

WATER MATTERS. M. J. Drake and M. Stimpfl, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721-0092, USA, drake@lpl.arizona.edu

Introduction. Water matters. It is essential to life, it modulates climate, and yet its origin on Earth and the other rocky planets is uncertain. It has long been accepted that temperatures in the accretion disk in the region of the terrestrial planets were too high for hydrous phases to exist [1]. Thus the view is widespread that the Earth and other terrestrial planets accreted “dry” from anhydrous materials, and accreted water from comets or hydrous asteroids. There are problems with both sources that require special, but not impossible, circumstances to make them credible sources of Earth’s water [2].

What’s wrong with comets? The D/H ratio of cometary water is a useful tool for examining cometary contributions of water. The most straightforward interpretation of the D/H ratios in comets is that comets cannot have provided a significant fraction of Earth’s water (Fig. 1). Further, the Ar/water ratios (all but one upper limits) measured by [3, 4] in several comets, if both accurate and representative of all comets, limits cometary addition of water to Earth to at most 1%.

It has been pointed out that cometary ratios are similar to the lowest measured Martian D/H ratios, which Leshin et al. [5] conclude are representative of the Martian interior. However, Mars does not exhibit plate tectonics and it is possible that values measured at the surface and in the atmosphere are reflecting exogenous delivery over 4.5 Ga and that the D/H ratio inherent to Mars is unknown [2]. In any case, why Mars would end up with a different D/H ratio than Earth is unexplained.

It is also unclear if the D/H ratios measured spectroscopically and with the Giotto spacecraft mass spectrometer are truly representative of the interiors of comets. Laboratory experiments by Moores et al. [6] and Weirich et al. [7] show that the measured D/H ratio of sublimating water ice is strongly dependent on the physical nature of cometary material (Figs. 2, 3). Even if spectroscopically measured D/H ratios are representative of the bulk comets, it is possible that none of them are representative of cometary material hitting Earth and the other terrestrial planets 4.5 Ga ago.

What’s wrong with asteroids? Hydrated asteroids have been postulated as a source of Earth’s water [8]. It certainly seems probable that a small fraction of asteroidal material from the Main Belt collided with Earth at the end of accretion. For water to remain at the surface, such delivery of water would have to be made after effective segregation of metal in the core, else the water would be broken down into hydrogen, which would form iron hydride and be sequestered in the core, and OH, which would oxidize the mantle [9]. Thus the fate of late accreting water is inextricably connected by timing to the source of the highly siderophile element “late veneer” [10].

The late delivery of water from asteroids can be examined by looking at the Os isotopic signature of the “late veneer”. Figure 4 shows that Os isotopes in both Earth and Mars are quite unlike any hydrous meteorite falling to Earth today. Os isotopes in Earth’s primitive upper mantle (PUM) have an ordinary chondritic signature, while Os isotopes in Mars are unlike any known meteorites.

The fact that Mars does not resemble any meteorite falling to Earth today could be used to argue that hydrous asteroids colliding with the terrestrial planets 4.5 Ga ago were unlike those currently bombarding the inner solar system, and comparison with present day meteorite types is therefore irrelevant. We must also remember that anhydrous ordinary chondritic meteorites hitting the Earth today could come from a metamorphosed exterior of an S-type asteroid that is still hydrous in its interior, raising the possibility of reconciling Os isotopes in Earth’s primitive upper mantle with the delivery of water from the same body.

The promise of adsorption. Because of the problems raised with cometary and asteroidal sources of water in the Earth and other terrestrial planets, Drake [2] considered other sources. In particular, he noted that grains in the accretion disk were bathed in an atmosphere of hydrogen, helium, oxygen, and some hydrogen and oxygen combined to form water. Thus adsorption of water onto grains in the accretion disk might be the source of some or all of the water in the terrestrial planets. This concept has been developed quantitatively by Stimpfl et al. [11, 12] and will only be summarized here. Water adsorbs onto olivine grains forming bonds of ~50 kJ/mole to greater than 200 kJ/mole. Strong bonds favor the retention of water during impacts. Further, Canup and Pierazzo [13] showed that significant fractions of water were retained in some giant impacts, although not in late grazing impacts of the sort currently favored to explain the origin of the Moon. Thus it seems promising that some water in the terrestrial planets was obtained directly from the gas in the accretion disk.

Obvious questions not yet addressed are whether the observed D/H ratio in Earth’s oceans can be obtained directly by adsorption? If not, will mixing with a cometary or asteroidal reservoir yield the observed ratio? Further, can approximately 5 Earth oceans of water [14] be obtained by adsorption? If Leshin et al. [5] are correct and Mars really does have a different inherent D/H ratio than Earth, why are two planets that are so close in heliocentric distance so different in their water sources?

Conclusions. The questions raised in this work are testable with more measurements on natural materials, laboratory experiments, and numerical calculations. Measurements of D/H and Ar/water ratios in more comets is of obvious importance. Is it simply a coinci-

dence that comets Halley, Hyakutake, and Hale-Bopp have the same D/H ratio? Direct measurements of the D/H ratio in Martian ice are essential, and will hopefully be made by the Phoenix spacecraft. Laboratory measurements of the evolution (if any) of the D/H ratio of sublimating water ice in a realistic cometary simulant are needed. Finally, numerical experiments on the adsorption of water onto grains are only in their infancy [11, 12].

References.

