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Morphological study of Insoluble Organic Matter from carbonaceous chondrites: Correlation with petrologic grade

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Abstract

The major form of organic material delivered to Earth from an extraterrestrial origin is Insoluble Organic Matter (IOM). A morphological study of IOM in the CR (Renazzo-type) and CM (Mighei-type) carbonaceous chondrites was performed in order to constrain its origins and processing history. IOM residues from the following CR chondrites: GRO 95577 (CR1), Al Rais (CR1/2), EET 92042 (CR2), QUE 99177 (CR3) and the CM chondrites: MET 01070 (CM2.2), Cold Bokkeveld (CM2.3), Murchison (CM2.4) and QUE 97990 (CM2.5) were studied using Annular Dark Field STEM imaging. Characteristic features of the IOM, organic nanoglobules, were manually identified and measured for their abundances and size distributions. The IOM residues were also compared holistically for their degree of average 'roughness' or 'coarsening' using fractal image analysis. Manually identified nanoglobules have abundances making up less than 10% of the total IOM, which is consistent with previous studies. Their measured abundances do not correlate with petrologic grade. Thus parent body processing did not systematically deplete their abundances. The IOM is however on average 'smoother' or 'coarser' in the more altered chondrites, demonstrated by a lower fractal dimension using fractal box counting (D_B). The D_B values for the IOM in the CR chondrites are distinctive: QUE 99177 has the largest D_B value (average = 1.54 ± 0.004) and GRO 99577 has the lowest (average = 1.45 ± 0.011). Al Rais and EET 92042 have IOM with average D_B values within this range (average, 1.46 ± 0.009 and 1.50 ± 0.006). The CMs record a similar but less distinctive trend in D_B, with QUE 97990 having the largest value (1.52 ± 0.004), MET 01070 the lowest (1.45 ± 0.019), and Cold Bokkeveld (1.50 ± 0.011) and Murchison (1.49 ± 0.017) equivalent to one another within error. The identified nanoglobules in the IOM of the CM chondrites are on average larger than those in the CR chondrites. The 'coarsening' or 'smoother' texture of the IOM (lower D_B) in the more altered chondrites coupled with a tentative increase in the size of large features (identified nanoglobules) demonstrates that the aqueous processes leading to the lower petrologic types also formed the overall IOM morphology. In addition, observations of fluid-like textures more frequently found in the more altered carbonaceous chondrite residues suggests that organic and aqueous fluids determined at least some of these morphologies. The polymerization of organic solutions is consistent with these morphologies. Their formation conditions are more favorable under the containment of carbonaceous chondrite parent bodies.

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1. INTRODUCTION

Insoluble Organic Matter (IOM) is an acid insoluble form of organic matter (OM) found in primitive extraterrestrial materials (Cody et al., 2002; Pizzarello et al., 2006; Alexander et al., 2007; Flynn et al., 2013). It is mostly found in the matrices of carbonaceous chondrites, constituting a major proportion (70–99%) of the total organic carbon. The remainder is of the soluble type (Pizzarello et al., 2006). It therefore represents the highest fraction of OM that would have arrived to the primordial Earth in similar meteoritic bodies during the late heavy bombardment (Chyba et al., 1990). It exists as solid macromolecular organic material (e.g. Naraoka et al., 2004) that is largely made up of small aromatic moieties with short, highly branched aliphatic moieties that forms side chains on and cross links between the aromatic moieties (e.g Cody and Alexander, 2005). Isotopic anomalies in IOM (enrichments in D/H and $^{15}N/^{14}N$ ratios relative to solar and terrestrial values, both in bulk and in μm-sized hotspots) point to an origin in cold molecular clouds and/or the cold outskirts of the protoplanetary disk (e.g. Robert and Epstein, 1982; Yang and Epstein, 1984; Alexander et al., 1998, 2007; Busemann et al., 2006; Nakamura-Messenger et al., 2006; Remusat et al., 2006; Gourier et al., 2008; Hashiguchi et al., 2013). However, it is not clear what type of material accreted onto the parent body and formed the observable IOM. A characteristic morphological component of IOM are nanoglobules – tiny (~50–1000 nm), often hollow, carbonaceous spheres (Nakamura-Messenger et al., 2003; Garvie and Buseck, 2004, 2006, Garvie, 2006; Garvie et al., 2008; De Gregorio et al., 2010, 2013). Some nanoglobules exhibit larger ^{15}N and D enrichments than the typical IOM from the same meteorites (Nakamura et al., 2006; De Gregorio et al., 2010, 2013). Most identified nanoglobules to date however do not exhibit any isotopic enrichment (De Gregorio et al., 2013).

