

Preface: Evolution of refractory grains, volatiles, and organic molecules from the interstellar medium to the early solar system

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Primitive extraterrestrial materials record the early evolution of the solar system that predated planet formation. They also preserve the interstellar heritage from prior to the Sun's birth in the form of presolar grains and potentially as isotopic signatures of light elements in organic matter and specific molecules. It is one of the key issues in cosmochemistry to link the birth and evolution of the solar system to the evolution of the interstellar medium (ISM) and the Galaxy. To address this issue, an interdisciplinary approach linking analysis of extraterrestrial materials including samples returned by spacecraft, laboratory experiments, astronomical observations, and theoretical studies is crucial.

This special issue arose from a session "Refractory Grains, Volatiles, and Organic Molecules Inherited from the Interstellar Medium" at the Goldschmidt Conference (Aug. 25–30, 2013, Florence Italy) and consists of six articles covering a wide array of topics and disciplines to explore various perspectives of cosmochemistry; astronomical observation, laboratory experiments, extraterrestrial organic chemistry, astrophysical modeling, in-situ isotopic analyses, chronology, and sample-return mission.

Dartois *et al.* (2014) summarize observational and laboratory studies on interstellar carbonaceous dust to explore the link between ISM carbonaceous dust and insoluble organic matter (IOM) found in chondrites and interplanetary dust particles (IDPs). Several forms of carbonaceous solids are observed in the ISM (polyaromatic hydrocarbons (PAHs), amorphous carbons, hydrogenated amorphous carbons (a-C:H), fullerenes, and ices that further turn into macromolecular organic residues after ice-sublimation), among which PAHs, a-C:H and/or macromolecular organic residues would be the main precursor of solar system carbonaceous materials. PAHs and a-C:H are more aromatic and contain less oxygen and nitrogen than solar-system IOM. Organic matter formed

by photolysis and/or radiolysis of ice in laboratories do not match the entire infrared spectral features of IOMs either. These lines of evidences indicate that further evolution of organic materials may have occurred in the early stage of solar-system formation from ISM carbonaceous dust as a precursor.

The evolution of organic matter in the early solar system may also be recorded in soluble organic components extracted from primitive meteorites. Yamashita and Naraoka (2014) report two homologous series of alkylpyridines ($C_nH_{2n-5}N$ and $C_nH_{2n-7}N$) identified in the methanol extract of the Murchison meteorite by liquid chromatography/high-resolution mass spectrometry. The organic components consisting of C, H, and N are likely to have escaped chemical oxidation during parent body alteration and may thus record the early stage of formation of meteoritic organic components. Laboratory simulation experiments involving HCHO, CH₃CHO, and NH₃ produced alkylpyridines, which provided a plausible synthetic pathway for meteoritic alkylpyridines via aldol condensation and Chichibabin-type reactions (alkylpyridine formation from aldehydes and NH₃). Their findings indicate the possible importance of aldehyde activity under alkaline conditions in the presence of ammonia for the chemical evolution of soluble organic matter in carbonaceous chondrites.

Water is one of the dominant volatile components in the solar system, and played many essential roles in solar system chemistry through interactions with minerals and organic matter. Tornow *et al.* (2014) model the formation, destruction and re-formation of water molecules during the earliest stage of star formation (a quasi-stationary molecular cloud core and its collapse to form a protostar) focusing on the evolution of the D/H ratio. Their model show that the D/H ratios of water in the gas and dust phases change spatially and temporally and that their D/H ratios are higher than the solar-system meteoritic water. The model thus infers that the relatively low D/H ratio of solar-system meteoritic water may be related to the later evolutionary stage of the protosolar disk.

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The inner solar system water might have had low D/H ratios, but it has not yet been clear how many water sources were present in the early solar system and how such water inventories interacted with each other. Yurimoto *et al.* (2014) report the first H and O isotope measurements of asteroidal liquid water, found as fluid inclusions in halite crystals from two H chondrites (Monahans and Zag), with a secondary ion mass spectrometer equipped with a cryo-sample stage (Cryo-SIMS). Highly variable H and O isotopic compositions were found in the fluids inclusions; $-400 < \delta D < +1300\text{‰}$ and $-20 < \Delta^{17}\text{O} < +30\text{‰}$. This indicates that asteroidal aqueous fluids had at least two sources (inner solar-system chondritic water and outer solar-system cometary water) and that the fluids with various mixing degrees were in isotopic disequilibrium before trapped into halite on the parent body (bodies) of H chondrites. Yurimoto *et al.* (2014) concluded that such various degrees of water-rock interaction on planetesimals may be the fundamental evolution pathway of planetary water. We should note that this new and challenging technological approach has allowed it to analyze the isotopic compositions of asteroidal fluids for the first time.

The dating of early solar-system materials is crucial to investigate the evolution of the solar system, and short-lived radionuclides such as ^{26}Al and ^{53}Mn have been used as high-precision chronometers. Nagashima *et al.* (2014) investigate Al–Mg isotope systematics in mineralogically pristine chondrules from unmetamorphosed CR2 (Renazzo-type) carbonaceous chondrites with secondary ion mass spectrometry. The CR chondrites are among the most primitive chondrites; they experienced various degrees of aqueous alteration, but largely avoided thermal metamorphism. Resolvable ^{26}Mg excesses, correlated with Al/Mg ratios, were observed in six out of 14 chondrules, and their inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios, $(^{26}\text{Al}/^{27}\text{Al})_0$, ranged from $\sim 1 \times 10^{-6}$ to $\sim 6 \times 10^{-6}$. Other eight chondrules showed no detectable ^{26}Mg excesses with an upper limit of $(^{26}\text{Al}/^{27}\text{Al})_0 \sim (2\text{--}3) \times 10^{-6}$. These lower $(^{26}\text{Al}/^{27}\text{Al})_0$ ratios for CR chondrules than those in other primitive chondrites indicate that high-temperature chondrule formation processes occurred in the CR chondrite forming region $\sim 1\text{--}2$ Myr later than other chondrite forming regions.

Sample-return missions such as Apollo, Stardust, Genesis, and Hayabusa, have contributed significantly to the progress of cosmochemistry. Tachibana *et al.* (2014) outline the Hayabusa2 sample-return mission to the C-type near-Earth asteroid 1999 JU₃ (2014–2020), focusing on the cosmochemical importance of returned samples from the asteroid. C-type asteroids are expected to preserve the most pristine materials in the solar system, a mixture of minerals, ice, and organic matter that interact with each other, and record the cosmochemical evolution from the interstellar medium to the early solar system. Space mis-

sions are the only way to obtain such pristine materials with geologic context and without terrestrial contamination. The samples from the surface of this asteroid will also provide a precious opportunity to study current surface geological activities and the orbital evolution of the asteroid. The Hayabusa2 and NASA's OSIRIS-REx sample-return mission to the B-type asteroid Bennu (2016–2023) (Lauretta *et al.*, 2014) will open a new era in cosmochemistry in the early 2020's.

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