

## Laboratory experiments on the weathering of iron meteorites and carbonaceous chondrites by iron-oxidizing bacteria

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**Abstract**—Batch culture experiments were performed to investigate the weathering of meteoritic material by iron-oxidizing bacteria. The aerobic, acidophilic iron oxidizer (*A. ferrooxidans*) was capable of oxidizing iron from both carbonaceous chondrites (Murchison and Cold Bokkeveld) and iron meteorites (York and Casas Grandes). Preliminary iron isotope results clearly show contrasted iron pathways during oxidation with and without bacteria suggesting that a biological role in meteorite weathering could be distinguished isotopically. Anaerobic iron-oxidizers growing under pH-neutral conditions oxidized iron from iron meteorites. These results show that rapid biologically-mediated alteration of extraterrestrial materials can occur in both aerobic and anaerobic environments. These results also demonstrate that iron can act as a source of energy for microorganisms from both iron and carbonaceous chondrites in aerobic and anaerobic conditions with implications for life on the early Earth and the possible use of microorganisms to extract minerals from asteroidal material.

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### INTRODUCTION

The flux of extraterrestrial materials that falls to Earth today is estimated to be in the order of 20,000–40,000 T/yr (Love and Brownlee 1993), the majority of which is in the form of extraterrestrial dust such as micrometeorites or interplanetary dust particles from asteroidal (Blanchard et al. 1980) or cometary sources (Tomeoka et al. 2003; Yada et al. 2006). When this material reaches the Earth's surface, it is subjected to varied physical and chemical weathering processes, attributable to its fall location.

Discerning the mineralogical and chemical signatures of this weathering has been a key goal of many previous studies in order to elucidate the true pre-terrestrial signatures of solar system evolution. In particular, work has focussed on the inorganic alteration characteristics and weathering rates (Bland et al. 1996) of common find locations where the majority of new research samples are sourced, i.e., hot deserts (Ash and Pillinger 1995; Bland et al. 1996; Al-Kathiri et al. 2005) and Antarctica (e.g., Dennison et al. 1986; Gooding

et al. 1986; Dennison and Lipschutz 1987; Velbel 1988; Grady et al. 1991; Tyra et al. 2007). The study of weathering products on meteorites has been proposed as the basis for examining terrestrial weathering rates (Bland 2006). However, very little attention has been paid to the role of biota in mediating the alteration of extraterrestrial materials and the extent to which those processes can be discerned from abiotic weathering.

Terrestrial weathering studies have identified that primary ferromagnesian minerals in stony meteorites are oxidized in both hot desert and Antarctic environments (Burns et al. 1995; Bland et al. 1998). Similarly, rusting of Fe-Ni metal and silicates from iron/stony-iron meteorites has been widely reported, generating metal and silicate-based rust (Gooding et al. 1986) including goethite (Marvin 1963; Buchwald and Clarke 1989), lepidocrocite, akagenéite, and maghemite (Buchwald and Clarke 1989), magnetite (Marvin 1963; Buchwald 1989) and jarosite (Gooding 1986). As microorganisms can use metals in various oxidation states as a source of electron donors and acceptors for growth and other

compounds such as nitrogen and phosphorus as a source of nutrients (Ehrlich 2002) they would be expected, in the natural environment, to act immediately on fallen meteorites and to contribute to alteration processes.

Alteration textures and minerals within meteorites have previously been assigned to biological activity, specifically alteration textures made by filamentous organisms in contact with pyroxenes (Benzerara et al. 2003, 2005). Meteorites are known to be colonized by the microorganisms (Steele et al. 2000). The microbial consortia associated with the Tatahouine meteorite (classified as a diogenite [Lacroix 1931]) from the Sahara was found to be a subset of that found in the surrounding soil (Benzerara et al. 2006), suggesting that the weathering populations within meteorites are distinct.

Elucidating the effects of microorganisms on meteoritic material is necessary to determine whether terrestrial biological weathering could be confounded with purely abiotic chemical weathering, particularly that which has occurred prior to meteoritic fall either in space or other planetary bodies. A particularly important case is meteoritic material from Mars in which there is controversy about Martian biological involvement in weathering.

Investigating microbe-mineral weathering interactions on meteorites is also relevant for assessing the potential of extraterrestrial meteoritic materials as a source of accessible nutrients and energy on the early Earth. The early Earth was subjected to bombardment from extraterrestrial material on the order of over 200 times greater than today's rate (Love and Brownlee 1993; Hartmann et al. 2000). It is believed that the early Earth's surface would have been relatively inhospitable to life, with regular sterilization from impacts (Nisbet and Sleep 2001). However, despite the destruction that the extraterrestrial infall may have brought (Sleep et al. 1989), it may also have contributed raw materials to the Earth's surface (Chyba and Sagan 1992; Jenniskens et al. 2000) that were essential to the beginning, and subsequent evolution, of microbial life.

For example, carbonaceous chondrite-type meteorites carry up to 5% organic material, including amino acids, carboxylic acids and sugar-related compounds (for a review see Sephton 2002). In addition to providing prebiotic materials for biological evolution, they might provide a source of energy to support an existing biota. Carbonaceous chondrites also contain phosphorus in the form of phosphates, phosphides and metal/sulfide inclusions (Pasek 2007) and nitrogen, mostly present as organic nitrogen with some contribution from nanodiamonds from an interstellar source (Pizzarello et al. 2006). Mineralogical studies have shown that the carbonaceous chondrite meteorites contain iron, which is present as anhydrous phases such as olivine, pyroxenes, or hydrous phases such as serpentines and magnetites (for a review see Brearley and Jones 1998). Mautner (2002) demonstrated that carbonaceous chondrites

can provide sufficient nutrients to germinate plant tissue cultures. Although this unusual study was intended to determine whether asteroidal material could be used for future agricultural purposes, its wider implications illustrate that the major nutrients for biological growth can be found in extraterrestrial carbonaceous meteorites.

Carbonaceous chondrites are not the only form of extraterrestrial infall; iron meteorites are composed of intergrown kamacite and taenite, alloys of iron and nickel, with minor contributions from carbon and phosphorus-containing minerals (Buchwald 1977). Despite their rarity, iron meteorites have longevity on the Earth's surface due to their relative resistance to weathering compared to carbonaceous and other stony meteorites.

A report by Gonzalez-Toril et al. (2005) suggested that acidophilic bacteria could be grown on iron meteorites. The authors used samples of the Toluca meteorite to support the growth of *Leptospirillum ferrooxidans*, an iron-oxidizing microorganism. The work provides important and tantalizing insights into the possible use of meteoritic materials by a microbiota, although the aerobic iron-oxidation performed by *L. ferrooxidans* would not be relevant to the anoxic early Earth.

In this study, we sought to investigate microbe-mineral interactions with extraterrestrial materials. Specifically, we examined the interaction of iron oxidizers with iron and carbonaceous meteorites to study their capability to cause weathering through oxidation of the extraterrestrial iron in aerobic and anaerobic environments.

## MATERIALS AND METHODS

### Organisms and Culture Media

Experiments were conducted on the ability of iron oxidizers to weather meteorites by oxidizing extraterrestrial iron. Experiments were carried out using the aerobic acidophilic iron oxidizer *Acidithiobacillus ferrooxidans* obtained from the DSMZ (Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH) (Braunschweig, Germany) (DSM 583). Growth media specific to the selected organisms was prepared which contained essential elements for microbial growth.

