

OXYGEN THREE-ISOTOPE MEASUREMENTS ON THE FIRST ARTIFICIAL METEORITES (THE ESA 'STONES' EXPERIMENT): CONTRASTING BEHAVIOUR OF DOLOMITE AND A SIMULATED MARTIAN SOIL. M. F. Miller¹, A. Brack², P. Baglioni³, R. Demets³, I. A. Franchi¹, G. Kurat⁴ and C. T. Pillinger¹, ¹Planetary Sciences Research Institute, The Open University, Walton Hall, Milton Keynes MK7 6AA, United Kingdom (e-mail correspondence: m.f.miller@open.ac.uk), ²Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron 45071 Orléans cedex 2, France. (e-mail correspondence: brack@cnrs-orleans.fr), ³ESA Directorate of Manned Spaceflight and Microgravity, ESTEC, Postbus 299, NL-2200 AG Noordwijk, The Netherlands, ⁴Naturhistorisches Museum, Postfach 417, A-1014 Wien, Austria.

Introduction: The 'Stones' experiment is an autonomous investigation of the Microgravity space flight program of the European Space Agency (ESA). It is led by Dr A Brack (Principal Investigator) and is designed to assess physical, chemical and isotopic modifications experienced by meteorites during their passage through the Earth's atmosphere, by measurements made on geological samples attached to the heat shield of a recoverable Foton space capsule. Such artificial meteorites offer a unique means of identifying changes that accompany atmospheric entry, by comparing well-defined materials with original (control) non-flown samples. The principle objective is to address the problem of why, amongst the 14 examples of SNC meteorites so far identified, none are of a sedimentary rock type (or, indeed, appear to originate from the surface of the parent body), despite evidence that the most probable parent body (Mars) was characterized by a warm and wet climate earlier in its history. By contrast, most lunar meteorites identified to date are regolith samples, in accord with their ejection from the lunar surface by impact.

In the case of Mars, the present-day surface is covered both by impact-generated regolith and by sedimentary rocks; the latter presumably deposited by flowing or still water. Thus, the presence of detrital deposits and evaporites would be expected. Furthermore, groundwater might be expected to compact loose sediments and regolith by filling pore space with evaporitic minerals. Such sedimentary hard rocks should be among the Martian meteorites, but none have yet been identified. It is postulated that consolidated sedimentary rocks may have survived ejection from the Martian surface, but did not survive terrestrial atmospheric entry because of decrepitation of the cementing matrix (most probably a sulfate). Furthermore, carbonate-rich sedimentary rocks may never have developed a fusion crust during terrestrial atmospheric entry: thermal decrepitation of carbonates is likely to produce a surface texture that is not recognizable as a fusion crust.

Samples and flight details: To address these issues, the 'Stones' experiment involved the attachment of three different rock types to the heat shield of a recoverable Foton capsule. These were: a basalt; a dolomite (fine-grained, sedimentary Ca-Mg carbonate, with minor quartz) and a 'synthetic Martian soil'. The latter consisted of comminuted basalt (<5mm grain-size)

cemented by gypsum (mixing proportion 80:20). The samples were attached to the heat shield of Foton-12, which was launched from Pletsetsk (Russia) on 9th September 1999 and flew for 16 days before re-entry. Nominal orbital parameters were: perigee 220km; apogee 380km; inclination 62.8°. The landing site was near the Kazakhstan/Russian border. Unfortunately, the basalt sample was lost during flight. However, the dolomite and 'Martian soil analog' survived and were successfully recovered.

Oxygen isotopes: We report here some preliminary results of oxygen three-isotope measurements on the recovered dolomite and 'Martian soil analog' samples, together with comparable data on the (post-flight) Foton-12 heat shield and the respective control samples. For reference purposes, oxygen isotopic data on the distinctive fusion crust and interior of an LL6 ordinary chondrite fall (Appley Bridge meteorite) are also presented. Measurements were undertaken at the Open University, using infra-red laser-assisted fluorination (by BrF₅) of 1-2 mg of sample. All samples were laser heated to fusion, in vacuo, prior to fluorination. After purification, the resulting O₂ was analyzed for ¹⁷O and ¹⁸O using a dual inlet mass spectrometer of high resolution (M/M~250) and abundance sensitivity. This system provides dual oxygen isotope ratio measurements to very high precision, such that the offset between different mass-dependent fractionation lines is <±0.02‰. Full details of the experimental procedure are given by Miller et al. [1].

The development of fusion crusts on meteorites during their passage through the Earth's atmosphere is universally recognized, but fusion crusts and their implications for the atmospheric reprocessing of extraterrestrial materials have not been extensively studied [2]. In particular, isotopic effects resulting from reaction with atmospheric O₂ do not appear to have been documented hitherto. It has recently been shown [3], however, that atmospheric O₂ is characterized by a mass-independently fractionated component, resulting from stratospheric photochemical processes and involving O₂, O₃ and CO₂. Of particular interest, therefore, is to assess the extent to which a terrestrial atmospheric oxygen signal may be identified in the flown 'Stone' samples and in the fusion crust of the LL6 ordinary chondrite sample, analyzed for comparison.

In terrestrial rocks and minerals, oxygen isotope fractionations ¹⁷O/¹⁶O and ¹⁸O/¹⁶O follow a mass-

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dependent relationship given by:

$$^{17}\text{R}_s/^{16}\text{R}_r = (^{17}\text{R}_s/^{16}\text{R}_r)$$

where ^xR refers to $^x\text{O}/^{16}\text{O}$, subscripts s and r represent *sample* and *reference* materials, respectively, and 0.52 [4,5]. In terms of the delta notation, in which oxygen isotope values are conventionally reported, the above expression is usually approximated to:

$$^{17}\text{O} = 0.52 \cdot ^{18}\text{O}$$

Departures from the terrestrial mass-dependent fractionation line are thence quantified in terms of ^{17}O , which is defined as $^{17}\text{O} - 0.52 \cdot ^{18}\text{O}$ [6].