It is established that bulk D and ^{15}N enrichments in IOM decrease with increased evidence of aqueous alteration in the host meteorite (Alexander et al., 2007). A similar trend has been observed for isotopic hotspots within IOM (i.e. average hotspot isotopic enrichment is greater in less altered chondrites; Busemann et al., (2006). Herd et al. (2011) showed that different stones from the Tagish Lake (C2) chondrite experienced varying degrees of aqueous alteration, as determined by the abundances of framboidal magnetite and phyllosilicates. There is a systematic decrease in the bulk δD value of the IOM from the least to most altered stones. They also suggested that nanoglobule abundances decrease between the most and least altered stones, relating to a processing history of preaccretionary organic nanoglobules that may have carried these enrichments. De Gregorio et al. (2013) performed coordinated Transmission Electron Microscopy (TEM)-Scanning Transmission X-ray Microscopy (STXM)-NanoSIMS analysis on the IOM of a range of carbonaceous chondrites that experienced various degrees of aqueous alteration. They analyzed 7 different carbonaceous chondrite IOM residues and identified in total 184 nanoglobules. They demonstrated that most nanoglobules were not ^{15}N-enriched and that most D and ^{15}N hotspots were not associated with identified nanoglobules.

The IOM residues are aggregates of demineralized material making up a complex network of OM with submicron to nanometre scale variation. Although the petrologic context is lost in these residues, they provide the possibility of rapid TEM-based characterization of their morphologies. We report a systematic investigation into the morphological properties of IOM as a function of degree of aqueous alteration in CM and CR chondrites. This study has attempted to identify the largest number of 'nanoglobules' to date (~1000 in total) and samples the largest area of studied IOM. Firstly, we aim to determine if the discrete spherical organic nanoglobules were the carriers of the isotopic enrichments and were subsequently destroyed or altered by parent body processing. In order to achieve this we determine their relative abundances and size distributions. Nanoglobules have been previously shown to make a minor fraction (~10%) of chondritic IOM (Pizzarello et al., 2006) and thus are not fully representative when comparing IOM. We also compare the IOM morphologies holistically from different meteorites by image-based fractal analysis, enabling us to assess if there are any other morphological relationships as a function of alteration type. This method of image analysis has not been reported in the study of planetary materials before. We show that morphological variations in the IOM correlate with the degree of parent body alteration in a chondrite group; the more altered CM and CR chondrites are 'smoother' or 'coarser' by exhibiting lesser morphological detail at finer scales compared to the less-altered meteorites. We also tentatively observe an increase in identified nanoglobule size from the most altered meteorites, and a distinctively larger average size in the CM chondrites when compared with the CR chondrites. We further discuss the implications of these results for the possible formation and/or alteration mechanisms that have affected IOM found in carbonaceous chondrites.

2. SAMPLES AND METHODS

IOM residues from the following CM (Mighei-type) and CR (Renazzo-type) chondrites were studied: Meteorite Hills (MET) 01070 (CM 2.0), Cold Bokkeveld (CM 2.2), Murchison (CM 2.5), and Queen Elizabeth Range (QUE) 97990 (CM 2.6); Grosvenor Mountains (GRO) 95577 (CR 1), Al Rais (CR 1/2), Elephant Moraine (EET) 92042 (CR 2) and QUE 99177 (CR 3). The petrologic types of the CM chondrites were taken from Rubin et al. (2007), and are consistent with the classifications made by Howard et al. (2009, 2011). The CR chondrite alteration types are from Alexander et al. (2007).

The IOM residues were prepared using the CsF method described by Cody et al. (2002) and Alexander et al. (2007). The resulting IOM residues consist of a fragile black powder. Several grains from each IOM residue were mixed with 99.9% pure S, embedded by melting the mixture to approximately 115 °C (the melting point of S) on a hotplate and then glued to epoxy stubs. A Leica EM UC7 ultramicrotome at the Naval Research Laboratory (NRL) was used