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MICROBIAL D/H FRACTIONATION IN EXTRATERRESTRIAL MATERIALS: APPLICATION TO MICROMETEORITES AND MARS. R. L. Blackhurst¹, M. J. Genge¹, and M. M. Grady² ¹Department of Earth Science and Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, UK; ²Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD. Email: rebecca.blackhurst@imperial.ac.uk.

Introduction: High D/H ratios in extraterrestrial materials are frequently considered to be indicative of an extraterrestrial origin. Deuterium (D) enrichments, for example, are common in many primitive meteorites and interplanetary dust particles and are thought to have been caused by isotopic fractionation in interstellar molecular clouds [e.g.1].

Studies on Earth show that stable isotope (D/H) fractionation can arise from anaerobic microbial processes [2]. Biological fractionation leads to unequal distribution of heavier and lighter isotopes between the reactants and products of a reaction [3]. In most cases the lighter isotope is preferentially used and the heavier isotope enriched in the residual substrate fraction. This is a well known phenomenon for CO₂ fixation in photosynthesis, methanogenesis and methane oxidation [3]. In this paper we evaluate the potential for microbial D fractionation in micrometeorites in the terrestrial environment and discuss its wider implications for other planetary materials including martian meteorites.

Micrometeorites and COPS Phases: Micrometeorites (MMs) are extraterrestrial dust particles that survive atmospheric entry to be recovered from the Earth's surface. Many MMs recovered by melting of Antarctic ice contain COPS phases, carbon-, phosphorous- and sulphur-bearing "dirty magnetites" [5]. These materials, which consist primarily of ferrihydrite, an iron oxyhydroxide, have textures that suggest formation during terrestrial alteration of the MMs [4]. An extraterrestrial origin for COPS phases in micrometeorites has, however, been suggested on the basis of their high D/H ratios ($D/H > 160 \times 10^{-6}$) [5]. Microbial fractionation of D may provide an alternative explanation for the origins of such materials that reconciles the textural evidence that implies a terrestrial origin with their D/H ratios. COPS in MMs illustrates that high D/H ratios are not necessarily indicative of an extraterrestrial origin but may also be a signature of biological activity.

Terrestrial Origin of COPS in MMs: COPS phases are found within the entire spectrum of MM types from fine-grained particles that have escaped melting during atmospheric entry to cosmic spherules that formed as molten droplets in the Earth's atmosphere. The presence of COPS as thick rims surrounding some cosmic spherules and as infillings of vesicles within

spherules and scoriaceous MMs implies that these materials form after cooling and deceleration of particles either in the atmosphere or during residence in Antarctic ice. The occurrence of COPS phases, therefore, suggests an origin as terrestrial alteration products of micrometeorites.

The most significant development of COPS phases are observed on coarse-grained MMs (cgMMs). These particles consist mainly of anhydrous silicates within a glassy mesostasis and thus evidently represent igneous materials. The irregular particle shapes of coarse-grained MMs and the presence of re-melted rims on some particles, indicates that these MMs have survived atmospheric entry without large scale melting. Type I cgMMs are often associated with large amounts of COPS, often as a layered external rim that surrounds the particle. COPS rims in Type I cgMMs occur as an outermost layer and are usually associated with an internal magnetite rim. Such magnetite rims are common on MMs and are known to form during atmospheric entry heating. The occurrence of COPS rims on cgMMs as an external layer, therefore, suggests they form after entry heating as terrestrial alteration products. Type I cgMMs are reduced igneous objects and, like Type I chondrules, often contain significant FeNi metal along with Mg-rich silicates. Relict FeNi metal objects, with irregular, embayed outlines, are often found within COPS phases in Type I cgMMs and thus suggest the formation of COPS by oxidation and hydration of FeNi metal within the terrestrial environment.