*A. ferrooxidans* was cultured in modified K medium at 28 °C (Silverman and Lundgren 1959) made by mixing two solutions in equal proportions. Solution A was comprised 3 g NH<sub>4</sub>SO<sub>4</sub>, 0.1 g KCl, 0.5 g K<sub>2</sub>HPO<sub>4</sub>, 0.5 g MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.01 g Ca(NO<sub>3</sub>)<sub>2</sub>, 1 mL 10N H<sub>2</sub>SO<sub>4</sub> in 500 mL ddH<sub>2</sub>O. Solution B was a source of reduced iron and was provided as 44 g FeSO<sub>4</sub>·7H<sub>2</sub>O in 500 mL ddH<sub>2</sub>O, which was filter sterilized as the iron is oxidized during autoclaving. The final growth medium was made by mixing solution A and B in a 50:50 ratio. In experiments when weathering of meteoritic materials was being examined, solution B was replaced by an equal volume of dd H<sub>2</sub>O in the medium.

An anaerobic iron oxidizer enrichment culture was provided to the Open University by the Centre for Applied Geoscience, University of Tübingen as described in Straub et al. (1996). These enrichment cultures are facultative anaerobes originally obtained from freshwater sediments in town ditches of Bremen, Germany, and a brackish lagoon of the Baltic Sea near Hiddensee, Germany. The enrichment culture was grown in a defined anaerobic medium consisting of 0.3 g  $\text{NH}_4\text{Cl}$ , 0.05 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.4 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.6 g  $\text{KH}_2\text{PO}_4$  and 0.1 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  per liter, supplemented with 1 mL selenite-tungstate solution (40 mg NaOH, 0.6 mg  $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ , 0.8 mg  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in 100 mL dd  $\text{H}_2\text{O}$ ), 1 mL trace element solution (5.2 g Na-EDTA, 30 mg  $\text{H}_3\text{BO}_3$ , 100 mg  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , 190 mg  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 24 mg  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 2 mg  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 144 mg  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 36 mg  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 1 L dd  $\text{H}_2\text{O}$ ), 1 mL vitamin solution (2 mg biotin, 2 mg folic acid, 10 mg pyroxidine, 10 mg riboflavin, 10 mg thiamine, 5 mg pantothenic acid, 5 mg nicotinamide, 10 mg B12, 5 mg PABA (para-amino benzoic acid), 6 mg lipoic acid in 1 L dd  $\text{H}_2\text{O}$ ) and 30 mL sodium bicarbonate (84 g  $\text{NaHCO}_3$  in 1 L dd  $\text{H}_2\text{O}$ ).  $\text{NaNO}_3$  was added to a final concentration of 4 mM and the medium was adjusted to pH 7.0. Tubes were incubated with a 90/10  $\text{N}_2/\text{CO}_2$  headspace at 28 °C. For the general culturing of organisms  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added to a final concentration of 10 mM. This was replaced with meteoritic material in experiments to investigate oxidation of meteoritic iron.

### Meteoritic Material

Samples of the Casas Grandes and Cape York (both IIIAB) iron meteorites were split in a Class 100 clean room, and rinsed with a dichloromethane:methanol solvent mix to remove terrestrial contamination. Both samples were provided by the Smales Collection. The Casas Grandes meteorite was found in Mexico in 1867 but has a terrestrial age of greater than 2300 years (Sprenkel 1959; Suess and Wänke 1962). The Cape York meteorite was found in West Greenland in 1818 but has a terrestrial age of ~1000 years (Nishiizumi et al. 1987). In addition to metallic alloys, Casas Grandes contains 1.5 mg/g phosphorus and Cape York contains 1.4 mg/g phosphorus (Moore et al. 1969).

Whole rock samples of the Murchison and Cold Bokkeveld (both CM2) carbonaceous chondrites were split and crushed in a Class 100 clean room using an agate pestle and mortar. The Cold Bokkeveld meteorite sample was supplied by the Natural History Museum, London. The Murchison meteorite fell in Australia in 1969, and was rapidly collected after fall. It contains 2.7 wt% carbon (Pearson et al. 2006), 0.14 wt% nitrogen (Pearson et al. 2006), ~22 wt% iron (Jarosewich 1971) and 1–1.5  $\mu\text{g/g}$  phosphorus (Fuchs et al. 1973). Cold Bokkeveld fell in South Africa in 1838. It contains 2.16 wt% carbon (Pearson et al. 2006),

0.08 wt% nitrogen (Pearson et al. 2006), ~20 wt% iron (Wiik 1956) and 0.8–1.4  $\mu\text{g/g}$  phosphorus (Michaelis et al. 1969; Genge and Grady 1999).

### Cell Enumerations and Localization

To count the cells in the iron meteorite experiments aliquots were removed and stained with Syto 9 DNA binding dye according to the manufacturer's instructions (Invitrogen, Paisley, UK). As acidic conditions were found to interfere with staining, the cells were first washed with dd  $\text{H}_2\text{O}$  on a 0.2  $\mu\text{m}$  polycarbonate filter prior to staining the cells on the filter. Filters were observed with a Leica DMRP microscope equipped with epifluorescence (Leica Microsystems, Bensheim, Germany). Stained cells exhibited green fluorescence using an excitation waveband of 450–490 nm (Leica filter cube I3) and an emission long band cutoff filter of >515 nm. For each flask in the experiment four separate aliquots (10  $\mu\text{L}$ ) were counted in 50 fields of view.

### Batch-Culture Experimental Protocol

#### *Iron Meteorite Experiment*

Samples of iron meteorite (Cape York and Casas Grandes) were broken into pieces and weighed. The meteorites were flame sterilized prior to the experiments. For aerobic iron oxidation experiments, meteorites were placed into 50 mL diluted solution A in 100 mL Erlenmeyer flasks. For anaerobic experiments, the meteorite was placed into 20 mL of anaerobic culture medium in Hungate tubes and the tubes were immediately purged with 90/10  $\text{N}_2/\text{CO}_2$  for five minutes. For each experiment, an inoculum of 400  $\mu\text{L}$  of cells at a concentration of  $\sim 1 \times 10^7$  cells/cm<sup>3</sup> was added. Cells were previously washed by centrifugation at 10,000 g twice in dd  $\text{H}_2\text{O}$  at 21 °C. For the anaerobic experiments, the tubes were again purged with 90/10  $\text{N}_2/\text{CO}_2$  for five minutes. All experiments were conducted at 28 °C. Experiments were repeated in triplicate.

In the aerobic iron oxidation experiments the following controls were run: 1) Solution A with meteoritic material and no *A. ferrooxidans* (to compare abiotic changes in meteoritic material in growth medium with the biological experiment), 2) Solution A with *A. ferrooxidans* and no meteoritic material (to show that the organisms required meteoritic material), 3) Solution A with solution B with *A. ferrooxidans* (to show that solution A sustained biological oxidation of iron when a defined, non meteoritic source of reduced Fe was provided to organisms), and 4) solution A with solution B with no *A. ferrooxidans* (to compare abiotic oxidation of  $\text{Fe}^{2+}$  with control number 3). In the anaerobic iron oxidation experiments the same controls were run in which solution A corresponded to the anaerobic growth medium without iron and solution B to the addition of iron to the growth medium.

