

## Isotopic compositions of asteroidal liquid water trapped in fluid inclusions of chondrites.

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### Introduction:

The origin of the water of terrestrial planets remains one of the primary issues of planetary sciences. It is believed that terrestrial planets formed inside of the water ice evaporation line (snow line) in the solar nebula where it was difficult to trap water components. It is useful to use isotopic compositions as a tracer in order to discuss the origin and evolution of materials, but we have little knowledge of isotopic compositions of extraterrestrial water components. In particular, there is no report of isotopic compositions of extraterrestrial liquid water.

Aqueous fluid inclusions contained within crystals of halite in two ordinary chondrites are the only extraterrestrial liquid water samples available for laboratory measurements [1]. Because chondrites are primitive materials in the solar system and chondrite-like materials formed the terrestrial planets, isotopic compositions of chondritic liquid water provide a direct evidence to reveal the origin of water of terrestrial planets. The fluid inclusions were found in halite (NaCl) and sylvite (KCl) (hereafter collectively called "halite") from two ordinary chondrite regolith breccias (Monahans (1998), hereafter simply "Monahans" (H5), and Zag (H3-6)) [1, 2]. Both meteorites contain millimeter to centimeter-sized aggregates of blue to purple halite containing aqueous fluid inclusions in the matrix. The halite grains were dated by K-Ar, Rb-Sr and I-Xe systematics to be ~4.5 Ga [1, 3, 4], and thus the trapped aqueous fluids are at least as ancient. These halite grains are blue to purple owing to the gradual accumulation of trapped electrons in cation vacancies, resulting, probably, from the beta decay of <sup>40</sup>K. Since recently recrystallized halite would be colorless, fluid within the colored halite grains must be pre-terrestrial in origin. Heating/freezing studies of the fluid inclusions in Monahans halite grains demonstrated that they were trapped at approximately 25°C [1], and their presence in the halite requires their incorporation into the H chondrite asteroid after metamorphism, as heating would have released fluids from halite.

Large variations of hydrogen isotopic composition have been observed in hydrous minerals

from chondrites [5]. Cometary and interstellar water is highly D-enriched [6, 7], representing cloud or outer solar disk chemistry. The hydrogen isotopic composition of hydrous minerals in chondrites is believed to reflect inner solar system water.

Oxygen isotopes in the solar system are also highly variable [8, 9], reflecting contributions of an H<sub>2</sub>O component [10, 11]. However, it is impossible to measure isotopes of hydrogen and oxygen simultaneously in hydrous minerals, because they invariably contain structural oxygen not bound in water. Halite contains no structural oxygen or hydrogen, allowing the isotopic composition of oxygen and hydrogen in aqueous fluid inclusions to be measured. Thus, fluid inclusions in halite have the potential to reveal unique information regarding the origin and activity of aqueous fluids in the early solar system. This information contains, and perhaps uniquely identifies, the source of the aqueous fluid from which the halite precipitated.

Here we report direct measurement of the hydrogen and oxygen isotopic compositions of the aqueous fluid in halite fluid inclusion by cryo-secondary ion mass spectrometry (Cryo-SIMS), and discuss the origin of this water [12].

### Experimental:

The isotopic measurement of individual aqueous fluid inclusions in halite requires a secondary ion mass spectrometer equipped with a cryo-sample-stage, which is not a typical instrument configuration. A Cameca ims-1270 SIMS instrument equipped with a cryo-sample-stage at Hokkaido University was prepared for the measurements. The cryo-sample-stage (Techno. I. S. Corporation) was placed in the sample chamber in place of the original sample stage and cooled down to about -190°C using liquid nitrogen. At this temperature the aqueous fluid (a brine) in fluid inclusions was frozen. The operating vacuum in the sample chamber was maintained at less than 2x10<sup>-9</sup> Torr.

