SEARCHING FOR LIFE IN THE SULFUR ISOTOPIC ANALYSIS OF SURFACE SULPHATES ON MARS.
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Introduction: The search for evidence of life is a major goal of the exploration of Mars. Data from terrestrial systems suggests that isotopic fractionation can provide rigorous evidence for biological activity. Consequently, isotopic analysis has been proposed as an important tool in the search for life [1]. On Earth, numerous studies have identified biological activity on the basis of strong isotopic fractionation between sulfate and sulfide, especially where seawater sulfate is transformed by microbial sulfate reduction into sulfide minerals [2]. However, making such measurements depends upon sampling both parent sulfate and product sulfide, which may be unrealistic. Sulfides on Mars, which are predicted to be widespread [3], are very probably oxidized within accessible range of the surface [4]. Realistically, sampling is therefore limited to the sulfates. Intriguingly, sulfates are widespread on the martian surface, evident from both landers and remote sensing [5], and instrumentation for isotopic measurement is being developed accordingly [6,7].

Analogue study in Haughton Impact Structure: Here we present an analogue study which shows that isotope fractionation can demonstrate biological activity, using sulfate samples from a transect through the Haughton impact structure on Devon Island, Canadian High Arctic. The structure was formed by a 39 Ma impact, producing a 23 km diameter crater in bedrock that included 470 Ma beds of the sulfate mineral anhydrite [8]. Impact breccias in the crater contain comminuted anhydrite/gypsum [8]. The crater was later (Eo-Miocene) filled with lacustrine sediment.

The impact breccias are pervasively mineralized by pyrite, and locally by marcasite and selenite (gypsum). These sulfur-bearing phases are interpreted as hydrothermal, induced by the residual heat of the impact [9]. The sulfides have sulfur isotope compositions that indicate microbial sulfate reduction, which occurred as the impact structure cooled down [10]. The sulfide-bearing deposits have experienced some oxidative weathering back to sulfates, including jarosite [10]. In order to simulate robotic sampling, a series of sulfate and sulfide samples were collected on a single traverse through the Haughton Crater, at accessible points (Fig. 1). At each location, the sampled phases are visible at a distance of at least 1m, and could therefore be readily sampled and visible to a robotic vehicle.

Progressing westwards through the crater, a total of 10 sampling stations are distinguished as follows: (A) Surface crust of gypsum, which crystallized at the surface. Occurs above bedded gypsum as in D; (B) Iron sulfide (marcasite) veins in the impact breccias; (C) Surface efflorescent sulfate precipitates (predominantly copiapite) associated with iron sulfides and probably weathered from them; (D) Bedded gypsum rock below the impact breccias, evidently part of the pre-impact succession; (E) Pyrite-rich impact breccia; (F) Selenite (gypsum) veins up to centimetres width, cutting the impact breccias; (G) Clasts of gypsum up to 5 cm size in the impact breccias; (H) Gypsum veinrock, below an impact-related hydrothermal vent; (J) Black, platy masses, centimetre-scale, of pyritic sandstone, eroded from crater-fill sediments; (K) Mixed gypsum-iron oxide crust above crater-fill sediments.

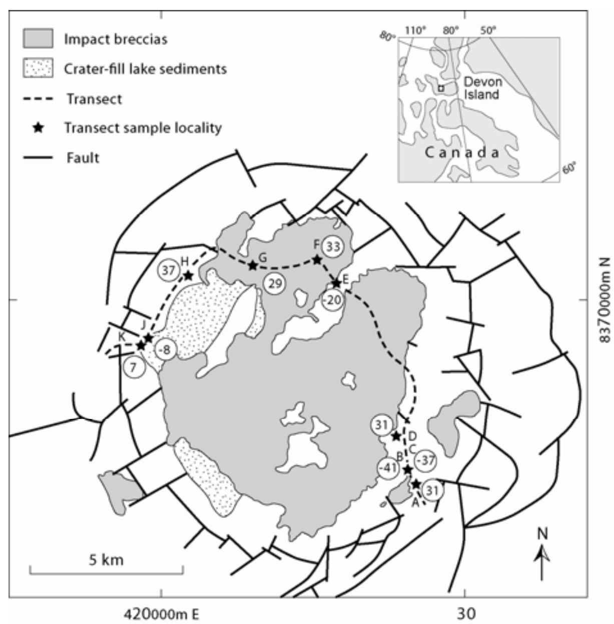

Fig. 1. Map of Haughton Crater showing sampling stations and mean sulfur isotope compositions.