### Carbonaceous Chondrite Experiment

The first experiment with carbonaceous meteorites (experiment 1) was conducted with 20 mg of meteorite material (the quantity of material we procured was such that we were limited to 20 mg for each experiment) in 1 mL of solution A using a 25  $\mu\text{L}$  inoculum of cells ( $\sim 1 \times 10^7$  cells/ $\text{cm}^3$ ) in 2 mL glass vials. As we had limited material and could not carry out replicates we repeated the experiment with the two different meteorites (Murchison and Cold Bokkeveld) to provide replication. However, initially we found that the concentration of iron was sufficiently low in the small amount of material we were able to use that the abiotic rate of oxidation of iron was indistinguishable to the biological rate. We repeated the experiment using 30 mg of meteorite and 200  $\mu\text{L}$  of solution A with ten times the  $\text{H}_2\text{SO}_4$  concentration in the stock solution to hold the  $\text{Fe}^{2+}$  in a reduced state to provide time for biological iron oxidation to occur (experiment 2). To increase biological activity we used a 50  $\mu\text{L}$  inoculum of cells.

### Ferrozine Assay

We chose to use a  $\text{Fe}(\text{II})$ -specific spectrophotometric assay with ferrozine as colorimetric agent (Stookey 1970) to examine the oxidation of the extraterrestrial reduced iron by the organisms. The ferrozine assay is a standard assay used to measure the changing concentrations of iron in solution. The oxidation as determined by this method can also be used as a proxy to show growth of the organisms, although the organisms might oxidize iron without growing or reproducing, so it is not conclusive with respect to growth. The ferrozine assay also allowed us to monitor the abiotic oxidation of  $\text{Fe}^{2+}$  to provide control  $\text{Fe}^{2+}$  oxidation rate corrections to our biotic experiments. By carrying out a reduction step in the assay we were able to determine how much oxidized Fe had been “lost” to the side of the tubes in precipitates and, therefore, the proportion that had been precipitated on surfaces and the proportion of oxidized iron that remained in solution.

A modified ferrozine method was used to monitor the  $\text{Fe}(\text{II})$  concentration over time as described by Viollier et al. (2000) for small volumes of natural waters. Three reagents were prepared to perform the ferrozine test: 1) ferrozine (3-[2-Pyridyl]-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid Na-salt) was prepared to a concentration of 0.01 M by adding 24.6 mg ferrozine to 5 mL of  $10^{-1}$  mol/L ammonium acetate (Stock ammonium acetate preparation: 0.38 g ammonium acetate in 50 mL  $\text{H}_2\text{O}$  adjusted to pH 9.9). 2) Reducing agent, 1.4 M hydroxylamine hydrochloride ( $\text{H}_2\text{NOH.HCl}$ ), was prepared by adding 0.97 g hydroxylamine hydrochloride to 10 mL 2 M HCl. 3) Buffer solution was prepared by adding 7.7 g ammonium acetate to 10 mL  $\text{H}_2\text{O}$  and adjusted to pH 9.9 using 30% ammonium hydroxide.

An initial absorbance corresponding to the soluble reduced iron ( $A_1$ ) was obtained by adding 100  $\mu\text{L}$  of ferrozine

solution to 900  $\mu\text{L}$  of sample in a cuvette.  $A_1$  was recorded by use of a spectrophotometer (Helios Spectrophotometer, Thermo Scientific, UK) measuring at 562 nm. 800  $\mu\text{L}$  was then removed from the cuvette and placed in a clean cuvette. 150  $\mu\text{L}$  of the reducing agent was added. The samples were left for 10 minutes in order to allow reduction of  $\text{Fe}(\text{III})$  to  $\text{Fe}(\text{II})$ . The buffer solution was then added and the absorbance ( $A_2$ ) corresponding to the total iron ( $\text{Fe}(\text{II})$  from soluble  $\text{Fe}(\text{II})$  and reducible  $\text{Fe}(\text{III})$ ) was then recorded. The quantity of Fe in  $\mu\text{M}$  was determined by use of calibration curves obtained with standards using  $\text{FeSO}_4$ .

### X-Ray Diffraction

To investigate the oxidized material produced by *A. ferrooxidans* in the iron meteorite experiments we employed X-ray diffraction (XRD). Powder X-ray diffraction patterns were measured using a Siemens D5000 X-ray diffractometer operating with a Cu X-ray tube (K-alpha average wavelength = 1.5408 Angstrom). Data were measured in Bragg-Brentano mode from samples of powder sprinkled on a silicon wafer coated with a thin layer of silicone grease in steps of 0.02 degrees 2-theta from 5–80 degrees 2-theta with counting time of 12 s per step. X-ray diffractograms were compared to the 2002 release of the JCPDS release of the Powder Diffraction File using the Bruker axS software Diffrac.

### Iron Isotope Analysis

Samples of oxidized material produced by *A. ferrooxidans* in the iron meteorite experiments were dissolved and iron purified using anion exchange chromatography following the procedure described in Mullane et al. (2003). Iron isotope measurements were performed at LMTG-CNRS in Toulouse, France using a Thermo Electron Neptune MC-ICP-MS (Bremen, Germany). The analytical set up and the procedure followed for iron isotope measurements were those described in detail in Poitrasson and Freydier (2005). In short, the sample introduction system included a tandem quartz glass spray chamber arrangement together with a low-flow self-aspirating, PFA nebulizer. For improved sensitivity, the instrument was also fitted with X cones. The machine setup permitted simultaneous measurements of the three main iron masses (54, 56, 57), and mass 53 to monitor and correct for any Cr isobaric interference. Purified iron samples were analyzed in a 0.05 M HCl solution and were set to a concentration of 3 ppm, resulting in a signal of ca. 45 V for  $^{56}\text{Fe}$  in the medium mass resolution mode of the instrument. The Fe isotope measurements were mass bias corrected using the sample standard bracketing approach in this particular study. The international Fe standard used was IRMM-14. The Fe isotope data are reported in delta notation (in ‰) relative to the IRMM-14 iron isotopic reference material, where:

$$\delta(^{57}\text{Fe}/^{54}\text{Fe}) = \left( \frac{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{IRMM14}}} - 1 \right) \times 1000$$

Each sample was analyzed at least six times over a period of 4 months and an in-house hematite standard was also measured regularly to assess the long term external reproducibility on  $\delta^{57}\text{Fe}/^{54}\text{Fe}$ , which in the present case was better than 0.05‰ (2 $\sigma$ ). This hematite also serves to check data accuracy. The values obtained during this study were exactly the expected values previously reported (e.g., Poitrasson and Freyrier 2005).

## SEM

The surfaces of meteorite samples were examined by Scanning Electron Microscopy (SEM). Meteorites samples, both abiotically and biotically altered, were dried in a desiccator and attached to aluminium stubs. They were examined by SEM at 20 kV accelerating voltage and 7–15 mm working distance. The SEM was a Quanta 3D dual beam FIB SEM (FEI, Oregon, USA). Samples did not require carbon coating as the meteorites were found to be sufficiently conducting to prevent charging. Samples were also examined for alteration at the University of Tübingen using a LEO Model 1450 VP (Variable Pressure) with either Everhart-Thornley SE-detector or 4-quadrant BSE-detector (LEO Electron Microscope Ltd., UK). In both cases Energy Dispersive Spectroscopy (EDS) was carried out with a count time of 50–100 s. Data analysis was performed with the software, Inca (Oxford Scientific Instruments, Oxford, UK) to study the composition of the samples.

