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Clay mineral–organic matter relationships in the early solar system

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Abstract–As the solar system formed, it inherited and perpetuated a rich organic chemistry, the molecular products of which are preserved in ancient extraterrestrial objects such as carbonaceous chondrites. These organic-rich meteorites provide a valuable and tangible record of the chemical steps taken towards the origin of life in the early solar system. Chondritic organic matter is present in the inorganic meteorite matrix which, in the CM and CI chondrites, contains evidence of alteration by liquid water on the parent asteroid. An unanswered and fundamental question is to what extent did the organic matter and inorganic products of aqueous alteration interact or display interdependence? We have used an organic labelling technique to reveal that the meteoritic organic matter is strongly associated with clay minerals. This association suggests that clay minerals may have had an important trapping and possibly catalytic role in chemical evolution in the early solar system prior to the origin of life on the early Earth.

INTRODUCTION

The birth of the solar system was preceded and accompanied by a prolific organic chemistry that is evidenced by the presence of organic matter in primitive extraterrestrial objects such as asteroids and comets. The carbonaceous chondrite meteorites are naturally delivered fragments of primitive organic-rich asteroids and that contain a wide variety of extraterrestrial molecules (*e.g.*, Sephton, 2002). These meteorites allow us to study the products of early solar system prebiotic molecular evolution in the laboratory. Organic matter is most abundant in those carbonaceous chondrites that display the greatest amount of inorganic aqueous alteration products. Superficially, this correlation suggests a genetic link between organic material and aqueous alteration and/or its products. The association between organic matter and aqueous alteration is key to the interstellar-parent body hypothesis, where it is suggested that meteoritic organic compounds were initially interstellar organic molecules that underwent hydration by melting cometary ices accreted during parent body formation (Cronin and Chang, 1993).

Minerals have also been linked with the development of complex organic networks (Ponnamperuma *et al.*, 1982), considered to be the forerunners of biomacromolecules. Understanding the relationships and interdependence of organic and inorganic components is essential for comprehending the processes and mechanisms involved in the evolution of organic material in the early solar system. Despite this, very little work has been carried out to investigate whether a true organic–inorganic relationship exists and, if it does, which inorganic phases play a role.

We have studied four carbonaceous chondrites—Murchison, Orgueil, Ivuna and Tagish Lake—all of which are known to have undergone aqueous alteration on their asteroidal parent bodies. The aqueous event generated a number of oxidized and hydrated mineral phases from more reduced and anhydrous precursors. The hydrated minerals are found within the chondrite matrix together with significant amounts of organic matter. Murchison is a CM2 chondrite that has experienced partial alteration and matrix material surrounds incompletely altered anhydrous precursors. Orgueil and Ivuna are CI1 chondrites that have undergone more extensive aqueous processing and consist entirely of hydrated matrix. The classification of Tagish Lake is still in dispute, but mineralogical evidence indicates that it has been subjected to aqueous alteration at a degree intermediate to type 1 and 2 chondrites (Brown *et al.*, 2000).

In order to verify the existence of a relationship between organic and inorganic chondritic components, we have implemented a novel approach, which utilizes a labelling technique that highlights the location of organic material within whole-rock samples.

SAMPLES AND ANALYTICAL PROCEDURES

To determine the location of organic matter within the meteorites we impregnated samples with osmium tetroxide

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(OsO_4) vapor. Dry whole-rock samples of Murchison, Ivuna, Orgueil and Tagish Lake were held within OsO_4 vapor inside a sealed canister for 1 week. Reactions between the organic matter and OsO_4 vapor resulted in the localized incorporation of fine-grained osmium (Os) that is readily detected using analytical scanning electron microscopy (SEM).

Elemental mapping was carried out using a JEOL JSM-840 SEM fitted with an Oxford Instrument's e-XL energy dispersive (EDS) x-ray microanalyser.

To demonstrate that organic-free meteoritic minerals do not give spurious Os incorporation, terrestrial analogue minerals were exposed to OsO_4 vapor for 1 week. Olivine, two feldspars, two pyroxenes, four carbonates, gypsum, magnetite, hematite, montmorillonite, saponite and two serpentines showed no Os-staining, except for traces on organic inclusions within gypsum.

The utility of OsO_4 impregnation to locate organic matter has been illustrated in a wide range of recent and ancient terrestrial sedimentary rocks (Aplin *et al.*, 1992; Bishop *et al.*, 1992; Patience *et al.*, 1990).

