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Do meteoroids of sedimentary origin survive terrestrial atmospheric entry? The ESA artificial meteorite experiment STONE

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Abstract

The 18 SNC meteorites identified to date are all igneous rocks, being basalts or basaltic cumulates. The lack of sedimentary rocks in this inventory is therefore surprising, in view of the collisional history of Mars and the likelihood that Mars experienced warmer conditions, possibly with a significant hydrosphere, earlier in its history. To address the possibility that sedimentary rocks ejected by impact from the surface of Mars may have reached the Earth, but did not survive terrestrial atmospheric entry, an experiment was performed in which samples of dolomite, a simulated Martian regolith (consisting of basalt fragments in a gypsum matrix) and a basalt were fixed to the heat shield of a recoverable capsule and flown in low Earth orbit. Temperatures attained during re-entry were high enough to melt basalt and the silica fibres of the heat shield and were therefore comparable to those experienced by meteorites. The dolomite sample survived space flight and atmospheric re-entry, in part, as did fragments of the simulated Martian regolith, allowing detailed examinations of these 'artificial meteorites' to be conducted for chemical, mineralogical and isotopic modifications associated with atmospheric re-entry. Oxygen three-isotope measurements of the silica 'fusion crust' formed on the sample holder during atmospheric re-entry fit on a mixing line, with tropospheric O_2 and the interior of the sample holder as end members.

Because much of the surface of Mars is covered by clastic sediments, meteorites of Martian provenance might be expected to be mostly sedimentary rocks rather than igneous ones. However, in the absence of a readily identifiable fusion crust, the extraterrestrial origin of such sedimentary rocks on Earth would most probably not be recognised without detailed petrological-geochemical examination and, ultimately, isotope measurements. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Artificial meteorites; Atmospheric entry; Dolomite; Martian sediments; Isotopes

1. Introduction

Most of the approximately 25,000 meteorites identified to date are believed to originate from bodies in the asteroid belt. As of January 2002, there are 18 meteorites that with certainty come from the Moon. Another group, the SNC meteorites, of which 18 have so far been identified, are believed to originate from Mars (Wood and Ashwal, 1981; McSween, 1994). In contrast to the prevalence of regolithic samples among lunar meteorites, sedimentary rocks and regolith samples are absent from the SNC inventory, although it is quite possible that some of the basaltic shergottites are surficial flows from younger regions of Mars. The present-day surface of Mars appears to be covered by both impact generated regolith and by sedimentary rocks, the latter possibly having been deposited by flowing water or in basins, although deposition in a dry, subaerial setting in which atmospheric density and variations thereof mimicked a subaqueous, depositional setting cannot be excluded (Malin and Edgett, 2000). If water played a key role, the sedimentary rocks should be comprised of detrital

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deposits, as well as chemical sediments (evaporites). Furthermore, the presence of groundwater would be expected to have compacted—at least in part—loose sediments and regolith by filling the pore space with evaporitic minerals. On this basis, such consolidated sedimentary hard rocks should be among the Martian meteorites, but none have so far been identified. Therefore, the lack of sedimentary meteorite samples cannot be readily explained. Such material either does not survive the escape process which requires an escape velocity of > 5 km/s or does not survive terrestrial atmospheric entry. Or it is not readily identifiable as being of extraterrestrial origin.

In order to investigate the physical and chemical modifications to sedimentary rocks during terrestrial atmospheric entry, the STONE experiment was devised. Samples of terrestrial rock were secured to the heat shield of a recoverable spacecraft (Foton-12) and flown in low Earth orbit for a period in excess of 14 days, before atmospheric re-entry and recovery of the capsule. To the best of our knowledge, this is the first investigation to involve the creation of 'artificial meteorites'.

2. Samples and flight details

The samples selected for this investigation were as follows:

- A basalt (alkali basalt from Pauliberg, Burgenland, Austria, of Miocene age), to serve as an in-flight control and to demonstrate that the frictional heat was sufficient to form a fusion crust, although the re-entry speed of 7.8 km/s was considerably lower than the 12–20 km/s of typical meteoroids. This sample and its holder were not recovered after flight, unfortunately; they probably became detached from the spacecraft during the final stage of atmospheric re-entry.
- A dolostone, a chemical sedimentary carbonate rock consisting of dolomite and remnants of carbonate fossil shells, together with some quartz and feldspars debris. The rock is very fine-grained (< 50 μm), re-crystallised and dense. The sample (of Triassic 'Schlern-Dolomit') was collected at the base of the Lagazuoi Mountain in the bed of Rio Lagazuoi, just below Passo di Falzarego, Belluno, Italy. The chemical composition of the dolostone, determined (as respective oxides) by electron microprobe analysis, was: 31.0 wt% CaO, 22.1 wt% MgO, 0.10 wt% FeO and 0.04 wt% MnO.
- An artificial rock, simulating Martian soil. It was made in a proper mold by mixing 80 vol% alkali basalt crushed into fragments of < 5 mm with 20 vol% gypsum slurry. Basalts are representative of all juvenile planetary surfaces, being the primitive silicate liquids which form by partial melting of chondritic matter. The sample used in the artificial Martian regolith was an alkali olivine basalt from Pauliberg, a tertiary volcano in Burgenland, Austria. Sulphates and basalts are common at the surface of Mars, as is evident from Martian soil analyses by the Viking and Mars Pathfinder landers (Baird et al., 1976; Clark and Baird, 1979; Clark et al., 1982; Rieder et al., 1997); some Martian hardpans (cemented soil) can therefore be expected to be cemented by sulphates—analogous to terrestrial gypcretes.

