

## NANO-SIZED CO<sub>2</sub>-H<sub>2</sub>O FLUID INCLUSIONS IN CALCITE GRAINS OF THE SUTTER'S MILL CM METEORITE.

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**Introduction:** Aqueous fluids in the early Solar System are preserved in some H chondrites as aqueous fluid inclusions in halite (e.g., [1]). Candidates for fluid inclusions have been found in carbonate grains of carbonaceous chondrites (Ivuna CI and Sutter's Mill CM meteorites) using nano-microtomography [2]. These inclusions are typically a few micron meters in size and some of them have facets (negative crystals). However, further analysis using phase contrast tomography showed that they are empty probably because fluids have been already escaped even if fluid used to be present [3,4]. Instead, some inclusions are filled with insoluble organic matter (IOM) in the Sutter's Mill meteorite [5]. IOMs were also recognized in carbonate grains of different CM chondrites [6]. In this paper, we report the most probable presence of fluid as nano-sized inclusions in calcite grains of the Sutter's Mill meteorite.

**Experimental:** The Sutter's Mill CM meteorite contains calcite grains <~a few  $\mu\text{m}$  in size [4]. Thin sections of calcite ~400 nm in width were extracted using focused ion beam (FIB) system (Helios Nano Lab G3; Thermo Fisher Scientific) from a polished thin section of the meteorite. A thin section was also prepared from a box-shaped sample, which has been examined by nanotomography [5]. These sections were observed using a (S)TEM/EDS system (JEM-2100F/JED-2300T; JEOL) with a cryogenic holder (G636; Gatan).

**Results:** A large numbers of very tiny inclusions <100 nm in size were observed in TEM sections. Some of them have facets. They are distributed along twin boundaries or concentrated in regions of single crystals. The three-dimensional structure obtained by the nanotomography shows that they form a zonal structure.

Extra diffraction spots appeared at -100°C together with host calcite spots in selected area electron diffraction (SAED) pattern, which was obtained from a single crystal region including a nano-sized inclusion. These extra spots were disappeared when the temperature raised to the room temperature (~20°C). Then, additional extra spots appeared after the sample was kept at the room temperature overnight. When the temperature decreased to -100°C again, the first extra spot appeared again while the spots at the room temperature disappeared. The extra spots at -100°C cannot be indexed by any hexagonal and cubic H<sub>2</sub>O ice but indexed by CO<sub>2</sub> ice or CO<sub>2</sub> clathrate (CO<sub>2</sub>·nH<sub>2</sub>O; n=5.75 in the ideal formula). The additional spots at the room temperature can be indexed probably by aragonite but the possibility of ikaite or monohydrocalcite (CaCO<sub>3</sub>·H<sub>2</sub>O) cannot be excluded.

The EDS spectrum showed that C and O in the inclusion seem to be more abundant than those expected from the CaCO<sub>3</sub> stoichiometry. Some inclusions have tiny objects, which is rich in P and have diffraction spots indexed by apatite.

**Discussion:** The present SAED and EDS results strongly suggest that CO<sub>2</sub>-H<sub>2</sub>O fluid is present in the inclusion; CO<sub>2</sub> ice or clathrate formed by freezing the fluid at -100°C and melted at the room temperature. According to the phase diagram in the system CO<sub>2</sub>-H<sub>2</sub>O [7], the mole fraction of CO<sub>2</sub> in the fluid should be >~0.15 because no H<sub>2</sub>O ice was present at -100°C. The delayed appearance of CaCO<sub>3</sub> (or CaCO<sub>3</sub>·H<sub>2</sub>O) phase at the room temperature can be explained by the increase in the CaCO<sub>3</sub> solubility with decreasing temperature [8] and crystallization kinetics as follows. When the fluid inclusion saturated with calcite at the room temperature cooled some amount of calcite dissolved into the fluid due to higher solubility at lower temperature. The fluid, which experienced cooling, became supersaturated with CaCO<sub>3</sub> (or CaCO<sub>3</sub>·H<sub>2</sub>O) phase at the room temperature, but any CaCO<sub>3</sub> phase did not crystallized instantaneously at the room temperature due to the kinetic hindrance, and finally some CaCO<sub>3</sub> phase crystallized as time advanced.

It is most probably from the above discussion that we found early Solar System fluid in nano-sized inclusions in calcite of a carbonaceous chondrite, which suffered strong aqueous alteration. This early Solar System fluid contains CO<sub>2</sub> as well as H<sub>2</sub>O. We could not find any extra spots at -100°C for inclusions along twin boundaries, suggesting that fluid escaped along the twin boundaries over time. In contrast, fluid in very tiny inclusions in single crystals remained. Larger fluid inclusion candidates, such as negative crystals, should once contain CO<sub>2</sub>-H<sub>2</sub>O fluid, which has escaped over ~4.6 billion years.

**References:** [1] Zolensky M. E. et al. 1999. *Science*, 285:1377-1379. [2] Tsuchiyama A. et al. (2014) *Meteoritics & Planetary Science*, 49:A5152. [3] Zolensky M. E. et al. (2014) *Meteoritics & Planetary Science*, 49:1997-2016. [4] Tsuchiyama A. et al. (2016) *JpGU Meeting2016*, Abstract PPS12-11. [5] Tsuchiyama A. et al. (2017) *JAMS 2017 Annual Meeting*, Abstract. [6] Chan Q. H. S (2017) *Geochimica et Cosmochimica Acta* 201:392-409. [7] Longhi, J. (2005) *Geochimica et Cosmochimica Acta*, 69:529-539. [8] Plummer L. N. and Busenburg E. (1982) *Geochimica et Cosmochimica Acta*, 46:1-11-1040.