OBSERVATIONS

Using SEM, Os incorporation within the samples was mapped using the Os-M and Os-L x-ray lines (Fig. 1). Figure 1a displays a backscattered electron (BSE) image of a Murchison chondrule surrounded by a fine-grained accretion rim and matrix. In Murchison, enrichment in Os was observed in the chondrule accretion rims (Fig. 1b,c). These accretion rims have been heavily altered on the meteorite parent body and contain signatures characteristic of clay minerals such as serpentines (Mg, Fe, Si and Ni). There is an apparent decrease in the abundance of organic matter from the hydrated outer edges of the chondrule rims towards the unaltered cores. No evidence of Os incorporation was observed in the interior of the chondrules. Figure 1d displays a BSE image of the matrix-dominated Ivuna meteorite. X-ray mapping and microanalysis of the Os-impregnated surfaces of Ivuna reveal that Os-labelled organic matter is concentrated in the clay-rich matrix (Fig. 1e,f). Furthermore, there are distinct associations between Os and those elements characteristic of clay minerals (Mg, Fe, Si and Ni). Both CI1 chondrites (Ivuna and Orgueil) and Tagish Lake provided identical results.

Other aqueously generated mineral phases in the samples, such as magnetite (Fe, O; Fig. 1e,f), sulphides (Fe, Ni and S; Fig. 1f) and carbonates (Ca and Mg) (Fig. 1c) were also subjected to x-ray mapping but contained no Os-labelled organic matter. Our Os-labelling results were corroborated with spectra taken from these aqueously produced mineral phases, which also show no evidence for the presence of Os. These observations are inconsistent with previous reports of fluorescent organic coatings around magnetite grains in Orgueil (Alpern and Benkheiri, 1973). Recent transmission electron microscopy (TEM)-based analyses of Tagish Lake have identified the sites of certain carbon-bearing materials in this meteorite. Matrix sulfides in Tagish Lake appear to be coated by layers of graphitic carbon (Zolensky *et al.*, 2002) and sub-2000 nm carbonaceous globules are present in the phyllosilicate matrix (Nakamura *et al.*, 2001). However, these reports could not be substantiated by our method because the recalcitrant nature of graphite precludes it from being visualized by Os labelling and the carbonaceous globules are too small to be detected by our SEM-based approach.

Therefore, the Os-labelling data indicate that although organic material is linked to aqueous alteration processes that produce several hydrous mineral phases, the only organic–inorganic association of significance is that between the organic matter and the clay minerals.

DISCUSSION

Implications for the Interstellar-Parent Body Hypothesis

Current theories propose that significant amounts of meteoritic organic matter, or its precursor materials, were synthesized in an interstellar environment. The interstellar heritage of meteoritic organic matter is supported by noticeable enrichments in the heavy stable isotopes of C, N, and H (Cronin and Chang, 1993; Sephton and Gilmour, 2001). Subsequently, organic precursors synthesized in interstellar space were hydrolytically transformed to water-soluble organic compounds by aqueous reactions on the meteorite parent body. The influence that the interstellar and asteroidal environments appears to exert on the final constitution of meteoritic organic matter has led to this model being called the interstellar-parent body hypothesis (Cronin *et al.*, 1993). Our observation that there are no associations between organic matter and aqueously generated inorganic mineral phases, other than with clay minerals, suggests that aqueous processing alone, is not the key mechanism for controlling the organic evolution on the meteorite parent body. Rather, it is the ability of aqueous alteration to generate clay minerals in close proximity to organic-rich fluids that is important.

Parent Body Processes

Perhaps the simplest explanation for the clay mineral–organic matter association is that the clay mineral-containing matrix has a higher porosity than the more impermeable anhydrous mineral phases. Channelling of organic-rich solutions through the matrix may have allowed the preferential accumulation of organic matter in conduits within clay–mineral dominated areas.