Samples were fixed to the surface of the ablative heat shield of the Foton-12 capsule, around the stagnation (hottest) point. The material of the heat shield consisted of silica glass fibres embedded in urea formaldehyde polymer. All rock samples were shaped into disks 7 cm diameter (of which the central 5 cm was exposed), 1 cm thick, and clamped to the heat shield by a sample holder consisting of an annular disk of material similar to that of the heat shield. The sample holders were secured in place by bolts; no bonding adhesive was used. Foton-12 was launched on 9 September 1999 at Plesetsk (Russia) and landed on 24 September near Sudbodarovka, Orenburg (Russia). Flight duration was 14 days and 15 h. Orbital parameters were as follows: inclination 62.8°; perigee 225.1 km; apogee 405.4 km; orbital period 90.53 min.

3. Experimental methods

3.1. Mineralogical analysis

Polished thin sections of pre-flight and post-flight samples were prepared, and investigated by optical microscopy and analytical scanning electron microscopy. The phases were analysed with an ARL-SEMQ electron micro-analyser operated at 15 kV acceleration potential and 15 nA sample current. Phase analyses were performed with reference to natural and artificial minerals; standard correction procedures for matrix effects and drift were applied. The mineral content of the pre- and post-flight dolostone was determined from measurements made with a Siemens X-ray diffractometer. FT-Raman spectra were recorded using a Brucker IFS 66 instrument with a FRA 106 Raman module attachment. Excitation was effected at 1064 nm by a Nd^{3+}/YAG laser and spectra were recorded using up to 4000 accumulations, with a maximum of 20 mW at the sample surface and a spectral resolution of 4 cm^{-1}.

3.2. Isotope measurements

3.2.1. Bulk measurements of carbon yield (as CO_2) and carbonate isotopic characterisation

Standard experimental procedures based on those first described by McCrea (1950) were used for carbonate bulk carbon and oxygen isotope determinations. Finely ground samples were reacted overnight with '100%' orthophosphoric acid (SG 1.92) at 50°C; the $^{18}O/^{16}O$ fractionation between the reactant dolomite and product CO_2 at 50°C was taken as 1.01066 (Rosenbaum and Sheppard, 1986). Replicate analyses of carbonate reference materials gave $\delta^{13}C_{VPDB}$ reproducibility to better than 0.04‰, and $\delta^{18}O_{VSMOW}$ to 0.002‰, respectively.

3.2.2. *Stepped heating (pyrolysis) of dolomite for carbon yield (as CO_2) and carbonate isotopic characterisation*

Incremental in vacuo heating (100°C steps) of dolomite fragments was performed to investigate whether differences in the CO_2 release profile and associated isotopic composition were evident in samples selected from different zones of the flown dolomite, also for comparison with the control sample. The principle of stepped heating of carbonaceous materials, either in the presence of supplied oxygen or in vacuo, for release of CO_2 for isotopic analysis, has been extensively documented elsewhere (e.g., Wright and Pillinger (1989) and references therein). The technique is used primarily to remove contaminant carbonaceous matter of terrestrial origin from extraterrestrial samples, thus permitting isotopic characterisation of the residual, indigenous carbon phases. For the present work, the experimental procedure closely followed that advocated by Miller and Pillinger (1997). Isotopic measurements were conducted on a PDZ Europa GEO 20-20 mass spectrometer, operating in dual inlet mode.

3.2.3. *Oxygen triple isotope measurements*

After sample homogenisation by laser heating in vacuo to melting, O_2 was extracted from 1–2 mg of the oxygen-bearing matrix by infrared laser-assisted fluorination, using BrF_5 as the fluorinating agent (after Clayton and Mayeda, 1963). Following purification, the released O_2 was analysed for $\delta^{17}O$ and $\delta^{18}O$ isotopic composition using a VG Isotech PRISM III dual inlet mass spectrometer. Analytical precision, at the 1σ level, for replicate measurements of reference materials using the combined extraction and isotopic analysis procedures, was about 0.08‰ for $\delta^{18}O$, 0.04‰ for $\delta^{17}O$, and 0.03‰ for $\Delta^{17}O$. Further details are given by Miller et al. (1999). Gypsum samples were thermally decomposed by laser heating to form calcium oxide, prior to fluorination of this component. Some isotopic fractionation occurred during this process, on the basis of $\delta^{18}O$ values obtained for the NBS127 barium sulphate reference being ~ 1‰ lower than the accepted value of +9.3‰. Similar findings, but on a significantly greater scale, have been reported elsewhere (Bao et al., 2000). However, such isotopic fractionation (which arises from non-quantitative conversion) conforms to mass-dependent behaviour and therefore does not influence the associated $\Delta^{17}O$ measurement. Duplicate analyses of NBS127 gave $\Delta^{17}O$ results of 0.031‰ and 0.014‰, which are essentially zero within the analytical precision of the measurements.

4. Results and discussion

4.1. *Dolostone*

4.1.1. *Mineralogy*

The dolostone sample was retrieved intact, although reduced to a depth of about 3 mm, some 30% of its original thickness. The exposed surface was ablated in a manner comparable to etching. Although molten heat shield material (mostly silica) must have been continuously flowing over the dolomite surface during atmospheric entry (Fig. 1), there was no residue of it remaining. The mineralogy of the rock was dramatically modified at the exposed surface: the original dolomite thermally decomposed to CaO and MgO (periclase), with concomitant escape of CO_2, thereby forming a very fine-grained intergrowth (Fig. 2a, b). The lack of a fusion crust is attributed to the highly refractive nature of the solid oxides formed (melting temperatures are 2927°C for CaO and 2826°C for MgO), the physical weakness of the oxide mixture and the chemical instability of CaO in the terrestrial atmosphere. No calcium or magnesium silicates were detected. X-ray diffraction of the fresh surface showed only the presence of MgO, CaO, $Ca(OH)_2$ and traces of quartz, phases which were also identified in the fresh polished thin section by analytical scanning electron microscopy. Raman spectroscopy performed two weeks later did not identify CaO but instead detected portlandite and calcite. We note that CaO is hygroscopic and converts into portlandite in the terrestrial atmosphere and subsequently reacts with atmospheric CO_2 to form calcite.