[1] Boss A.P. (1998) *Ann. Rev. Earth Planet. Sci.* **26**, 26-53.
 [2] Drake M.J. (2005) *Meteoritics and Planetary Science* **40**, 519-527.
 [3] Weaver H.A., Feldman P.D., Combi M.R., Krasnopolsky V., Lisse C.M. and Shermansky D.E. (2002) *Astrophys. J.* **576**, L95-L98.
 [4] Stern S.A., Slater D.C., Festou M.C., Parker J.W., Gladstone G.R., A'Hearn M.F., and Wilkinson E. (2000) *Astrophys. J.* **544**, L169-L172.
 [5] Watson (Leshin) L., Hutcheon I.D., Epstein S., and Stolper E.M. (1994) *Science* **265**, 86-90.
 [6] Moores J.E., Brown R.P., Lauretta D.S., and Smith P.H. (2005) *Lunar and Planetary Science XXXVI*, # 1973.
 [7] Weirich J.R., Brown R.H., and Lauretta D.S. (2004) *Bull. Amer. Astron Assoc.* **36**, 1143.
 [8] Morbidelli A., Chambers J., Lunine J.I., Petit J.M., Robert F., Valsecchi G.B., and Cyr K. (2000) *Meteoritics and Planetary Science* **35**, 1309-1320.
 [9] Okuchi T. (1997) *Science*, **278**, 1781-1784.
 [10] Chou C-L., Shaw D.M., and Crocket J.H. (1983) *Jour. Geophys. Res.* **88**, A507-A518.
 [11] Stimpfl M., Walker A.M., Drake M.J., de Leeuw N.H., and Deymier P. (2006) *Journal of Crystal Growth* **294**, 83-95.
 [12] Stimpfl M., de Leeuw N.H., Drake M.J., and Deymier P. *Lunar and Planetary Science XXXVIII* (this volume).
 [13] Canup R.M. and Pierazzo E. (2006) *Lunar and Planetary Science XXXVII*, # 2146.
 [14] Ohtani E. (2005) *Elements* **1**, 25-30.
 [15] Drake M.J. and Righter K. (2002) *Nature* **416**, 39-44.

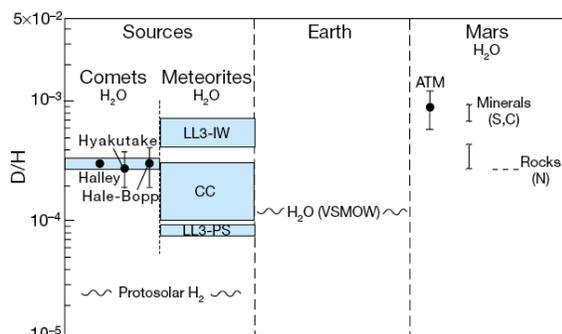


Fig. 1. The D/H ratios in H₂O in three comets, meteorites, Earth (Vienna standard mean ocean water - VSMOW), protosolar H₂, and Mars. "CC" = carbonaceous chondrites, "LL3-IW" = interstellar water in Semarkona, "LL3-PS" = protostellar water in Semarkona. After [15].

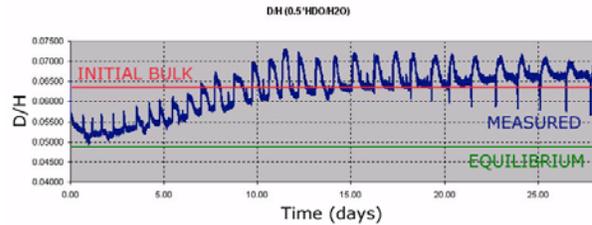


Fig. 2. Measured D/H ratios of pure deuterated water ice as a function of time during sublimation. From [6].

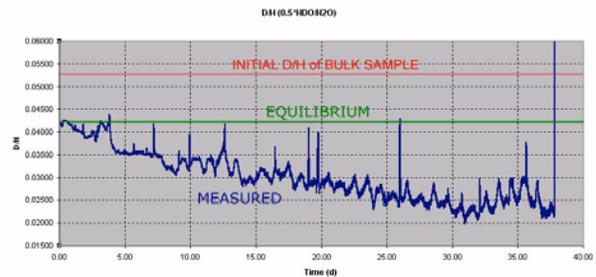


Fig. 3. Measured D/H ratios of 75% deuterated water ice and 25% TiO₂ as a function of time during sublimation. From [7].

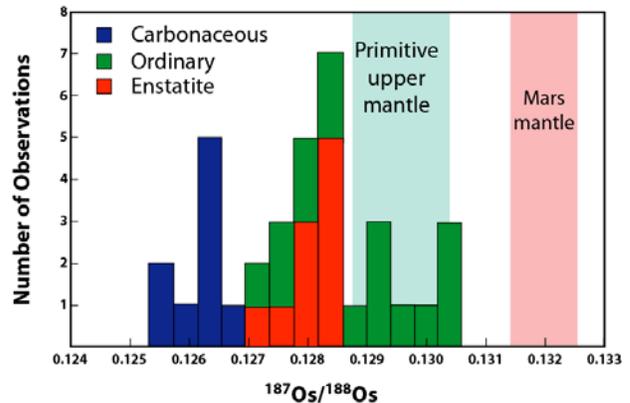


Fig. 4. ¹⁸⁷Os/¹⁸⁸Os ratios in carbonaceous, ordinary, and enstatite chondrites, and in the Earth's primitive upper mantle (PUM), are distinct and are diagnostic of the nature of the Earth's "late veneer". Mars is not plotted because the uncertainty in its initial ¹⁸⁷Os/¹⁸⁸Os ratio is larger than range of the X-axis. After [15].