## TEM

TEM analysis was carried out on *A. ferrooxidans* from a culture in the presence of Murchison meteorite to investigate whether the cells were isolated or associated with the meteorite fragments and to assess their state (i.e., isolated, clumped and/or attached to meteorite minerals). Samples of the culture were dried down onto copper grids. TEM analysis was carried out on a JEM 1400 (Jeol, Herts, UK) working at an operating voltage of 120 kV. Images were captured on a 11 megapixel lens-coupled AMT XR60 digital camera (Deben, Suffolk, UK).

## RESULTS

### Batch Culture Experiments

#### *Iron Meteorite Experiment*

Figure 1, which shows two representative experiments, shows that in the presence of meteorite sample there was a rapid release of reduced iron during the first day, which over the following 15–20 days was oxidized by the organisms as shown by the lack of oxidation of the liberated iron in the

control with Solution A and meteorite, but no organisms. The quantity of iron in solution was approximately 50 times less than in the  $\text{FeSO}_4$  experiments. Although no  $\text{Fe}^{2+}$  was detected in the control with Solution A and organisms and no meteorite, as expected (Fig. 1b), a small quantity (<4  $\mu\text{mol/L}$ ) of reducible iron was detected which might be attributable to iron released from the organisms used in the inoculation (either as intracellular iron or minerals attached to the cells).

The total iron measured during the experiments fell to approximately a third of the initial soluble iron after 20 days. We attribute this 'lost iron' to the formation of iron oxyhydroxides which precipitate on the sides of the tubes and are therefore not included in the aliquot removed for the ferrozine assay. They were conspicuous as platy orange/red precipitates on the side of the tube. The measured oxidized iron component was likely to be fine particulate matter that remains in the bulk solution. In both experiments we observed that the total iron increased again up to 40 days, which we attribute to the formation and then disaggregation of iron oxides on the surface of the tubes.

The results with Cape York meteorite were qualitatively identical to the results shown for Casas Grandes (data not shown).

Initial cell numbers in the control biological experiment with iron supplied as  $\text{FeSO}_4$  and the meteorite experiment with organisms ( $1.01 \pm 1.34 \times 10^7$  cells/mL and  $9.80 \pm 0.23 \times 10^6$  cells/mL respectively) had increased to  $5.05 \pm 0.90 \times 10^7$  and  $5.43 \pm 0.40 \times 10^7$  cells/mL after 20 d showing that  $\text{Fe}^{2+}$  from the meteorite supported growth. However, we found cell enumerations to be difficult on account of interference from particles and shielding of organisms by iron precipitates, particularly at later stages of the experiments.

In the anaerobic enrichment culture experiments using the anaerobic enrichment culture with Casas Grandes meteorite, after 90 d the quantity of reduced iron in the control and enrichment cultures was  $0.82 \pm 0.01$  and  $1.23 \pm 0.03 \mu\text{M}$  respectively and the quantity of total iron was  $4.53 \pm 0.34$  and  $13.22 \pm 0.45 \mu\text{M}$ . There was precipitate on the sides of the tube in the biological experiment and oxidized iron was visible as small flakes of suspended material which was not observed in the abiotic control.

#### *Carbonaceous Chondrite Experiment*

The amount of carbonaceous chondrite we used was such that only small (<112  $\mu\text{M}$ ; Table 1) amounts of reduced iron were released into solution. In experiment 1, after four days the iron in both the control and organism-containing experiments had been oxidized (data not shown). However, by increasing the concentration of the acid in experiment 2 the reduced iron was sufficiently stable to monitor biotic iron oxidation compared to abiotic control (Table 1). After 9 d 35% of the control  $\text{Fe}^{2+}$  from the Cold Bokkeveld had been oxidized compared to 97% in the experiment containing A.