The dolomite decomposition products formed grain-like units, which were considerably smaller than the original dolomite grains and highly porous. The degree of pyrolytic conversion to oxide ranged from complete at the exposed surface, to essentially zero at the bottom of the disk (about 3 mm distant), indicating the presence of a very steep temperature gradient during re-entry. Alteration visible with high-contrast back-scattered scanning electron imaging extends to only about 1.5 mm into the sample. Thermal breakdown of carbonate during re-entry was also indicated by electron microprobe analysis, which revealed respective CaO and MgO contents of up to 39.5 and 29.2 wt% near the exposed surface, considerably higher than the corresponding values recorded for the control (non-flown) dolostone. The low total of 68.7 wt% for the analyses of the pyrolysed dolomite indicated the presence of abundant pore space, of $Ca(OH)_2$, and possibly of some carbonate, not observable in the SEM. CO_2 yield from phosphoric acid reaction (performed for bulk isotopic analysis) also confirmed that the leading surface of the flown dolomite was depleted in carbonate, with 30 wt% loss of carbon relative to the control sample, whereas the ‘trailing’ surface (i.e., adjacent to the heat shield) experienced a reduction of only 20 wt%. It should be noted that the volume selected for carbon yield measurements (and carbonate isotopic characterisation) is likely to have included some secondary carbonate formed

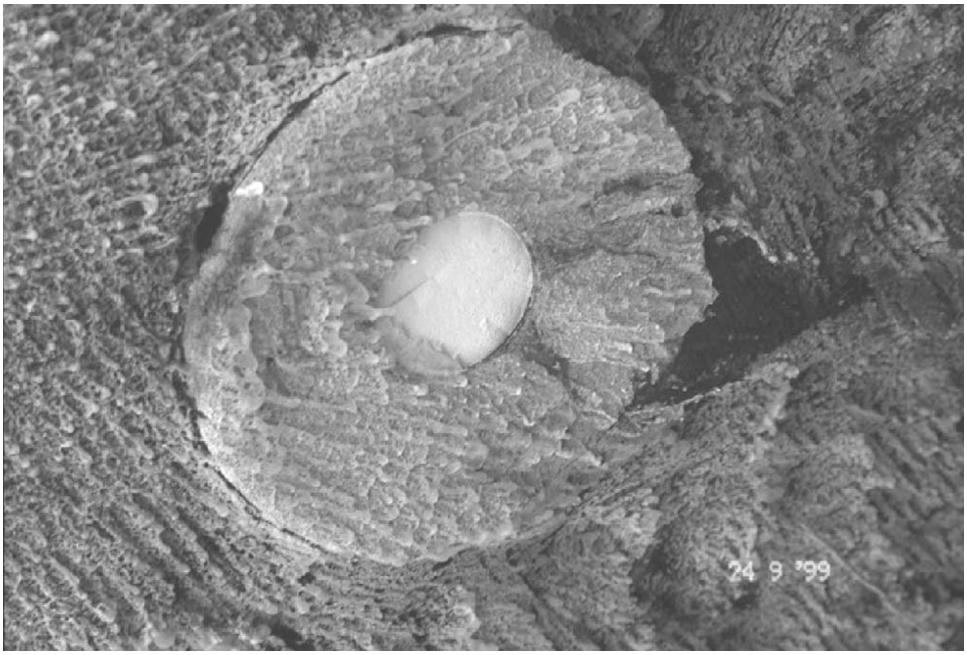

Fig. 1. Dolostone sample on the heat shield of the Foton-12 capsule. The sample (exposed diameter is 5 cm) is deeply eroded, surrounded by the sample holder and mounted in the heat shield. Sample holder and heat shield are covered by silica glass (grey to white, flowing from left to right) formed from silica fibres during atmospheric entry but the dolostone sample is free of such melts, except for some drops at the left side.

from the reaction of portlandite with atmospheric CO_2, as well as primary carbonate that survived atmospheric re-entry, because these analyses were conducted several weeks after recovery of the flown sample.

4.1.2. *Isotopic characterisation of the dolostone*

With regard to isotopic composition, carbonate carbon in SNC meteorites is notably enriched in ^{13}C compared to the vast majority of terrestrial counterparts, with $\delta^{13}C_{VPDB}$ values ranging up to +42‰ in ALH84001 (Romanek et al., 1994; Jull et al., 1998). In Nakhla, values from +23‰ to +49.6‰ have been reported (Jull et al., 2000). These are significantly higher than in any terrestrial analogue, with the possible exception of some diagenetic dolomitic limestones from deep marine environments (Murata et al., 1967). The experiments undertaken to measure the isotopic composition of carbonate in Martian meteorites were carried out on interior specimens, i.e. material away from the fusion crust and thus unaffected by entry heating. With the dolomite sample, we were able to analyse the carbon isotopic signatures on different zones of the residual carbonate. These measurements (Table 1) indicate that the leading and trailing surfaces experienced $\delta^{13}C$ reductions of 0.80‰ and 0.25‰, respectively, relative to the control (non-flown) material. Although this is in accord with kinetic isotopic fractionation having accompanied thermal degradation of the dolomite during re-entry, we note that secondary carbonates formed by post-flight reaction with atmospheric CO_2 ($\delta^{13}C_{VPDB} \sim 7‰$), as discussed in Section 4.1.1, would also be characterised by lower $\delta^{13}C$ values than the precursor dolomite. Stepped heating of the control and post-flight dolomite samples in vacuo gave rise to kinetic isotopic fractionation, as shown in Fig. 3. The isotopic shifts, however, were relatively small and thus would not be expected to disguise any distinctive, non-terrestrial carbon isotopic composition associated with sedimentary carbonates of Martian origin. Also evident from Fig. 3 is the substantially reduced carbonate content of the flown dolostone (especially of the leading surface), relative to the control sample.