However, recent advances in theories of how complex organic networks form in terrestrial rocks may provide a more sophisticated explanation. In terrestrial systems, clay minerals have a propensity to adsorb organic molecules (Hedges, 1977) and this property has led to a newly proposed mechanism for the formation of high molecular weight sedimentary organic

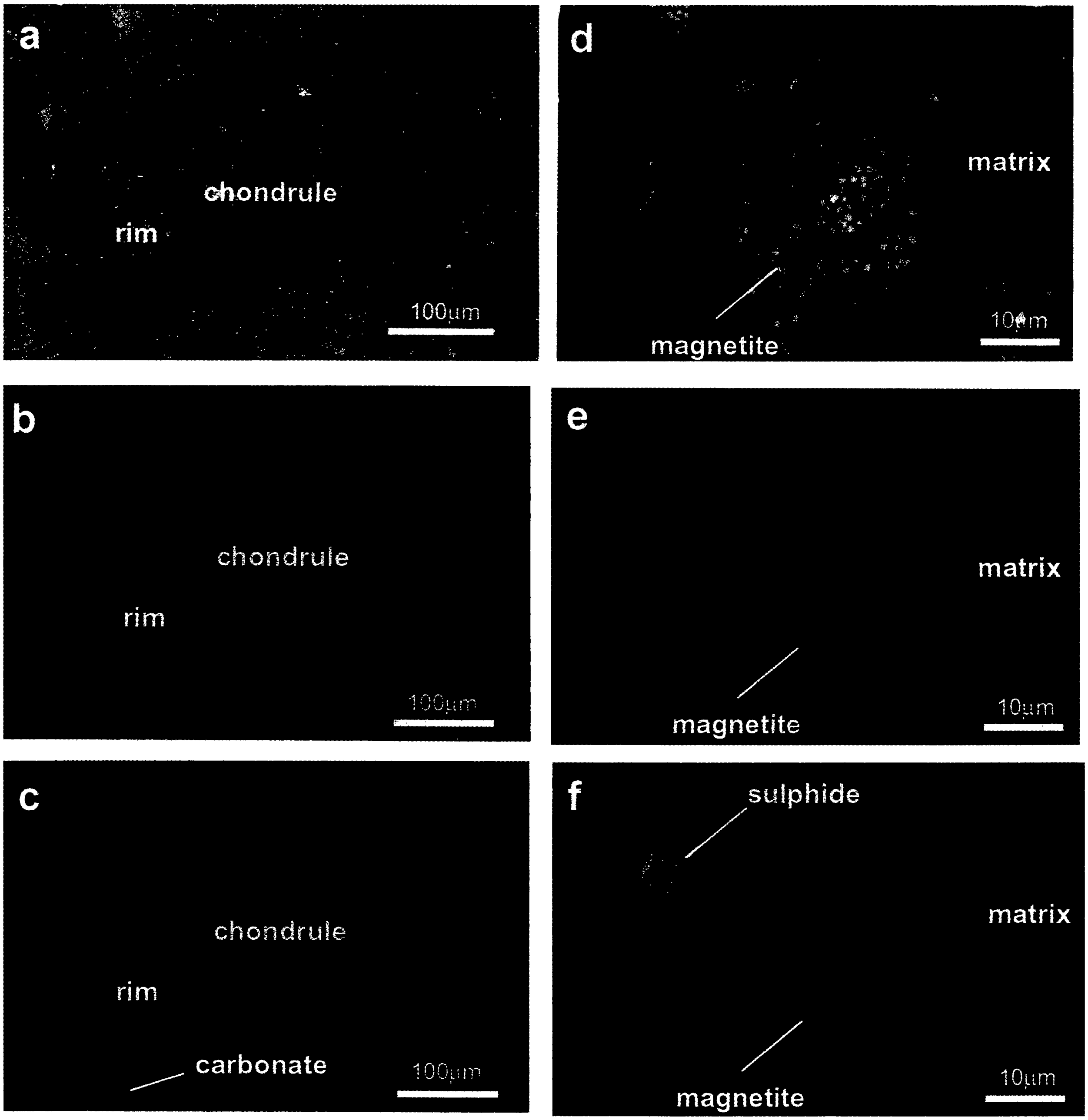

FIG. 1. (a) Backscattered electron image of a Murchison chondrule surrounded by a fine-grained rim and matrix. (b–c) Color coded x-ray maps of OsO_4 impregnated surfaces. (b) Os-stained organic matter (blue) is concentrated in the clay mineral-rich chondrule rim and matrix (mostly green) (Fe = green, Si = red, Os = blue). (c) Os-stained organic matter (blue) is not associated with the matrix carbonates (red) (Fe = green, Ca = red, Os = blue). (d) Backscattered electron images of Ivuna magnetite in fine-grained matrix. (e–f) Color coded x-ray maps of OsO_4 impregnated surfaces. (e) Os-stained organic matter (blue) is concentrated in the clay mineral-rich matrix (mostly red) and is not associated with magnetite (green) (Fe = green, Si = red, Os = blue). Note that the slight blue coloration on the sulphide grain is an artifact and appears because blue is a strong color and the other element signals in that region are low. Spectra of the sulphide grain indicate no Os incorporation. (f) Os-stained organic matter (blue) is not associated with sulphides (mostly red) (Fe = green, S = red, Os = blue).

matter. The so-called sorptive protection mechanism involves the adsorption of labile organic matter onto mineral surfaces (Collins *et al.*, 1995) and between clay layers (Salmon *et al.*, 2000) followed by their condensation into larger organic networks. It is possible that, during aqueous processing on the carbonaceous chondrite parent bodies, the sorptive protection mechanism was operating, leading to the trapping and modification of organic matter in coeval clay minerals.