Results:

Reference materials. For 11 analyses of isotopic reference materials (consisting of NBS-28 and an obsidian, secondary standard), undertaken at the same time as the ‘Stones’ samples, a mean ^{17}O value of $0.026 \pm 0.032 \text{‰}$ (1 σ) was obtained, on the basis of the ‘exact’ mass-dependent fractionation relationship between ^{17}O and ^{18}O , and using a slope value () of 0.5248, as measured for silica samples at the Open University. The ^{17}O of atmospheric O_2 was measured using tank oxygen gas: five replicate analyses gave a value of $-0.323 \pm 0.032 \text{‰}$ (1 σ). For the atmospheric oxygen ^{17}O calculations, the same value was used as for the terrestrial silicates.

‘Stones’ - ‘Martian soil analog’. Basalt grains and gypsum from the control (non-flight) samples predictably gave ^{17}O values of essentially zero. (Basalt gave a value of 0.058‰; duplicates of the gypsum cement gave -0.009 and -0.022‰ respectively.) A very limited quantity of post-flight material was available, consisting of a few small grains and a fine powder, which made it virtually impossible to assess whether any fusion crust had formed. Results of ^{18}O measurement confirmed that the coarser grains consisted primarily of the basalt (initial $^{18}\text{O} \sim 5.8\text{‰}$) whereas the fine-grained material consisted largely of the gypsum matrix (initial $^{18}\text{O} \sim 8.2\text{‰}$). No change in ^{17}O from zero was detectable in either fraction, however, within the limits of experimental precision. Overall, six replicate measurements produced a mean ^{17}O value of $-0.012 \pm 0.030 \text{‰}$ (1 σ).

‘Stones’ - sample holder (heat shield). Although the ‘Martian soil analog’ samples apparently displayed no isotopic interaction with the atmosphere during re-entry, it was observed that the heat shield material used to secure these samples to the Foton-12 capsule had itself developed a well-defined crust of silica during flight. Samples of this silica crust and also the (apparently carbonaceous) interior of the sample holder were therefore also subjected to oxygen three-isotope analysis, for comparative purposes. Whereas the interior exhibited no difference in ^{17}O value from a terrestrial silicate or oxide (measured ^{17}O value 0.011‰), analysis of the silica crust showed that some isotopic exchange with the Earth’s atmosphere had occurred: replicate ^{17}O values of -0.212 and -0.208 were obtained.

‘Stones’ - Dolomite sample. It was observed that a significant proportion of the leading face of the post-flight dolostone had apparently been ablated away. Furthermore, this surface was white in color, whereas a cross-section through the sample revealed distinct stratification into a ‘grey’ zone (interior) which, in turn, preceded a darkly-colored section, located adjacent to the heat shield. For present purposes, duplicate sub-samples were taken from all three zones. It should be noted that direct measurement of ^{17}O in carbonates is not feasible using laser-assisted fluorination procedures; CO_2 is evolved during sample heating and its associated ^{17}O value cannot be determined without the complexity of converting the CO_2 into O_2 . Therefore, ^{17}O measurements are undertaken on the residual oxide, formed by extended heating of the carbonate, and assuming that the carbonate-to-oxide conversion conforms to mass-dependent fractionation behavior. In the case of the ‘Stones’ dolomite sample, significant conversion to CaO and MgO will have occurred during the heating that accompanied re-entry of the capsule through the Earth’s atmosphere.

Isotopic measurements revealed that the ‘white’ (leading edge) was depleted in ^{18}O ($^{18}\text{O} 30.0 \pm 1.5 \text{‰}$) relative to the other two zones ($^{18}\text{O} 35.7 \pm 0.2 \text{‰}$). Interestingly, all zones displayed isotopic exchange with atmospheric oxygen, as evidenced by a mean ^{17}O value of $-0.241 \pm 0.075 \text{‰}$ (1 σ). Note that this value is comparable to that observed for the silica crust formed on the sample holder.

Appley Bridge meteorite. A mean difference of 0.214‰ was found between the respective ^{17}O values of the distinctive fusion crust ($1.151 \pm 0.053 \text{‰}$, 1 σ precision, four replicates) and interior (1.348‰ , 1.382‰ ; duplicate measurements) of this meteorite. Isotopic exchange between the fusion crust and atmospheric oxygen during infall is implicated.

Conclusions: The preliminary findings presented here show that, whereas a meteorite consisting primarily of carbonate minerals would not be expected to develop a fusion crust during entry through the Earth’s atmosphere, oxygen three-isotope measurements will clearly allow such a material to be identified from a non-meteorite specimen, by virtue of high temperature isotopic exchange having occurred with atmospheric oxygen. This appears not to be the case for the synthetic ‘Martian soil’ sedimentary rock flown on Foton-12, however. Further, detailed examination of these samples is presently in progress.

References: [1] Miller M. F. et al. (1999) *Rapid Commun. Mass. Spectrom.* 13, 1-7. [2] Genge M. J. and Grady M. M. (1999) *Meteoritics & Planet. Sci.*, 34, 341-356. [3] Luz B. et al. (1999) *Nature* 400, 547-550. [4] Craig H. (1957) *Geochim. Cosmochim. Acta* 12, 133-149. [5] Matsuhisa Y. et al. (1978) *Geochim. Cosmochim. Acta* 42, 173-182. [6] Clayton R. N. and Mayeda T. K. (1988) *Geochim. Cosmochim. Acta* 52, 1313-1318.