It is well established (Sharma and Clayton, 1965) that thermal breakdown of carbonate gives rise to CO_2 enriched in ^{18}O relative to the parent material, with concomitant ^{18}O depletion in the residual solid. In contrast, secondary calcite formation via reaction with atmospheric CO_2 ($\delta^{18}O_{VSMOW} \sim +41‰$) would be expected to increase the bulk $\delta^{18}O$ value of the sample. Our observations (Table 1) show that latter effect predominates, with the $\delta^{18}O$ value of the leading (exposed) surface being 0.61‰ greater than that of the control sample. It is unfortunate that the reactive nature of the dolomite pyrolysis products, with respect to terrestrial atmospheric moisture and CO_2, serves to obscure some of the changes which occurred during atmospheric entry.

4.2. *Martian soil analogue*

4.2.1. *Mineralogical modifications*

The simulated Martian sediment sample disintegrated before recovery. The extensive ablation of the associated sample holder and surrounding heat shield shown in Fig. 4 was

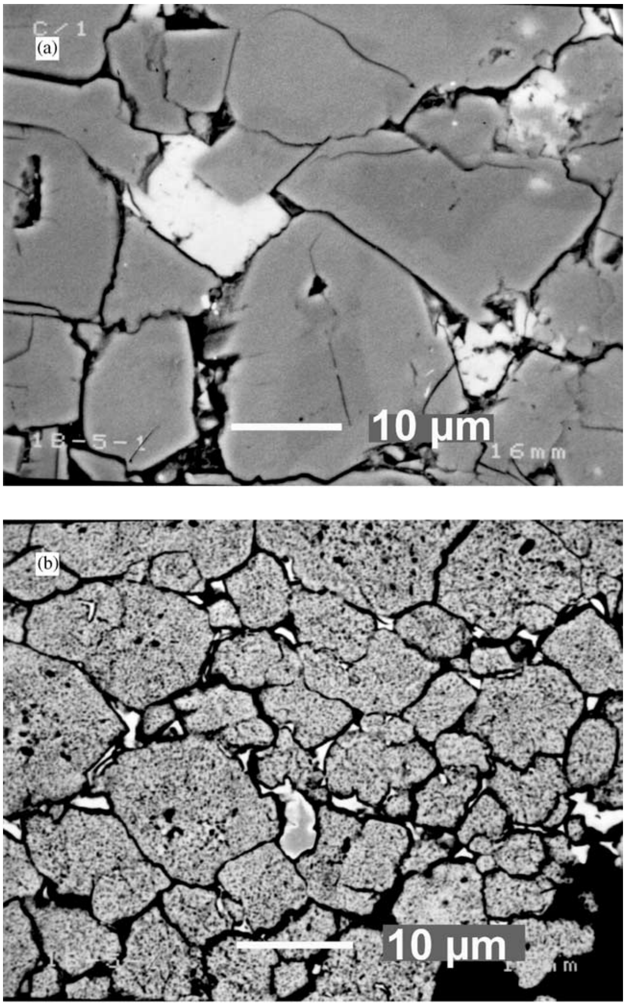

Fig. 2. (a) Scanning electron microscope (SEM) image (BSE mode) of pre-flight dolostone consisting of dolomite (grey) and a few silicates (white). (b) Similar image of post-flight dolostone. The original dolomite grains were transformed during thermal degradation into CaO (light) and MgO (dark) giving them a mottled appearance. Silicates appear white, pore space has increased (black).

Table 1

Bulk carbon and oxygen ($\delta^{18}O$) isotopic compositions of different zones of the flown dolomite, together with the control sample, as determined from measurements on the CO_2 liberated by orthophosphoric acid reaction at 50°C

	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ CO_2 (‰)	$\delta^{18}O_{VSMOW}$ residual solid (‰)
Pre flight (*control*)	4.03	10.02	30.26
Post-flight, leading	3.23	10.62	30.87
Post-flight, trailing	3.78	9.33	29.56
Post-flight, interior	3.95	9.88	30.12

apparently due to the release of small sample fragments during atmospheric re-entry, thus indicating that the sample was not disintegrated via gypsum dehydration during spaceflight, i.e. before re-entry. It proved possible to retrieve small pieces of the flown sample rock from underneath the sample holder. Most fragments were covered by a melt (Fig. 5); furthermore, the abundant pore space within the gypsum component was partly filled with melt. The fusion crust consists basically of a three layer structure: (i) an outermost melted crust, (ii) a partially melted outer substrate and (iii) an inner substrate in which heating affected mainly the gypsum cement.

The melted crust consisted of glass with abundant lath-like to dendritic phenocrysts of a calcium-rich silicate mineral, probably vesuvianite, $Ca_{10}Mg_2Si_7O_{34}(OH)_2$, together with some iron-titanium oxides. Isolated areas within the melted crust and at the boundary with the underlying substrate consisted of fine-grained porous materials that contained unidentified calcium-rich silicate, as well as oldhamite (CaS), potassium-bearing aluminosilicate glass, and an iron-titanium oxide component. In parts, the melt cover contained glassy silica fibres, remnants from the heat shield.