Isotopic Analysis: Mean sulfur isotope compositions (V-CDT) calculated for each group of samples are shown in Fig. 1. In summary, 5 of the 7 sets of sulfate have similar compositions in the range +29 to +37‰. The 3 sets of sulfide and the remaining 2 sets of sulfates have compositions which are isotopically lighter (lower $\delta^{34}S$) than the group of 5 sulfates.

Comparison of the mean values highlights some remarkable fractionation, particularly in the sulfides relative to most of the sulfates, strongly implicating biological activity [10]. To make the case study more relevant to Mars, we should omit the 3 sets of sulfide data (B, E, J), on the assumption that sulfides would not survive oxidation at the martian surface. Sulfates, however, are widespread, so interpretation of the Haughton sulfates is a valuable test of how we could assess sulfates on Mars. Focussing solely on the 7 sets of sulfate data, it is apparent that 5 of the 7 are comparable. The 2 sets that are different are 2 of the 3 soil zone precipitates.

If we were presented with the same set of contextual observations and isotopic data on Mars, a logical interpretation could progress as follows:

(i) The data for the pre-impact bedded gypsum (D) represents the 'baseline' composition, to which all other, younger, compositions should be compared.

(ii) The clasts in the impact breccia (G) have a similar composition, and can be inferred to be redeposited fragments of the bedded gypsum, excavated by the impact.

(iii) The vein selenite (F) and veinrock gypsum (H) also have similar compositions, and represent precipitation from groundwaters.

(iv) The three soil zone precipitates have distinct compositions. One (A) is comparable with the baseline bedded gypsum, and appears to be directly remobilised from it.

(v) The two remaining soil zone precipitates are very different from the baseline and from each other. One (C) exhibited a mean composition of -41‰. The other (K) has a mean composition of +7‰. The compositions for these two sites cannot reflect simple remobilisation, and indicate that some more complex process is responsible.

The actual values for these 2 soil zone precipitates are sufficiently high that on Earth they indicate biological activity, as the maximum fractionation induced by non-biological processes is about 20‰ [2]. Furthermore, the clear difference between the 2 indicates that, although both indicate biological activity, there were different pathways to the final product. These 2 sulfates exhibiting strong fractionation were derived by weathering of sulfides precipitated by microbial sulfate reduction. The sulfates weathered from marcasite shows a similar composition (-37‰) to the marcasite (-41‰), i.e. it has inherited the isotopic composition. The sulfate (K) weathered from crater-fill sulfides is heavier (+7‰) than the crater-fill sulfide data reported at station J here (-8‰). This reflects an additional component of weathering of a second crater-fill pyrite, which was omitted from the transect described above because it would not be visible to robotic sampling. Weathering of the 2 crater-fill sulfides can explain the composition of the resulting sulfate. In summary, the 2 soil zone sulfates carry a signature of biological activity, inherited from the sulfides from which they were weathered. In the case of the highest level of fractionation (C), detection of this anomalous composition could focus investigation, and lead to the discovery of the microbially-mediated sulfides (B). If we could not observe the parent sulfides, we would still suspect biological activity, and weathering of biologically-mediated sulfides would be the simplest way to explain the data. Thus, on Mars, a similar pattern of data would be of great interest.

Potential application to Mars: If there is life on Mars today, the microbial sulfate reduction which is the basis of the isotopic fractionation on Earth is conceivable. Some of the bedded sulfates on Mars date back to 3.5 Ga when the surface was warmer and wetter than now. However there has been repeated dissolution and reprecipitation of sulfates through the geological history of Mars [11], so there would have been opportunities for involvement and entrapment of later-evolving microbial communities. On Mars, any microbial activity that had evolved to engender sulfate reduction is likely to have caused isotope fractionation. The level of fractionation would reflect the concentration of sulfate available, which on Mars was high, and the time available for evolution to occur, which was probably much more limited than on Earth. However, even greatly reduced levels of isotope fractionation on Mars, for example 5 to 10‰, would indicate processing of sulfur species by some means that could include biological activity. Such anomalous compositions could be identified during robotic exploration, and therefore could contribute to decisions about where to focus other types of analysis.

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