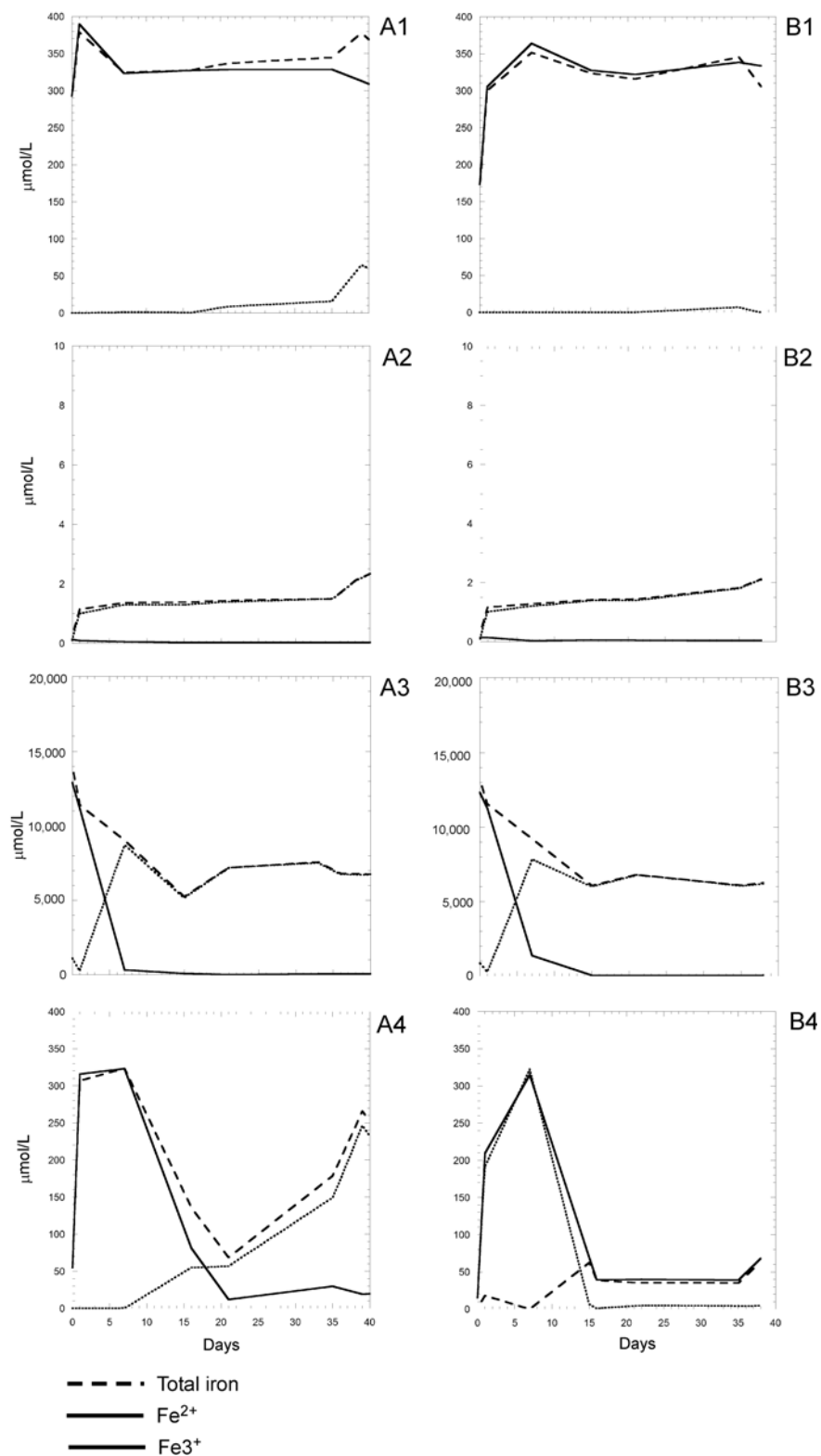


Fig. 1. Two representative experiments (A and B) showing oxidation of iron released from Casas Grandes meteorite by *A. ferrooxidans*. A1 and B1 are experiments with solution A and meteorite, but without organisms; A2 and B2 are solution A and organisms without meteorite (iron source); A3 and B3 are control experiment with solution A, B (FeSO<sub>4</sub>) and organisms; A4 and B4 are experiments with solution A, meteorite and organisms.

Table 1. Oxidation of reduced iron from carbonaceous chondrites by *Acidithiobacillus ferrooxidans*. Values measured by the ferrozine assay. The values for t = 0 and t = 9 d (t = time) are shown for each experiment (values are  $\mu\text{M}$ ). "Control" experiments had no organisms, but all other conditions were the same as experiments that included organisms.

Experiment	$\text{Fe}^{2+}$		Total iron	
	t = 0	t = 9	t = 0	t = 9
Cold Bokkeveld control	97.1	62.6	92.3	65.8
Cold Bokkeveld ( <i>A. ferrooxidans</i> )	104.2	2.6	96.5	15.1
Murchison control	104.9	44.7	101.3	51.3
Murchison ( <i>A. ferrooxidans</i> )	111.6	13.6	104.3	19.9

Table 2. Fe isotopic composition of samples analyzed in the present study. SE = standard error. Errors on hematite measurements (n = 48) are reported in terms of 2SD.

Sample type	$\delta^{57}\text{Fe}/^{54}\text{Fe}$	2SE	$\delta^{56}\text{Fe}/^{54}\text{Fe}$	2SE
Abiotic meteorite scraping	0.25	0.03	0.15	0.02
Abiotic flask wall precipitates	0.32	0.03	0.21	0.01
Biological expt. met. scraping	0.59	0.03	0.38	0.03
Biological expt. wall precipitates	-0.09	0.04	-0.07	0.03
Iron meteorite (Casas Grandes)	0.03	0.03	0.02	0.01
Hematite (in house standard)	0.75	0.09	0.51	0.05

*ferrooxidans*. In the experiment with Murchison meteorite these values were 57% and 88%, respectively.

Almost all of the oxidized iron produced during the experiment precipitated on the sides of the tubes, accounting for a reduction in total iron at the end of the experiment (Table 1).

### X-Ray Diffraction

The primary peaks in the experiment in which Casas Grandes was exposed to organisms corresponded to lepidocrocite and goethite and a minor peak corresponding to butlerite ( $\text{Fe}^{3+}(\text{OH})(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ ). In the experiment using Cape York only goethite with some vivianite was observed. In the non-biological control the primary phase was lepidocrocite with both Cape York and Casas Grandes, although with Cape York some vivianite and maghemite was also observed.

### Iron Isotope Analysis

The Fe isotope data on the meteoritic samples from Casas Grandes used as a starting material in the aerobic experiments are listed in Table 2 and shown in Fig. 2. It is apparent that the iron meteorite and the products of biological and abiological experiments have clearly resolvable and distinct Fe isotopic compositions and that Fe isotopes are fractionated in both experiments. The extent of fractionation is greater in the biological case compared to the abiological case (Fig. 2). In the abiological experiment, Fe-rich scrapings consisting of iron oxyhydroxides collected from the surface of the meteorite as well from the walls and the floor of the experimental flask show almost identical Fe isotopic composition. Given that no iron was originally present in the

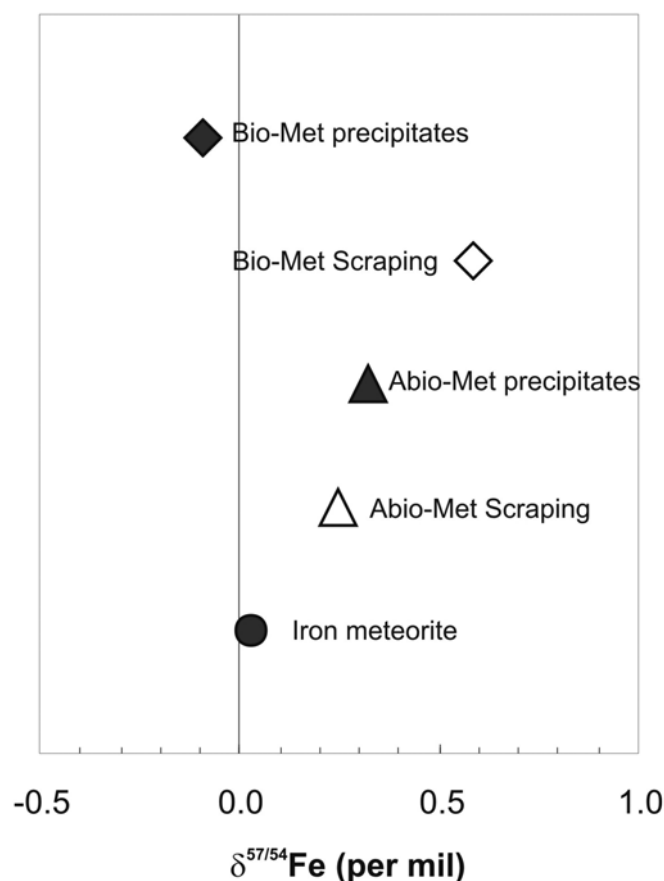


Fig. 2. Diagrammatic representation of data shown in Table 1 showing fractionation of iron isotopes collected from: scrapings at the surface of the meteorite in biotic (Bio-Met Scraping) and abiologic (Abio-Met Scraping) experiments, and precipitates from biotic (Bio-Met precipitates) and abiologic (Abio-Met precipitates) experiments.

solution, this means that iron transport in the solution after partial meteorite dissolution did not induce any extra isotopic fractionation. Hence, the inorganic chemical precipitates on both the meteorite surface and reactor walls record the same Fe chemical pathways during dissolution and precipitation, as revealed by a similar isotopic signature. However, in the case of biological experiment, the scrapings from the meteorite surface shows heavier Fe isotopic signature whereas precipitates collected from the walls and the floor of the experiment vessel shows the lightest Fe isotopic composition measured in this study (Fig. 2).