The partially melted outer substrate was laterally discontinuous and consisted of embayed olivine, pyroxene and plagioclase crystals contained in vesicle-bearing glassy veins of alkali aluminosilicate. The textural relations and compositional variation within relicts suggest that non-equilibrium partial melting of all silicate phases occurred. Within the inner substrate, the basalt fragments were largely unaltered. Magnetite was locally present and preferentially covered the surfaces of basalt rock fragments (Fig. 6). Some gypsum survived; the remainder was converted to anhydrite. Basalt fragments close to the melted crust also contain vesicles, due to the mobilisation of the alkali-aluminium-silicate glass of the basalt. These areas also contained manganese-bearing iron spinels.

The chemical composition of the glass varied substantially, ranging from highly silicic to Fe-, Ti- and Mg-rich (Table 2). However, the most common glass was characterised by a composition approaching that of the original basalt, but enriched in SiO_2, CaO and K_2O, yet depleted in TiO_2, FeO and MgO. This indicates that the glassy matrix of the basalt was preferentially melted and that this melt was additionally enriched in CaO from the gypsum and in SiO_2 from the silica glass fibres of the heat shield. A glass with the composition of the original basalt was not encountered, which indicates that preferentially partial melting of the basalt occurred and mixing with silica and gypsum decomposition products was unavoidable. The layered structure of the crust confirms that a significant temperature gradient occurred across the thickness of the sample disk during atmospheric re-entry. Surface melting of basalt fragments within the substrate below the fusion crust, however, indicates heating by a super-heated gas that pervaded the pore spaces. Gases within the bow shock envelopes of meteoroids may experience heating to several thousand degrees; if they penetrated pore spaces created by degassing of the sulphate matrix, such a mechanism could account for the surface-correlated heating of basalt fragments deep within the artificial Martian regolith sample and underneath the protective sample holder.

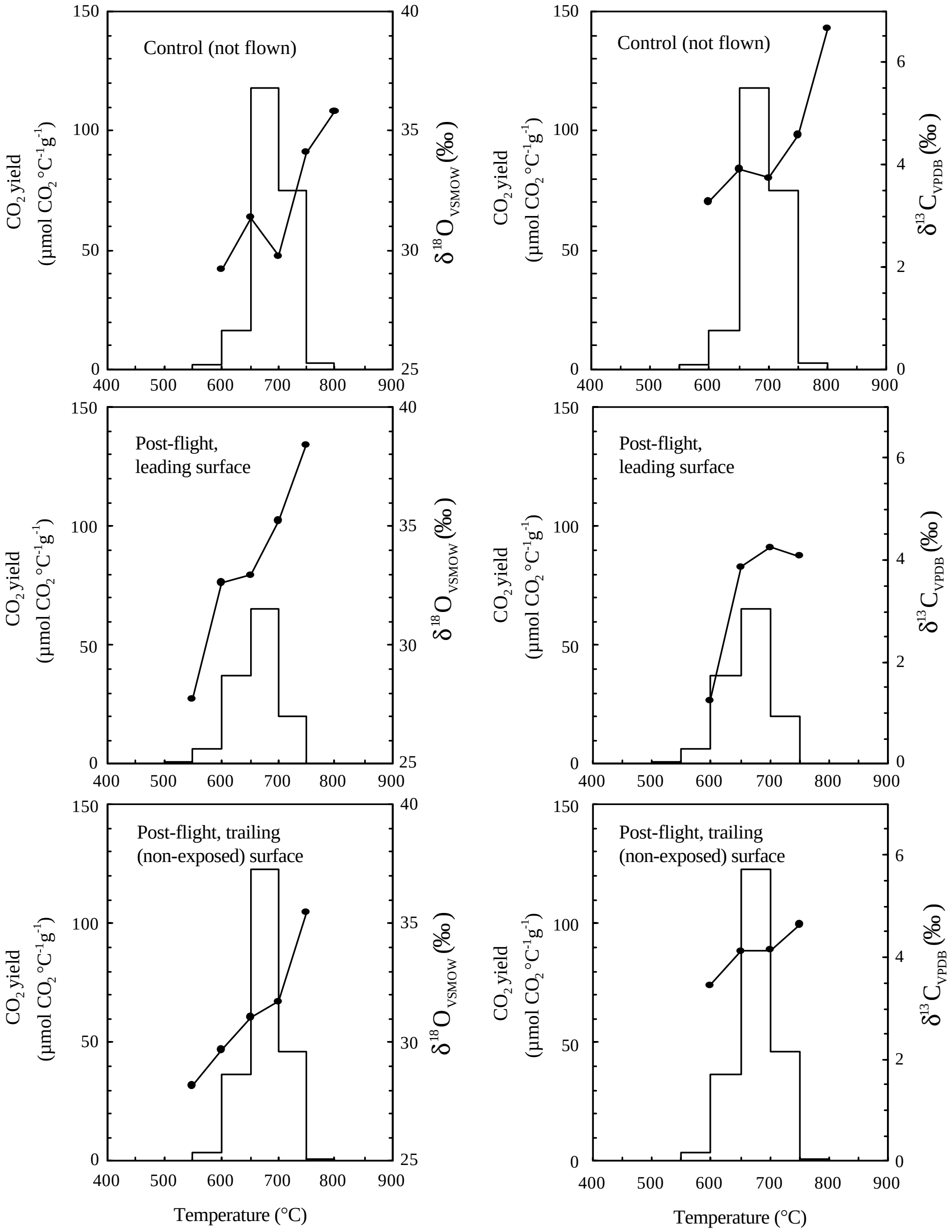

Fig. 3. Stepped heating profiles (in vacuo pyrolysis) of pre- and post-flight dolomite, showing normalised CO_2 yields (histogram) as a function of temperature, together with the isotopic characteristics of the CO_2 released.

