement of water ice relative to CO gas in the disk midplane outside the snow line, followed by radial migration of icy bodies towards the proto-Sun and their evaporation at the snow line led to significant enrichment in ¹⁶O-depleted water, which then spread through the inner solar system (Cuzzi & Zahnle, 2004). Bulk O-isotope compositions of chondrites are narrower than those of their components and are largely defined by compositions of chondrules and matrices, suggesting that both experienced extensive O-isotope exchange during transient heating events in an ¹⁶O-poor gas. None of the known chondrites represents the postulated initial O-isotope composition of the disk, suggesting that thermal processing of dust in an ¹⁶O-poor gas was a fundamentally important process in the inner solar system. Aqueous alteration experienced by some chondrite groups (CI, CM, CV, CO) modified their bulk O-isotope compositions to a relatively small degree. Bulk O-isotope compositions of the terrestrial planets and different achondrite groups are uniform relative to chondrites, suggesting extensive homogenisation during planetary igneous processes.

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The contribution of comets to water on Mars and Earth

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The oxygen-carbon inventories at the Earth's surface already suggest that comets cannot be the major source of the Earth's oceans (Owen and Bar-Nun) a conclusion confirmed by the difference between D/H in cometary H₂O and in SMOW (Meier and Owen). How much water comets could have brought depends on the D/H in the other sources of water accumulated by the planet. The noble gas abundances and isotope ratios will provide clues as to the fraction of Earth's volatiles that comets actually delivered, once these powerful discriminators have been evaluated in comets. Meanwhile, there are intriguing clues that comets may have delivered heavy noble gases to both Earth and Mars, making the possible recent delivery of water to the surface of Mars long after the planet's accretion especially interesting. This possibility is based on the isolation of the Martian lithosphere and the values of D/H in SNC minerals.

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The role of water in early solar system evolution: Insights from primitive chondritic meteorites

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Evidence from primitive chondritic meteorites shows that water was widely available in the inner solar system during the earliest stages of solar system formation. Over the last 15 years, it has become widely recognized that meteorites from essentially all the chondrite groups retain a record of interaction with liquid water early in solar system history. For many chondrites, this process occurred at low temperatures (<50°C) and resulted in replacement of primary high temperature phases by an assemblage of phyllosilicates, carbonates, sulfides, sulfates and oxides. However, recent evidence of a more cryptic nature also indicates some chondrites such as the CV, CO and ordinary chondrites experienced fluid-assisted metamorphism at temperatures in excess of 200°C.

A major topic of discussion concerns the environment under which interaction of nebular solids occurred. Many workers have proposed that the bulk of alteration occurred after accretion of asteroidal parent bodies. In this model, nebular dust accreted into asteroids along with significant quantities of water ice. Subsequent asteroidal heating resulting from the decay of short-lived radionuclides such as ²⁶Al initiated melting of the ice and the formation of liquid water. However, an alternative scenario is that at least some alteration could have occurred in the solar nebular or in ephemeral protoplanetary bodies prior to final parent body assembly. This evidence to support this so-called preaccretionary alteration is largely textural in character and is, in many cases ambiguous. These two models have interesting implications for the reservoirs of water that may have been present in the raw building blocks of the terrestrial planets. For the asteroidal alteration model, hydrous phases would have required a finite time to develop on asteroidal parent bodies. Mn – Cr dating of carbonates indicates that alteration started within ~4 Ma of CAI formation. On the other hand, for the preaccretionary model, hydrous materials (probably phyllosilicates) would have been present within the first 1-2 Ma of solar system history. In either case, it seems likely that a significant amount of water would have become sequestered in phyllosilicate phases within 10 Ma of molecular cloud collapse and been available in a relatively stable form for accretion into the terrestrial planets.

The history of water on Venus

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Remote sensing and in-situ measurements give an atmospheric water abundance of 30 PPM on Venus. The D/H ratio (150 times terrestrial) indicates a history of water loss (Donahue et al. 1997). Venus is commonly thought to have experienced an early transition from a wet, more Earth-like past to its current highly desiccated state (Kasting, 1988). The randomly distributed and relatively pristine crater population reveals a later transition, with a rapid decrease in resurfacing rate between 300 and 1000 Myr ago (Schaber et al, 1992; McKinnon et al, 1997). The accompanying decline in outgassing rate would have caused large climate changes (Bullock and Grinspoon, 2001) and globally synchronous plains deformation (Solomon et al, 1999). We are exploring the possibility that these two apparent transitions may be part of a single, continuous planetary transformation. The loss of water through evaporation, photodissociation and H escape would have led to a change from plate tectonics to single plate behavior, as the shut-off of subducting hydrated sediments led to the desiccation of the mantle and loss of an asthenosphere. Current estimates of the timescale for water loss are highly uncertain. We are modeling clouds in wet, hot atmospheres in an effort to better constrain the albedo, energy balance and timescale for water loss. If clouds stabilized the moist greenhouse and Venus' oceans persisted for several billion years, rather than the canonical (but unconstrained) hundreds of millions, then the loss of water could have initiated changes in global convective style which led directly to the observed surface features. This might mean that Venus was a (conventionally defined) habitable planet for most of its history.