## SEM

The surface of the control meteoritic material (Fig. 3A) was not uniformly flat on account of the milling procedure used to remove sections from the original meteorite. After 20 days, meteorite exposed to *A. ferrooxidans* medium, but without organisms, was covered by 4–6  $\mu\text{m}$  near-spherical structures that formed aggregates (containing Fe, P, S by EDS) (Fig. 3B). In the experiment with *A. ferrooxidans* the surface became covered in both near-spherical aggregates of minerals and also spherical mineral aggregates covered by  $\sim 2$   $\mu\text{m}$  long needle-like crystals (Figs. 3C, 3D). If the organisms were directly associated with these crystals this could not be distinguished. In the experiment with the anaerobic enrichment culture, the control did not display surface precipitates and resembled the original meteorite. The meteorite surface exposed to the anaerobic enrichment culture displayed patches of fine ( $\leq 2$   $\mu\text{m}$ ) spherical and plate-like aggregates (Fig. 3E). EDS revealed them to be iron oxides with variable oxygen contents of between 45 and 60%. The mean of five such aggregates gave a composition of 51.4% O, 27.5% Fe, 8.1% P and 1.87% Ni as the four major elements (s.d.  $<20\%$ ). Platy flocculates were also produced in the biological experiment (Fig. 3F) which were observed floating in solution. They had a composition, determined by EDS, similar to the surface of the biologically altered meteorite.

## TEM

TEM analysis was first used to determine the size and expected morphology of the organisms in the control experiment (solution A and B with organisms) (Fig. 4A) prior to investigating the presence of *A. ferrooxidans* cells associated with minerals from Murchison meteorite (Fig. 4B). Cells were isolated and usually embedded within the meteorite minerals. The cells were covered in small mineral aggregates.

## DISCUSSION

### Microbial Weathering of Meteorites

The weathering of meteoritic material by microorganisms has importance for both understanding the

weathering and fate of extraterrestrial materials that land on the Earth and the potential of meteorites to provide energy and nutrient sources to a biota during early planetary history when impact fluxes were higher. In this work we investigated the aerobic and anaerobic biological weathering of meteoritic materials by iron-oxidizing microorganisms.

The experiments presented here show that organisms can play an active role in iron oxidation, and therefore potentially mineral weathering, in extraterrestrial materials in both aerobic and anaerobic conditions, and in acidic and neutral conditions. It has been recognized for a long time that iron meteorites can be oxidized in terrestrial conditions to yield iron oxide coatings (Shannon 1927). Bland (2006) showed that the degree of weathering of meteorites is correlated to their residence time on Earth, with an initial fast weathering rate that is then reduced, presumably due to a passivation effect, which is attributed to the formation of secondary weathering products in pore spaces. Although the weathering rate of meteoritic material is likely to be related to the physical environmental conditions (Lee and Bland 2003; Bland 2006), a role for microbiological weathering must also be considered.

Our data show that biological oxidation of iron in meteorites can be rapid once colonization occurs, in both iron and carbonaceous meteorites. In the case of the iron meteorite experiment with *A. ferrooxidans*, despite the fact that the initial soluble iron concentration is about 50 times higher in the control experiment compared to the experiment with meteorite, the complete oxidation of the iron occurs after  $\sim 7$  d in experiments which use  $\text{FeSO}_4$  as the reduced iron source, in contrast to the meteorite experiment, where oxidation is only complete after 15–20 days. We explain this by the slow release of  $\text{Fe}^{2+}$  from the meteorite reacting with the acid. Release rates would become slower as the surface of the meteorite is oxidized, thereby retarding  $\text{Fe}^{2+}$  release. Such a passivation effect has been reported by Bland (1998, 2006) during the weathering of ordinary chondrites.

Iron isotopic signatures of bulk meteorites may be influenced by the type of weathering imposed by the environment in which they fall. Whereas Fe isotopes signatures of ordinary chondrites from hot deserts have been perturbed by weathering (above grade W2: Saunier et al., Forthcoming), this does not seem to be the case for some meteorites from Antarctica (Poitrasson et al. 2004). The iron isotope data we obtained showed that in the biological experiments the bacterial Fe processing induced a distinct isotopic fractionation due to additional Fe processing. Previous work has shown that iron redox changes and/or complexation with organic ligands are efficient ways to produce Fe isotope fractionation (e.g., Brantley et al. 2001; Johnson et al. 2002; Beard et al. 2003; Wiederhold et al. 2006). Notably, there is a strong isotopic fractionation effect between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , ferric Fe being isotopically heavier by  $\sim 4.5\%$  in  $\delta^{57}\text{Fe}$  relative to ferrous iron at equilibrium in aqueous solution at 25 °C (Johnson et al. 2002; Welch et al.