The loss of the matrix probably led to large ablative mass loss rates of loosened particles. Only those basalt fragments that remained in situ would be expected to retain a melted crust; this explains why the fusion crust on the artificial Martian regolith is restricted to small areas of partially-exposed surface. (Note that we were only able to obtain fragments from underneath the sample holder). The irregular topography thus created may have increased contamination of the sample by gases derived from the heat shield, since it may have provided channels through which contaminants (including SiO_2 melt) could penetrate to various depths. This situation apparently led to the unexpected formation of exotic minerals and to a high mobility of all elements during the heating event. Part of the sulphate from the gypsum was reduced (presumably by the carbonaceous resin from the heat shield), forming sulphides of calcium (oldhamite), magnesium (Mg, Fe, Ca monosulphide and oxysulphides) and iron (FeS, pyrrhotite). In meteorites, sulphides of strongly lithophilic elements such as Ca and Mg are only known to occur in highly reduced enstatite meteorites. Their presence indicates highly reducing conditions locally and high sulphur fugacity. Transport of the reactants is likely to have occurred via a vapour phase, promoting rapid reaction. The absence of metallic iron within relatively Fe-rich olivines, however,

Fig. 4. Martian soil analogue (basalt regolith ‘gypcrete’) in place on the Foton-12 capsule. The exposed sample (5 cm diameter hole in centre of sample holder) has been lost, exposing the underlying heat shield material. During its disintegration, basalt fragments eroded the protective heat shield on the lee side (lower centre). Air flow was from top to bottom as marked by silica glass flow pattern. Sample fragments were recovered from underneath the sample holder.

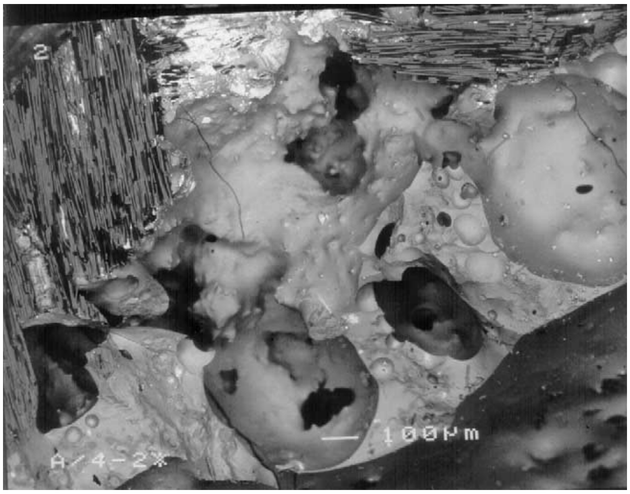

Fig. 5. SEM image of melt (grey, smooth surface) and fragments of silica glass tissue (striped areas on upper left and right), on the surface of the simulated Martian regolith sample (Foton-12A). The glass has a wide range of compositions but commonly is basaltic with enrichments in Ca and Si (obviously admixtures from the gypsum matrix and silica fibres of the heat shield, respectively).

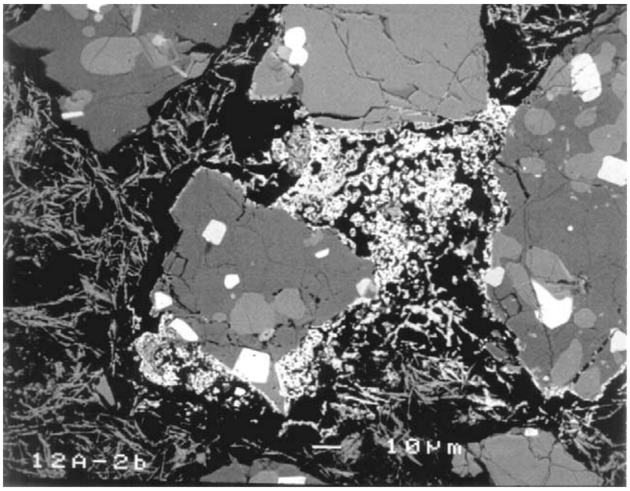

Fig. 6. SEM image of polished simulated Martian regolith sample Foton-12A. Basalt fragments show varying amounts of olivine, pyroxene and glass (different shades of grey) and bright Ti-magnetite grains. The matrix is porous (black) and contains gypsum crystals (grey rods). The matrix has been locally enriched in Fe oxides during the re-entry heating event, presumably via the vapour phase. Note the decoration of basalt fragments (centre and right) by Fe oxides (magnetite).

even in the partially melted outer substrate, suggests that the reduction was not pervasive and did not affect the silicates. This may be due to the brevity of events, being insufficient to allow diffusion of Fe to the silicate surface, where reaction with the reducing vapour could occur. Conditions elsewhere within the same sample were clearly more oxidising, apparently dominated by air, and caused the precipitation of various amounts of magnetite (Fig. 6). The precipitation of many small magnetite grains at the surface of basalt fragments is puzzling; this feature is typical of micrometeorites (Kurat et al., 1994). Apparently, mobilisation of Fe oxides (from the melt and/or from the basalt fragments) was particularly widespread and effective; it is also very likely to have occurred via a vapour phase—in accordance with chondrite vaporisation experiments (Gooding and Muenow, 1977).