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Meteoritical evidence for the timing of surface or near-surface liquid water on Mars

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There is widespread photogeological evidence for ubiquitous water flowing on the surface of Mars. Despite this observation, the absolute age of surface and near-surface water cannot be deduced from photogeology, because the uncertainty in the absolute calibration of the Martian crater flux results in uncertainties of ± 1.5 Ga in the middle period of Martian geologic history. Aqueous alteration of primary igneous minerals produces secondary minerals in Martian meteorites. Here we use the ages of secondary alteration minerals in Martian meteorites to obtain absolute ages when liquid water was at or near the surface of Mars. We find definitive evidence in Martian meteorites for aqueous alteration events at 3929 ± 37 Ma, 633 ± 23 Ma, and 0-170 Ma. These ages are based on absolute Rb-Sr and Pb-Pb ages of carbonates in ALH84001, Rb-Sr and K-Ar ages of iddingsite in two nakhlites, and the presence of secondary alteration products in several of the 170 Ma shergottites. These events appear to be of short duration, suggesting episodic rather than continuous aqueous alteration. Furthermore, the amount of secondary mineralization that is present in the meteorites appears to be decreasing with time. The 4500 Ma ALH84001 is made up of $\sim 1\%$ carbonates, the 1330 Ma nakhlites have obvious iddingsite alteration products that make up trace amounts of the meteorites, whereas some of the 170 Ma shergottites have vanishingly small amounts of various salts and clays. Although not definitive, this correlation is certainly consistent with the hypothesis that Mars has become dryer through time. The high $^{129}\text{Xe}/^{132}\text{Xe}$ ratio in the Martian atmosphere compared to Martian meteorites indicates fractionation of I from Xe within ~ 100 Ma after nucleosynthesis of ^{129}I . Such fractionation is difficult to achieve through magmatic processes. However, water very efficiently fractionates I from Xe, raising the intriguing possibility that Mars had a liquid water ocean within its first 100 Ma.

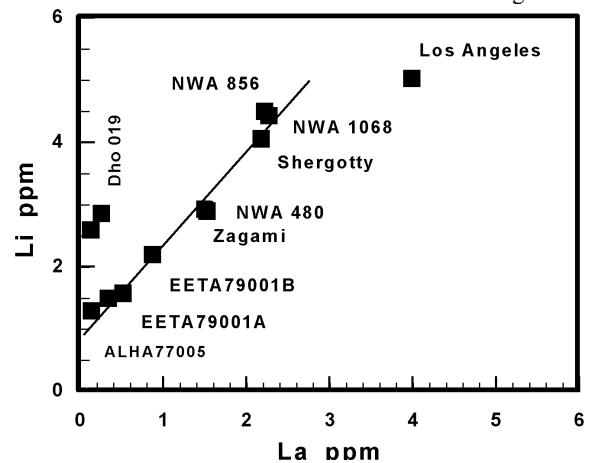
LI, CL, and BR in Martian (Shergottite) basalts: No evidence of water loss

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Shergotty and Zagami, Martian basalt meteorites (shergottites), are nearly anhydrous but may have crystallized from water-rich magmas. *McSween et al.* [2001] and *Lentz et al.* [2001] argued that decreasing abundances of Li and B, core-to-rim, in pyroxenes of Shergotty and Zagami reflect loss of an aqueous fluid from their parent magmas during crystallization. Losses of Li and B are inferred at 60-75% for Shergotty and $\sim 30\%$ for Zagami. The bulk compositions of Shergotty and Zagami should be similarly depleted in Li and B, and also be depleted in other elements that would be lost to an aqueous fluid, like Cl and Br. However, whole rock abundances of Li (Fig. 1), Cl, and Br in the shergottites show no evidence that Shergotty and Zagami were depleted (no analyses for B are available). Thus, core-to-rim decreases in Li and B in shergottite pyroxenes do not imply loss of a fluid phase, and must reflect other processes.

Fig. 1. Abundances of Li and La, both highly incompatible elements, in bulk shergottites. Nearly all fall on a single trajectory, suggesting that Shergotty and Zagami are not depleted in Li. Los Angeles is inhomogeneous. High Li in Dho019 and DaG476 is ascribed to desert weathering.



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Shock devolatilization of terrestrial impactites: Loss of fluid inclusions due to impact processing

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While impacts provided the flux of materials needed for planetary accretion, shock processing may have significantly reduced the volatile content of early planetismals. Fluid inclusions, which are abundant in terrestrial rocks, have only been observed in a few meteorites. In the past, the apparent lack of fluid inclusions has been interpreted as a lack of fluids on the parent body. However, recent experiments demonstrate that low to moderate shock pressures can effectively erase any evidence of fluid inclusions (Elwood Madden et al 2004).