In this context, it is interesting to note that while free or solvent-extractable organic matter may make up as much as 30% of the total carbon and nitrogen in carbonaceous chondrites, only a portion is readily extracted by solvents from whole-rock samples. The remainder is released following the removal of their inorganic surroundings by acid demineralization procedures (Becker and Epstein, 1982), a characteristic that is consistent with organic matter being bound within clay layers.

Implications for Nebula Catalytic Synthesis

The lack of an association between organic matter and inorganic phases such as magnetite and sulphides allows the relevance of other proposed theories for the origin of extraterrestrial organic matter to be constrained. Fischer–Tropsch type (FTT) catalysis has often been suggested as a method for the generation of simple organic materials in the solar nebula (Studier *et al.*, 1968). FTT involves the production of organic compounds from CO and H_2 on the surfaces of mineral catalysts. Once produced, these compounds may be thermally processed to achieve an organic distribution similar to that seen in meteorites. Traditionally, Fe- and Ni-rich metals and sulphides have been suggested as possible nebular catalysts for this reaction. If FTT synthesis involving Fe/Ni catalysts were a dominant organic compound-forming mechanism in the early solar system, then the purported mineral catalysts found in carbonaceous chondrites would be coated with organic matter. However, in this study metals and sulphides appear to have no relationship with organic matter. Clay minerals are themselves a possible FTT catalyst but appear to have formed on the meteorite parent body and not in the nebula (Bunch and Chang, 1980) although their precursor silicates may have been important nebula catalysts.

Significance for Prebiotic Molecular Evolution

The discovery that meteoritic organic compounds may be trapped and protected within a clay mineral matrix has implications for our understanding of prebiotic molecular evolution in the early solar system (Bernal, 1951). The carbonaceous chondrites contain a wide variety of water-soluble organic compounds (Cronin and Chang, 1993; Sephton, 2002). During aqueous alteration on the meteorite parent body, clay minerals may have trapped and concentrated organic compounds thereby promoting polymerization reactions (Ponnamperuma *et al.*, 1982). Extrapolating forward from the snapshot of prebiotic molecular evolution recorded in carbonaceous chondrites, the accumulation, protection and consequent polymerization of organic species within a clay–mineral matrix may have facilitated the development and preservation of primitive biopolymers that laid the foundations for early life.

The recognition of clay mineral–organic matter relationships in ancient extraterrestrial samples has a bearing on the possible ubiquity of life in the early solar system. Chondritic material would have been a common component of the inner solar system shortly after its formation. Thus, the biologically useful products of clay mineral–organic matter interactions would have also been widespread, and delivered to planetary surfaces through the accretion of carbonaceous asteroids (Chyba *et al.*, 1990). Life, therefore, may have originated on planets other than the early Earth, if suitable conditions were temporarily available. The most obvious example of which may have been the warm and wet environments of early Mars.

CONCLUSIONS

We have applied a novel Os labelling technique to locate organic material within aqueously altered carbonaceous chondrites, in order to investigate the role of aqueous processing in organic evolution. X-ray mapping of Os-stained surfaces of Murchison (CM2), Ivuna (CI1), Orgueil (CI1) and Tagish Lake (CI2?) indicate a strong affiliation between Os-labelled organic matter and hydrous clay minerals. No such relationships were observed between Os-labelled organic matter and any other aqueous mineral phases. Although aqueous alteration has been considered a key process in the accumulation of organic material on the meteorite parent body, we suggest it is the ability of aqueous processes to generate clay minerals that influences the abundance of organic material in carbonaceous chondrites. Clays may act as absorbents and catalysts for the polymerisation of organic interstellar precursor molecules into the complex organic networks found in carbonaceous chondrites. This organic–inorganic link may have provided a means to trap, protect and polymerise biologically useful molecules within the early solar system prior to their delivery to planetary surfaces and possible role in the origin of life.

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