Table 2
Martian soil analogue sample Foton12A

	4/1 #1	4/1 #5	4/1 #4	3 #1	3 #2	2/1 #1	4/1 #3	Basalt
SiO_2	83.8	63.0	53.3	**51.9**	**49.7**	**48.1**	44.6	45.9
TiO_2	1.3	1.2	5.6	**2.1**	**3.4**	**3.8**	9.2	3.9
Al_2O_3	1.0	2.1	3.2	**12.5**	**10.7**	**13.3**	3.1	11.1
Cr_2O_3	0.0	0.4	0.0	**0.0**	**0.1**	**0.1**	0.0	0.1
MnO	0.0	0.0	0.5	**0.0**	**0.1**	**0.2**	0.5	0.2
FeO	0.9	4.9	8.7	**5.2**	**9.1**	**5.7**	10.3	11.4
CaO	6.4	17.3	15.6	**17.2**	**17.6**	**16.7**	19.4	10.7
MgO	1.0	1.6	1.2	**4.4**	**3.5**	**4.8**	0.7	9.5
K_2O	3.5	3.0	4.2	**2.2**	**2.2**	**1.6**	2.4	1.5
Na_2O	2.1	6.2	7.7	**3.8**	**3.3**	**5.6**	8.5	2.9

Selected EDS-analyses of glasses (in wt%, normalised to total = 100%); **bold**: most common glasses with basaltic composition. Pauliberg basalt analysis from Poultidis and Scharbert (1986).

4.2.2. Oxygen triple isotope measurements

The development of fusion crusts on meteorites during their passage through the Earth's atmosphere has long been recognised, but the implications of fusion crust development for the atmospheric reprocessing of extraterrestrial materials have not been extensively studied (Genge and Grady, 1999). In particular, isotopic exchange between fusion crust silicate and atmospheric oxygen does not appear to have been documented hitherto. It has recently been shown (Luz et al., 1999) that atmospheric (tropospheric) O_2 is characterised by a mass-independently fractionated isotopic component, derived (at least in part—see Miller, 2002) from stratospheric photochemical processes and involving O_2, O_3 and CO_2. Of particular interest, therefore, was to assess whether evidence for oxygen isotopic exchange during terrestrial atmospheric entry may be identified in the components of the flown sample of simulated Martian regolith. The associated sample holder was found to have developed a substantial 'fusion crust' of reasonably pure silica (from silica glass fibres constituting the bulk of the heat shield material) during atmospheric re-entry and was therefore subjected to oxygen triple isotopic measurements, as was the interior of the sample holder, for comparison. To assess whether this procedure may be used to trace isotopic exchange with atmospheric oxygen during fusion crust formation in the case of a natural meteorite, samples of the well-preserved silicate fusion crust and interior of an LL6 ordinary chondrite fall (Appley Bridge) were similarly analysed.

Terrestrial rocks and waters generally conform to mass-dependent fractionation of $^{18}O/^{16}O$ relative to $^{17}O/^{16}O$; departures from the associated fractionation line are characterised by $\Delta^{17}O$ (Clayton and Mayeda, 1988). In rigorous terms, $\Delta^{17}O = 1000 \times [[1 + (\delta^{17}O/1000)] - [1 + (\delta^{18}O/1000)]^{\lambda}]$, where $\lambda \sim 0.52$ (Matsuhisa et al., 1978; Miller et al., 1999; Miller, 2002). Using a value of 0.5247 for λ (Miller, 2002) in the case of terrestrial rocks and waters, in conjunction with 23.5‰ and 11.92‰, respectively, for the $\delta^{18}O_{VSMOW}$ and $\delta^{17}O_{VSMOW}$ values of tropospheric O_2 (Luz et al., 1999), gives $\Delta^{17}O = -0.34$‰ for tropospheric O_2.

Table 3
Results of oxygen triple-isotope measurements of comminuted basalt fragments from the Martian soil analogue control and flown samples, together with comparable data from the silica 'fusion crust' and interior of the associated sample holder. Also shown are data from the fusion crust and interior of an LL6 ordinary chondrite fall

	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{17}O_{VSMOW}$ (‰)	$\Delta^{17}O$ (‰)
Martian soil analogue, pre-flight			
Basalt grain	5.78	3.09	0.059
Martian soil analogue, post-flight			
Coarse grain fraction (primarily basalt)	6.19	3.27	0.027
Duplicate	5.54	2.92	0.016
Sample holder, post-flight			
Silica 'fusion crust'	16.62	8.48	− 0.211
Duplicate	16.57	8.45	− 0.206
Carbonaceous interior	6.55	3.44	0.011
Appley Bridge LL6 ordinary chondrite			
Fusion crust	4.44	3.48	1.153
Duplicate	4.20	3.36	1.162
Interior	4.44	3.72	1.383
Duplicate	4.21	3.56	1.348

Basalt fragments and gypsum from the control sample (not flown) predictably gave $\Delta^{17}O$ values indistinguishable from zero. Recovered post-flight material consisted of only a few small fragments (comparable in size to the original comminuted basalt grains) and a fine powder. Results of $\delta^{18}O$ measurement confirmed that the larger fragments consisted primarily of the basalt (initial $\delta^{18}O_{VSMOW} \sim 5.8$‰). No change in $\Delta^{17}O$ from zero was detected in either fraction, however, within the limits of experimental precision. The salient results are presented in Table 3 and Fig. 7, which show that, although no mass-independent isotopic component was detected in the basalt from the Martian soil analogue sample, the silica 'fusion crust' from the associated sample holder was characterised by a $\Delta^{17}O$ value of close to -0.208‰. The corresponding interior exhibited no offset from a terrestrial silicate or oxide (measured $\Delta^{17}O$ value

