Highly variable ¹⁵N-enrichments in Solar System reflect different routes of interstellar N isotopic fractionation

BONAL L.*, HILY-BLANT P., FAURE A. AND QUIRICO E.1

¹IPAG , Institut de Planétologie et d'Astrophysique de Grenoble, UJF-Grenoble 1 / CNRS-INSU, France, [lydie.bonal@obs.ujf-grenoble.fr]

Large nitrogen (N) isotopic variations are observed in our Solar System ($^{14}N/^{15}N \sim 50$ to 450), with most of the objects being ¹⁵N-enriched compared to the presolar nebula (PSN, $^{14}N/^{15}N = 442$) [1]. We suggest that these variations originate from distinct sampled N interstellar reservoirs. Indeed, Nbearing molecules detected towards dark clouds may be divided into two groups, whether they carry the amine (-NH) or nitrile (-CN) chemical function. Our recent observations towards interstellar dense clouds, together with a review of data from the literature, suggest these two reservoirs are characterized by distinct isotopic ratios [2]. Compared to the PSN, (i) nitrile carriers (e.g., HCN) might be systematically enriched in ¹⁵N ¹⁴N/¹⁵N=100-320 and (ii) amine carriers (e.g., NH_3) are characterized by comparable isotopic ratios ($^{14}N/^{15}N$ \sim 400). Gas-phase chemical networks suggest that nitriles derive from N while amines are formed via N⁺, product of the dissociative ionization of N₂. The ¹⁴N/¹⁵N exchange reactions are therefore different for nitriles and amines, most likely with different timescales and efficiency [2], explaining the differential fractionation of these two reservoirs.

The proposed scenario [2] appears to explain several observations on Solar System objects. In particular, the absence of significant ¹⁵N-enrichments in interstellar clouds, as previously assumed, is no longer a valid argument to reject an interstellar origin of organic precursors in primitive cosmomaterials.

[1] Marty et al (2010) GCA 74, 340 [2] Hily-Blant et al. (2013) Icarus 223, 582.

A bimodal crystallite size distribution for mackinawite (FeS)

BONE, S.E.¹ SPOSITO, G.¹ AND BARGAR, J.R.²

¹University of California, Berkeley, CA ²Stanford Synchrotron Radiation Lightsource, Menlo Park, CA

The nanomineral mackinawite (tetragonal FeS, space group P4/nmm), ubiquitous in sulfidic sediments, impacts the cycling of metals and metalloids through sorption and reduction reactions. The crystallite size, hence the specific surface area, of FeS precipitated from supersaturated solutions is poorly described; variations in crystallite size may arise from differences in mineral synthesis conditions and from differences in measurement techniques used to estimate crystallite size. Transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns have been used to study FeS crystallite size. However, XRD is sensitive to the largest crystallites and identification of small crystallites in TEM images can be difficult when the crystallites are embedded in a matrix of aggregated particles.

In this research, we employ a combination TEM, XRD, and Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy to estimate the size of FeS crystallites formed under varying conditions of pH, ionic strength and reaction time. X-ray absorption spectroscopy is sensitive to the smallest crystallites, providing an estimate of size that is complementary to TEM and XRD. Furthermore, we calculate crystallite size distributions that are able to reconcile the XRD-, TEM-, and EXAFS spectroscopy-derived estimates of size. We suggest that the crystallite size may be bimodal, with a larger number of crystallites less than 2 nm in size than has previously been estimated using TEM and XRD. The presence of numerous small (< 2 nm) crystallites will have large ramifications for the properties of FeS, including its solubility and the rate and mechanism of particle growth. Lastly, the crystallite size distribution can be used to inform studies of particle reactivity by constraining the reactive surface area and the number of surface sites.

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