D/H Ratios of COPS: Engrand et al [5] report that COPS phases within MMs have high D/H ratios typical of those of the matrices of carbonaceous chondrites and thus have suggested an extraterrestrial origin for these materials. The occurrence of COPS, as described above, however, clearly indicates that these materials formed after atmospheric entry heating and is, therefore, inconsistent with such an interpretation. The high D/H ratios of COPS, however, must also be explained and are not consistent with terrestrial hydration and oxidation of FeNi metal. One possible explanation for the high D/H ratios of COPS might be the derivation of the (D,H)₂O present within the component ferrihydrite of COPS from an extraterrestrial source, for example, by condensation of water vapour generated by the degassing of the particle during entry heating

(Engrand, pers. communication). Although fine-grained MMs are likely to contain abundances of H₂O sufficient to generate the observed COPS phases it seems unlikely that water vapour degassed from heated particles would be recondensed efficiently enough to explain the significant volume of hydrated COPS material. The occurrence of large amounts of COPS associated with Type I cgMMs is also significant in regard to the origin of the water since these particles are originally igneous and would, therefore, contain negligible H₂O. The source of water involved in the hydration of FeNi metal to form COPS in cgMMs is demonstrably terrestrial. The high D/H ratios of COPS in MMs, thus, implies that D/H fractionation can occur in the Earth's atmosphere or in Antarctic ice during hydration of FeNi metal.

Microbial Fractionation of D: The fractionation of hydrogen isotopes can occur in several biological processes including methanogenesis, homoacetogenesis and methane oxidation. In the case of methane oxidation, fractionation of carbon and hydrogen isotopes has been shown to occur by methane-oxidizing bacteria. Bacterial methane oxidation is associated with a kinetic isotope effect; ¹²C and ¹H are preferentially used from the methane reactant pool, resulting in enrichment of ¹³C and D in the residual methane [6]. A study by Coleman et al., [7] showed that enriched cultures of methane-oxidizing bacteria fractionated both carbon and hydrogen isotopes resulting in the residual methane being enriched in the heavy isotopes [7].

Methanogens belong to the domain Archaea and are anaerobic organisms that use hydrogen as an energy source to convert dissolved carbon dioxide to biomass, giving off methane as a byproduct [8]. H₂-consuming autotrophs are thought likely to have been a dominant sink for H₂ on the early Earth [9]. Autotrophic methanogenesis has also been suggested as a potential energy source for organisms on Mars [10].

Methanogens are thought to make up the communities found in deep crystalline rock aquifers within the Columbia River Basalt Group [11]. These microbes appear to get energy from hydrogen generated in a reaction between iron-rich minerals in basalt and ground water [8]. In their study Stevens and McKinley [11] evaluated dissolved organic carbon in ground water samples and found it to be increasingly enriched in ¹³C, consistent with the preferential removal of ¹²C by methanogenic microorganisms. It is probable that these organisms also cause deuterium enrichment. Landfill waters are enriched in deuterium and this has been attributed to methanogenesis [12], e.g. a study by Siegel et al., (2001) found methanogenesis enriched the deuterium content of leachate from New York

City's Fresh Kills landfill to D/H 166.6 x 10⁻⁶ or δD +70‰ (VSMOW) [13].

Application to MMs and Extraterrestrial Materials: The ability of microbes to cause deuterium enrichment through metabolic processing might provide an appropriate explanation for the high D/H ratios of COPS phases within MMs since microbial fauna are known to be present within Antarctic ice. COPS also forms due to alteration of iron-rich phases, a similar scenario to methanogens within basalts. Given the difficulties in fractionating D during aqueous alteration, and the observation that microbes are capable of causing D enrichments, it seems entirely possible that microbial action may explain the high D/H ratios in alteration products in MMs.

Ferrihydrite dominated terrestrial alteration products are found in many weathered Antarctic meteorites and are broadly similar to the COPS phases described above. No measurements of their D/H ratios have yet been made, however, if D enrichments in MMs have a microbial origin then we may also expect these materials to be fractionated. Due to the finely dispersed nature of alteration products throughout the matrices of meteorites they potentially represent a source of terrestrial contamination that could be misinterpreted as having an extraterrestrial signature.

In addition to extraterrestrial materials exposed to the terrestrial biosphere, inorganic materials present on other planetary bodies such as Mars could also be subject to D fractionations if methanogenic bacteria are present. Microbial processing can, therefore, be added to the list of mechanisms by which D/H ratios can be moderated and in the absence of evidence for other explanations may represent a possible biomarker.

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