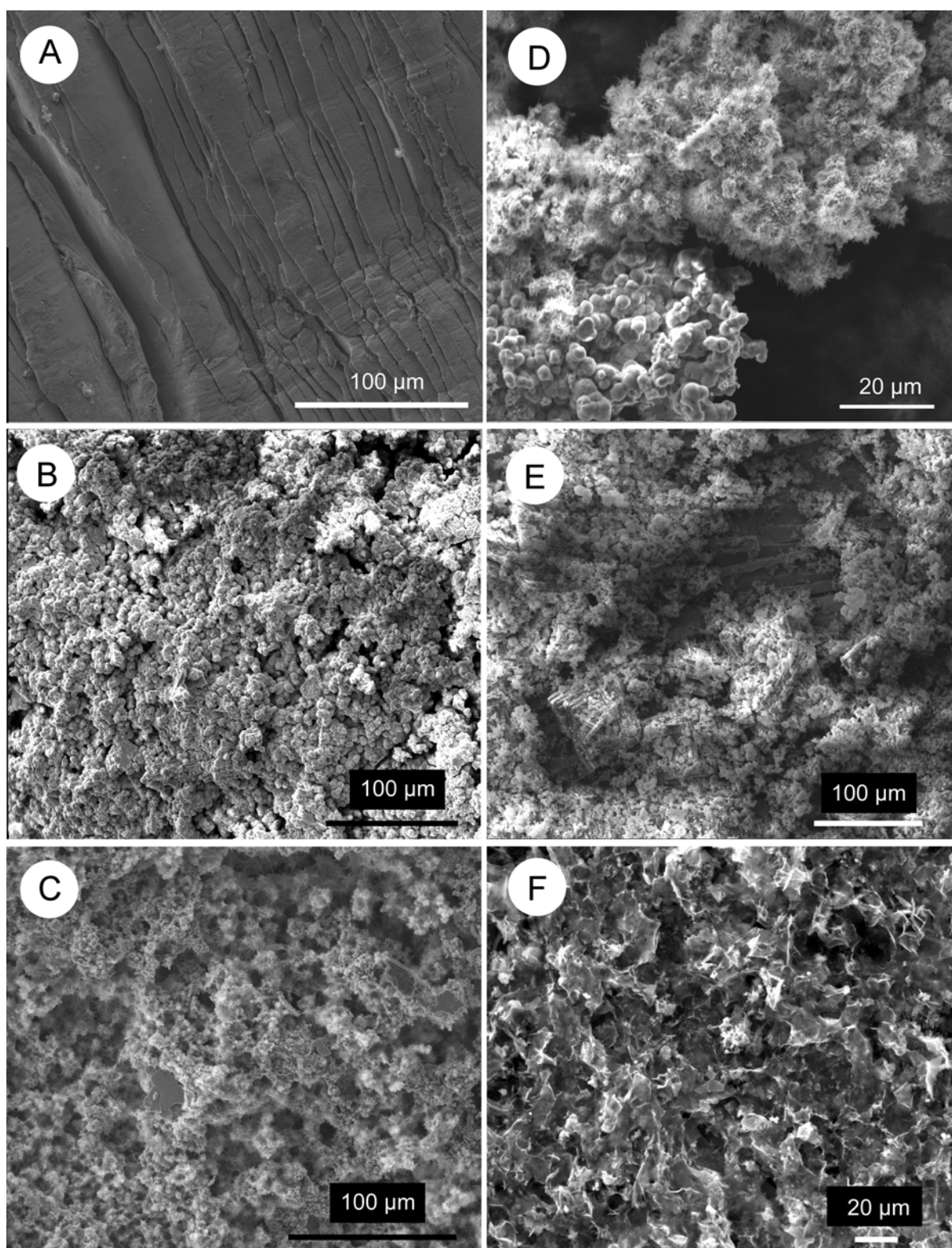


Fig. 3. The surface of the Casas Grandes meteorite. A) Example region of meteorite before experiments, B) Surface of control meteorite exposed to *A. ferrooxidans* medium, but with no organisms. C) Surface of meteorite in experiment with *A. ferrooxidans*. D) Surface of meteorite in experiment with *A. ferrooxidans* showing close-up of spherical aggregates covered by needle-like crystals. E) Surface of meteorite in experiment with anaerobic iron oxidizer enrichment culture. F) Flocks of iron oxides produced in experiment with anaerobic iron oxidizer enrichment culture.

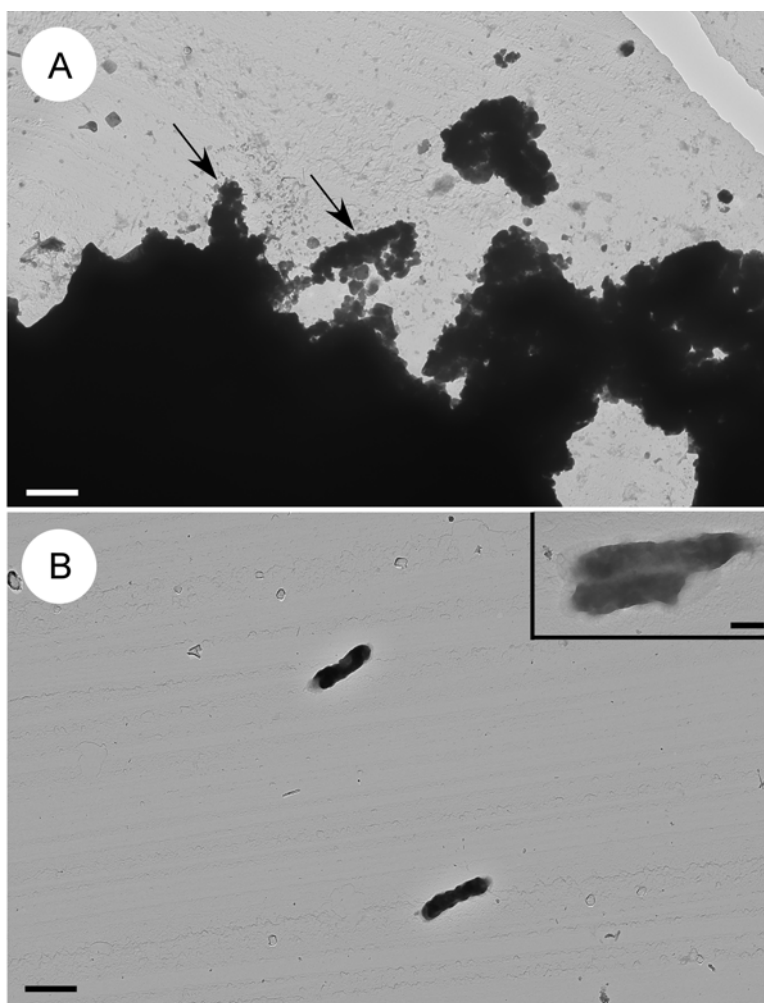


Fig. 4. TEM images of *A. ferrooxidans*. A) Associated with fragments of Murchison meteorite shown as arrows. B) Organisms from a control culture using  $\text{FeSO}_4$  as the electron donor (to provide control scale for organisms in A). Scale bar is 1  $\mu\text{m}$ . Inset in (B) shows magnification of *A. ferrooxidans* cells in control experiment (scale bar 100 nm).

2003; Anbar et al. 2005). In our experiments, abiological iron meteorite dissolution involved oxidation from  $\text{Fe}^0$  in the meteorite to  $\text{Fe}^{2+}$  released in solution, and subsequent reprecipitation of  $\text{Fe}^{3+}$  as oxyhydroxides on the meteorite surface and flask walls. The observed heavier Fe isotope composition of the precipitate can therefore be understood in the framework of previous experimental and computational knowledge. However, mass balance constraints suggest that some isotopically light Fe remained in solution during the abiological experiment. This has yet to be verified.

In the biological experiment, bacterial iron processing in solution affected the Fe isotope signature of the precipitates given that it has a different isotopic composition depending on whether it is located on the meteorite surface or flask walls. Previous experiments have shown that bacterial Fe oxidation produces isotopically heavy oxyhydroxides relative to the starting iron (Croal et al. 2004). This biological factor can therefore explain why the iron oxyhydroxide precipitates on the meteorite surface are isotopically heavier than those of

the experiments without bacteria (Fig. 2). This can also explain the larger isotopic contrast between the oxyhydroxides on the meteorites and flask walls in the biological experiments: the isotopically lighter precipitate on the flask walls would represent some of the iron leftover in solution after bacterial processing that has become increasingly light because the heavier iron was precipitated by the bacteria on the meteorite surface. Hence, the lighter Fe isotope composition of the precipitates found on the flask walls, relative to their counterpart in the abiological experiment, can simply be explained in terms of mass balance.

Further investigations are required to investigate reproducibility, analyse the aqueous solution after the experiments to have a complete budget of the Fe involved, and to investigate the reaction kinetics and check the attainment of equilibrium. At this stage, however, it can be concluded that biological processing has an imprint on Fe isotope signatures of the oxyhydroxide products of the

meteorite weathering and that such isotopic changes might be used to determine a biological role in natural meteorite weathering.

The presence of needle-like iron oxides in the biological experiments with iron meteorite and *A. ferrooxidans* as shown by SEM which were not observed in the abiotic experiments show that specific mineral phases and morphologies may be associated with biological alteration. XRD suggests a preferential biological production of goethite. Some weathering products can persist for a long time. Calcite clusters associated with pyroxenes within achondrites are long-lived and have been assigned to biological weathering (Benzerara et al. 2003). Combined mineralogical and isotopic approaches may be a potentially effective way of determining the involvement of iron oxidizers in weathering meteorites.

