

## CO<sub>2</sub>-bearing fluid discovered in a meteorite: evidence of dynamic evolution of the solar system

Water is abundant in our solar system. Even outside of our own planet, water of different states and quantities has been detected, for example, ice on the moon, in Saturn's rings and in comets, liquid water on Mars and under the surface of Saturn's moon Enceladus, and traces of water vapor in the atmosphere of Venus. Water played an important role in the early evolution and formation of the solar system.

Many researchers have searched for evidence of liquid water in extraterrestrial materials such as meteorites. Most meteorites originate from asteroids that formed in the early solar system (e.g., [1]). It is widely accepted that minerals and ice were accreted together to form asteroids outside the snowline where it was cold enough for volatile components such as H<sub>2</sub>O to condense into ice grains. Aqueous alteration by reactions of melted ice with anhydrous minerals occurred. This was recorded in some primitive meteorites called carbonaceous chondrites in which water is mostly present as hydroxyls and molecules in hydrous minerals, which are basically crystalline with some ionic or molecular water incorporated within them. Liquid water is expected to remain as fluid inclusions in minerals that precipitated in aqueous fluid. However, thus far, the only fluid inclusions from the early solar system have been those in salt (NaCl) crystals in less primitive ordinary chondrites [2], although their origin is not clear.

In searching for water inside meteorites, we focused on mineral grains of calcite  $(CaCO_3)$  in the Sutter's Mill meteorite, which is categorized as an aqueously altered Mighei-type (CM) carbonaceous chondrite. We reported the presence of  $CO_2$ -bearing fluid inclusions in a calcite grain for the first time and

used the results to infer the origin of the meteorite parent body [3].

We conducted a specific analysis protocol to search for fluid inclusions, systematically combining scanning electron microscopy (SEM), focused-ion beam (FIB) microsampling, synchrotron radiationbased X-ray computed nanotomography (SR-XnCT) and transmission electron microscopy with a cryostage (cryo-TEM). We examined polished sections of the Sutter's Mill meteorite and searched for calcite grains appropriate for the present analysis (Fig. 1(a)). Grains ~30  $\mu m$  in size were selected and extracted using FIB. The samples were imaged using SR-XnCT to obtain their three-dimensional (3D) images with absorption and phase-shift contrasts at SPring-8 BL47XU (e.g., [4]) with the spatial resolution of ~100 nm. Then, we found many inclusions larger than a few micrometers (micron-sized inclusions) inside the calcite grains (Fig. 1(b)). Most of them have facets suggesting the presence of water inside the inclusions. However, unfortunately, the inclusions were empty. The water that used to be there must have escaped sometime over the last 4.6 billion years.

When we took a much closer look, we found innumerable nanosized inclusions in the calcite (smaller than 1  $\mu$ m) (Fig. 1(b)), where water might remain. We extracted areas containing these nanosized inclusions using FIB and TEM sections were made (Fig. 2(a)). If water is to be found there, it must have been frozen in there at low temperatures; then, TEM would be able to detect the crystalline ice using electron diffraction at low temperatures. In the TEM observation, in addition to finding diffraction spots that indicated calcite crystals at room temperature (20°C), new spots appeared at -100°C (Figs. 1(b,c)).



Fig. 1. SEM and XCT slice images of calcite grains. (a) Backscattered electron SEM image showing a typical calcite grain in matrix (a). (b) Absorption XCT image at 7 keV showing micron-sized inclusions and a large number of nanosized inclusions.



Fig. 2. TEM images of nanosized inclusions in calcite and SAED pattern of a nanosized inclusion in cryo-TEM. (a) Bright-field image of nanosized inclusions in calcite. They are distributed as bands. (b) STEM image. One inclusion (arrowed) has extra diffraction spots in cryo-TEM observation. (c) Selected-area electron diffraction (SAED) pattern of an area including the nanosized inclusion in (b) (arrow) cooled at 173 K. Yellow arrows show spots appearing only at 173 K.

These spots were identified not as ice formed by freezing water (H<sub>2</sub>O) but as ice that is called CO<sub>2</sub> ice or CO<sub>2</sub> hydrate (CO<sub>2</sub>•5.75H<sub>2</sub>O). That is, the liquid in the inclusion was not simple liquid water (H<sub>2</sub>O) but a fluid that contained CO<sub>2</sub>. The ratio of CO<sub>2</sub> was found to be above 15% on the basis of the phase diagram of the system CO<sub>2</sub>-H<sub>2</sub>O. In addition, such CO<sub>2</sub>-bearing fluid should exist at pressures of possibly >~200 bars that corresponds to the depth of an asteroid deeper than ~100 km.

From the existence of the  $CO_2$ -bearing fluid, it is possible to narrow down the area in which the asteroid or a meteorite's parent body was formed. In the early solar system, the low-temperature regions far from the sun had snow lines where ice of H<sub>2</sub>O, CO<sub>2</sub>, and CO would appear in that order. The present finding



Fig. 3. H<sub>2</sub>O, CO<sub>2</sub>, and CO snow lines and formation of parent body of Sutter's Mill meteorite. During the evolution of the early solar system, the nebular accretion rate  $\dot{M}$  decreased with time and the distances of the snow lines from the Sun decreased. A possible region of formation of parent body of Sutter's Mill meteorite is bounded by CO<sub>2</sub> and CO snow lines and the ice-depleted region. Current orbits of Jupiter and Earth are also shown.

indicates that the parent body of the Sutter's Mill meteorite was formed outside the  $CO_2$  snow line but inside the CO snow line (Fig. 3).

In recent solar system formation theories, it is considered that planets and small celestial bodies did not remain in the same location as their formation, but rather, their orbits changed (or moved) after their formation [5]. Following this model, Jupiter would have been formed inside the current orbit and later moved to its current location. If we were to infer the formation regions of the celestial bodies from the snow line, the parent body of the Sutter's Mill meteorite would have been formed in the low-temperature region outside the region where Jupiter was formed. Then, along with Jupiter's orbital change, it moved inward towards the main asteroid belt between Mars and Jupiter. The discovery of water containing CO<sub>2</sub> also raised the credibility of the new dynamic solar system formation model.

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