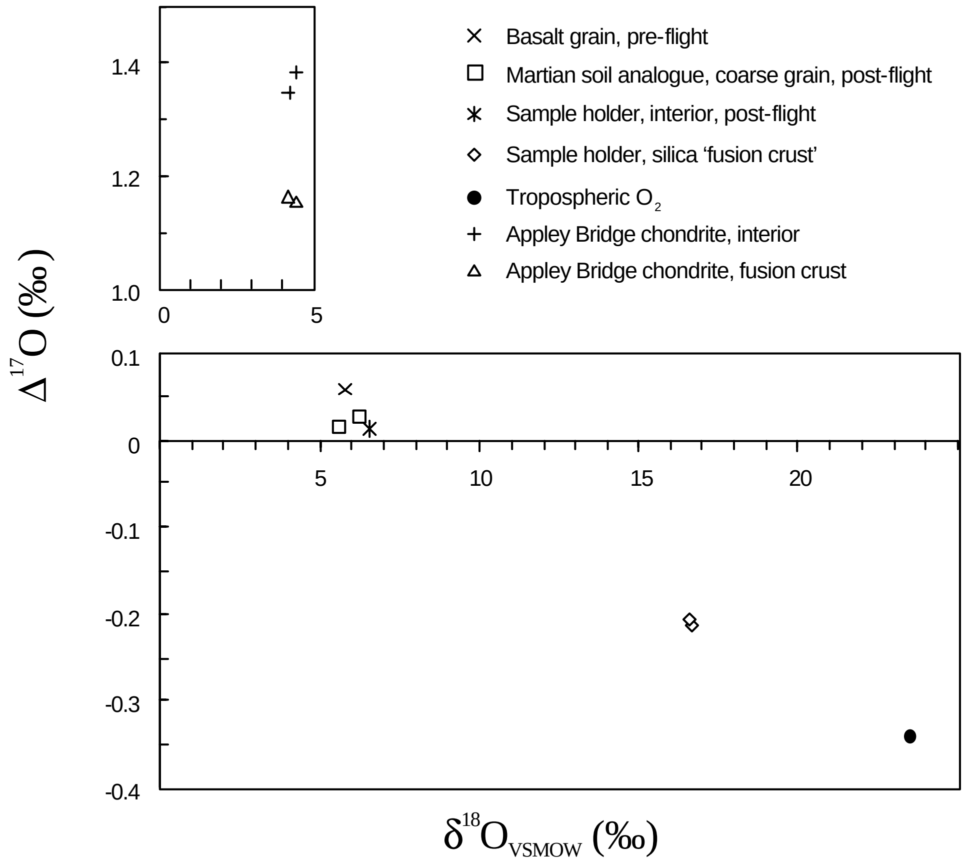

Fig. 7. Illustration of the offset ($\Delta^{17}O$) of 'STONE' samples from the terrestrial oxygen isotope mass-dependent fractionation line, reported as a function of the corresponding $\delta^{18}O$ values. Also shown are the corresponding data for tropospheric O_2 and the Appley Bridge chondrite (fusion crust and interior). Note that the external precision of the $\Delta^{17}O$ values determined for this paper is 0.057 at the 2σ level, hence all the reported 'STONE' results are indistinguishable from the terrestrial fractionation line, with the sole exception of the silica 'fusion crust' associated with the flown sample holder. Note also that this material lies on a mixing line defined by tropospheric O_2 and the carbonaceous interior of the sample holder.

0.011 ± 0.027‰, std. error). Fig. 7 shows that the silica 'fusion crust' oxygen isotopic data fit on a mixing line (regression coefficient $R^2 = 0.998$), with tropospheric O_2 and the interior of the sample holder as end members. Although a $\Delta^{17}O$ distinction of similar magnitude is evident between the interior and fusion crust of the Appley Bridge chondrite, there is no concomitant change of $\delta^{18}O$ value. Thus, the process in this case is evidently more complex and requires further investigation before a satisfactory explanation can be proposed.

5. Conclusions

In conclusion, temperatures attained at the heat shield of the Foton-12 capsule during atmospheric re-entry were high enough to melt basalt and pure silica glass and, therefore, were comparable to those experienced by meteoroids. In fact, the conditions experienced by Foton-12 during atmospheric re-entry closely mimicked those under which natural meteors occur. This assertion is supported by the observation of a fusion crust on the Martian soil analogue sample, the abundant and well-oriented regmaglypts on the heat shield, and the evidence for oxygen isotopic exchange with atmospheric O_2. The STONE experiment thus appears to be directly applicable to evaluating the feasibility of Martian sedimentary ejecta surviving terrestrial atmospheric entry. The results for the sedimentary carbonate (dolostone) indicate that the thermal instability of such rocks prevents the formation of a fusion crust and therefore precludes their ready recognition as meteorites. Only isotopic analyses could reveal their possible heritage from Mars.

The result for the consolidated clastic sediment (Martian soil analogue, 'gypcrete', a 'hardpan') is that such rocks, of size comparable to the flown disk, are unlikely to survive terrestrial atmospheric entry without fragmentation. Larger entities would be more likely to survive (several kg of the Tagish Lake meteorite were recently recovered, despite its low density of ~ 1.7 g cm^{-3} and significant friability), although these would probably be susceptible to rapid disintegration because of the terrestrial weathering characteristics of the most likely cements (mainly sulphates). Rapid disintegration of the rock will, of course, prevent its recognition as a meteorite. However, if observed during fall and collected soon thereafter, clastic sedimentary meteorites should be recognisable as such because of the development of a fusion crust—at least on the rock clasts. Because most of the Martian surface is covered by clastic sediments, meteorites of that composition should be present on the Earth, if indeed samples of Martian provenance are represented in the total meteorite inventory.

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