### Results and Discussion:

Hydrogen isotopes of the aqueous fluid inclusions ranged from -400 to +1300‰ on the δD scale. This distribution spans the entire range of

aqueously-altered minerals of chondrites and comparable to those of comets and icy satellites of outer planets, but is extremely D-rich compared with outer planets. Oxygen isotopes of the aqueous fluids fractionated mass-independently ranging from -15 to +30‰ in the  $\Delta^{17}\text{O}$  scale. The degree of  $^{16}\text{O}$ -depletion is larger in the aqueous fluid than the most  $^{16}\text{O}$ -depleted astromaterial magnetite formed by aqueous alteration on asteroids identified so far. The variation of oxygen isotopes of fluid inclusions is unique among solar system objects so far. The highly heterogeneous isotopic compositions between inclusions being heavily fractionated for hydrogen and mass-independently fractionated for oxygen, indicate that aqueous fluids were in isotopic disequilibrium before being trapped in halite.

None of our data are equivalent to isotopic compositions of ordinary chondrite water, demonstrating that these fluid inclusion fluids are not related to indigenous ordinary chondrite fluids. The isotopic compositions are highly scattered, but the D-rich fluids tend to be  $^{16}\text{O}$ -poor. These highly disequilibrium characteristics are consistent with highly disequilibrium mineralogy of solid inclusions also trapped in these halites, suggesting a relation to water/rock reactions in some carbonaceous chondrites.

Isotopic compositions of water in carbonaceous chondrites are in the range of -500 to +100‰ for  $\delta\text{D}$  [13] and -5 to +2‰ for  $\Delta^{17}\text{O}$  [9]. The halite fluid inclusion brines plot outside the region of estimated carbonaceous chondrite water. Therefore, a more D-rich and  $^{16}\text{O}$ -poor source is required for these fluids. Extremely D-rich water has been reported from comets. Another observation of extremely D-rich water is from Enceladus [14]. It is known that extremely  $^{16}\text{O}$ -poor oxygen has a close relationship with cometary water. Therefore, highly D-rich and  $^{16}\text{O}$ -poor water is expected in comets and icy satellites of outer planets (hereafter collectively called "cometary water").

The isotopic compositions of the Monahans fluids can be explained by results of water-rock interaction between cometary water and hydrous carbonaceous chondrite. The Zag fluids represent the direct mixing of carbonaceous chondrite water and cometary water. The isotopic compositions of fluid inclusion fluids suggest that the fluids are products of water-rock interaction with cometary water on carbonaceous chondrite parent asteroids.

The cometary water was delivered by impacting comets onto the asteroids. Aqueous fluid formed from the cometary ice percolating into the asteroids. The aqueous fluid reacted with surrounding rock containing phyllosilicates to change the isotopic compositions of the water. The fluid became supersaturated in halites to trap fluid inclusions at  $\sim 25^\circ\text{C}$  (Zolensky et al., 1999). Some cometary water directly mixed with indigenous water probably formed from dehydrated phyllosilicates or melted

interior ice that formed in inner solar system. The precipitated halites were delivered to ordinary chondrite parent asteroids of Monahans and Zag by impacts or cryovolcanoes [15].

The water-rock interaction also may occur on ordinary chondrite parent asteroids because enrichments of deuterium in water might occur during thermal processes on ordinary chondrite parent asteroids and the chemical compositions are also chondritic. If so, isotopic compositions of ordinary chondrite water may originally resemble carbonaceous chondrite water. However, the particular mineral assemblage and organic components of the solid inclusions observed in Monahans and Zag halite require carbonaceous chondrite-like asteroids for the water-rock interaction site [15]. In any case, because chondritic and cometary waters are believed to have originated in the inner solar nebula [5, 13] and outer solar nebula to molecular cloud [16], respectively, the isotopic compositions of the halite fluids suggest that dynamic delivery and accretion of water originated throughout the solar system and in the parent molecular cloud onto planetesimals was a fundamental mechanism in the evolution of present planetary water. Isotopic composition of lunar rock water [17] suggests that the global water mixing or delivery processes in the solar system continued at least until the time of the Moon's formation and early evolution.

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