This research investigates the effects of impact processing on fluids trapped in planetary materials by examining fluid inclusions in terrestrial impactites. Samples of crystalline basement rocks (granitic rocks and gneisses that experienced varying degrees of shock metamorphism) were collected from the Ries Crater and sedimentary rocks (Coconino Sandstone) were collected from Meteor Crater. Each lithology was then analyzed to determine its degree of shock-metamorphism and the percentage of quartz grains with fluid inclusions.

In both the crystalline basement and sedimentary rocks, fluid inclusions were abundant in quartz grains within samples that contained no shock features. Rocks containing planar fractures also contained fluid inclusions. Fluid inclusions were not observed, however, in samples with shock lamellae and diaplectic impact glass or in samples of partially melted Ries Crater crystalline basement rocks. However, fluid inclusions were observed within quartz grains entrained in glass in melted samples of Coconino Sandstone.

The correlation between shock and loss of fluid inclusions, plus examples of planar fractures offsetting solid inclusions, indicate volatiles trapped in fluid inclusions were lost from the rocks as a result of moderate shock deformation. This suggests that impact processing may lead to the loss of fluid inclusions and devolatilization of planetary materials.

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Oceanic temperatures recorded by the isotopic compositions of Precambrian cherts?

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"The world's oldest sedimentary rocks are cherts" [1]. As discovered by Knauth and Lowe [2] the least metamorphosed Precambrian cherts exhibit a regular increase in their $\delta^{18}\text{O}$ since 3.5 Gyr. that they attributed to the progressive cooling of the oceans.

Likely Precambrian cherts formed by the direct precipitation from seawater of amorphous silica, later transformed in micro quartz during sedimentary burial. As attested by the wide range of $\delta^{18}\text{O}$ for a given geological formation, the original isotopic signature of the amorphous silica may not be preserved during this transformation. Indeed, several isotopic exchange processes can modify the $\delta^{18}\text{O}$ of silica after its oceanic precipitation.

Since it is firmly established that all exchanges yield a decrease in $\delta^{18}\text{O}$, it has been proposed that the highest $\delta^{18}\text{O}$ values can be used as a proxy for oceanic temperatures. However it cannot be ruled out that cumulative post-depositional isotopic effects have progressively erased the original isotopic compositions of the cherts. Accordingly, the thermometric validity of oxygen isotopes in Precambrian cherts is considered by many workers as an open issue.

Cherts are made of silicon and oxygen (SiO_2). If an oxygen isotopic exchange took place between chert and water during diagenesis, its counter part for silicon isotopes can be evaluated. To try to make progress in this debate, we have measured the $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ at a micrometer scale with the 1270 Ion-microprobe in some of the Precambrian cherts having the highest known $\delta^{18}\text{O}$. We will show that (i) $\delta^{30}\text{Si}$ correlates with the highest $\delta^{18}\text{O}$ and that (ii) this correlation can be used to discuss the paleotemperatures of the archaic oceans.

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***In situ* use of microwaves to determine remotely the water content of minerals**

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The rovers Spirit and Opportunity are equipped with instruments to determine the chemistry of the minerals found on Mars. An emphasis has been placed on trying to correctly identify water-bearing minerals. While the Alpha-Particle-X-Ray spectrometer is used to determine elemental chemistry of minerals it cannot detect hydrogen. It also cannot determine the structure the minerals. These two drawbacks inhibit the direct determination of water in the samples. We propose to expose minerals to a microwave source and measure their heat gain as a method to determine if they contain water. A small microwave source and pyrometer could be included on future missions to determine if minerals contain water. To test this method we used a commercial microwave oven (2.4 GHz and 1000 Watts) and pyrometer to determine heating trends of several rock-forming minerals.

Minerals with higher amounts of water and/or hydroxide content should heat more than those with less amounts of water when exposed to microwaves over the same period of time. Minerals showed different heating patterns based on their water and or hydroxide content. Minerals that contained no water or hydroxide in their structure (i.e. quartz, calcite, anhydrite) showed little temperature increase with microwave heating. Clay minerals and zeolites showed a general increase in temperature with time. Borate minerals showed patterns of heating with time based on the amount of water and/or hydroxide contained in their structure.

Generally, minerals showed heating trends based on their water and/or hydroxide content: minerals with little or no water heated less over time, while minerals containing abundant water heated more over time. There were exceptions to the hypothesis, which indicate that other bonds may be microwave active. More experiments and a better theoretical understanding of the interactions of microwaves with minerals are needed before this method could be used to remotely determine water content. However the method shows promise as a means to determine the water content of rock-forming minerals, and possibly, by changing the frequency of the microwaves, to determine other chemical constituents of minerals.