The reduced iron liberated from carbonaceous chondrites can also be oxidized by *A. ferrooxidans*. However, the soluble iron is a small percentage of the total iron in the material. In the Murchison meteorite, a range of iron contents between 204 to 237 mg/g is reported in five studies (Ehmann et al. 1970; Jarosewich 1971; Fuchs et al. 1973; Genge and Grady 1999; Wolf and Palme 2001) with a mean of 218.8 mg/g. Four studies report ranges of 194 to 234 mg/g in the Cold Bokkeveld meteorite (von Michaelis et al. 1969; Wilk 1969; Genge and Grady 1999; Wolf and Palme 2001) with a mean of 209.6 mg/g. Based on these reported values we expected ~6 mg of Fe in the experimental vials in the carbonaceous chondrite experiment. The initial total iron that we measured in solution by the ferrozine assay was ~0.02% of this as soluble  $\text{Fe}^{2+}$ . The discrepancy might be accounted for by the majority of the iron being bound into the meteorite minerals. The calculations for the ferrozine assay assume the iron is completely dissolved in a soluble state. This iron would be recalcitrant against the reduction step in the assay. The presence of *A. ferrooxidans* cells attached to meteorite fragments, revealed by TEM, would be consistent with the iron being locally available in meteoritic material. The higher rate of iron oxidation induced by the organisms compared to the abiotic controls shows that they can induce oxidative weathering reactions in carbonaceous meteorites as well as iron meteorites.

The results we obtained with anaerobic iron oxidation and iron meteorites show that anaerobic microorganisms can also mediate the weathering of iron meteorites. Meteorites that land in anoxic water bodies or terrestrial environments (just a few centimeters deep in soils or in ponds/lakes in some environments) would be subject to alteration by this class of organisms.

This result might be understood by reference to previous work on metal corrosion in anaerobic environments (Hamilton 1985; Potekhina et al. 1986; Iverson 1987; Lee et al. 1995). The anaerobic corrosion of iron in sterile water is known to be very slow (Bockris and Reddy 1970). It can be initiated via the oxidation of the metallic Fe to  $\text{Fe}^{2+}$  and  $2\text{e}^-$ .

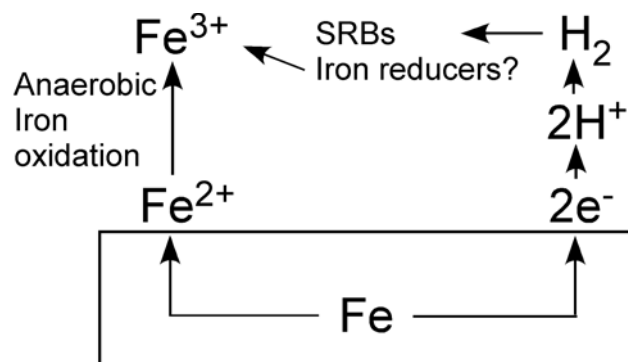


Fig. 5. A hypothetical scheme for the role of anaerobic iron oxidizers in the weathering of iron meteorites. Scheme also shows potential for anaerobic oxidation of cathodic  $\text{H}_2$  by sulfate-reducing bacteria (and iron reducers which could potentially use the  $\text{Fe}^{3+}$  produced by iron oxidizers to produce  $\text{Fe}^{2+}$ , resulting in an iron cycle).

Previous experiments studying the role of microorganisms in anaerobic metal corrosion have suggested that the hydrogen produced via the combination of protons produced from this reaction can be used by anaerobic organisms (principally sulfate-reducing bacteria, SRBs) as an electron donor (Hardy 1983; Pankhania et al. 1986), resulting in the biologically assisted corrosion of metallic iron (Deckena et al. 1992; Dinh et al. 2004). The combination of hydrogen atoms formed from the reaction  $2\text{e}^- + 2\text{H}^+$  is the rate limiting step (Bockris and Reddy 1970).

Iron oxidizers have not previously been suggested as agents of iron corrosion, although they are found in diverse environments (Straub et al. 1996, 2004; Weiss et al. 2003; Kappler et al. 2005; Emerson and Moyer 1997, 2002).  $\text{Fe}^{2+}$  produced by oxidation of metallic iron might be used by the anaerobic iron oxidizers (Fig. 5) as an electron donor. The removal of the reduced iron would favor further oxidation of the metallic iron surface. This would provide a mechanism for how the organisms in our experiments were able to oxidize iron from a metallic source. The experiment also raises the possibility of an iron cycle within iron-rich meteorites (and metals generally) (Fig. 5). The  $\text{H}_2$  produced by the oxidation of the metallic iron would be used by iron reducers and the  $\text{Fe}^{2+}$  produced used by anaerobic iron oxidizers, with the two redox states of iron produced from the meteorite exchanged between the organisms.

### Implications for Early Earth Biota

As well as studies on weathering, the experiments support the conclusions that meteorites can supply a source of iron for microbial growth as we observed increases in cell numbers in the experiment using iron meteorites and *A. ferrooxidans*. González-Toril et al. (2005) have reported that acidophilic iron oxidizers can use iron meteorites as a source of reduced iron. However, the reduced iron is primarily provided by the acidic conversion of metallic Fe to  $\text{Fe}^{2+}$  rather than the organisms directly using metallic Fe from the meteorite.

In a recent paper examining the potential availability of nutrients and redox couples in Martian soils using a numerical model, Jepsen et al. (2007) suggest that  $\text{Fe}^{2+}$  is the first element to become limiting to chemolithoautotrophic life. However, if  $\text{Fe}^{2+}$  can be supplied exogenously then this limitation would be mitigated until another element became limiting. The authors did not apply their model to the early Earth, but their theoretical data, when considered with our experimental data, shows that local limitations in  $\text{Fe}^{2+}$  to life can be overcome by extraterrestrial sources in both aerobic and anaerobic environments. Pasek and Lauretta (2007) estimate that the present-day flux of carbonaceous chondrites and iron meteorites to the Earth's surface is 600 and 13,000 kg per year, respectively. On early Earth this might have been  $8 \times 10^7$  and  $3 \times 10^{10}$  kg, respectively (Pasek and Lauretta 2007). Ignoring the other meteorite classes, assuming that the iron concentration of these two groups is 200 mg/g and 900 mg/g respectively and assuming that the material is delivered uniformly over the surface of the early Earth, these two classes of meteorites would have delivered 0.03 and 52.8 kg/km<sup>2</sup> of iron. In reality the surface of the early Earth would have experienced large localized increases in iron and nutrients at the point of impact.

### Practical Applications

Finally, we speculate that the experiments have applications to the human exploration and settlement of space. Asteroidal material is known to harbor platinum group elements, volatiles and a variety of potentially useful resources for both human space settlements and terrestrial industries (Kryzanowski and Mardon 1990; Sonter 1997; Busch 2004). On Earth, both copper and gold, for example, are now harvested using acidophilic iron oxidizers in "biomining" operations (Norris et al. 2000; Stott et al. 2003). Particularly in sulfide ores, iron oxidizers provide a source of  $\text{Fe}^{3+}$  which causes oxidation of the sulfidic minerals (Clark and Norris 1996; McGuire et al. 2001), producing sulfuric acid that sustains further rock dissolution, breaking apart the rock matrix to facilitate acquisition of useful minerals (e.g., Pronk and Johnson 1992; Schroeter and Sand 1993; Solisio et al. 2002; Rawlings 2005). The first step of successful biomining of iron-containing minerals is therefore to demonstrate the ability of iron-oxidizing microorganisms to oxidize reduced iron without the parent material being toxic to the very organisms carrying out this transformation.

As we show here, *A. ferrooxidans* can oxidize reduced iron in carbonaceous chondrites. Meteoritic materials contain sulfides as well as iron, which might provide a source of sulfuric acid to sustain the leaching reactions, similarly to sulfidic ores on Earth. Material could be ground into a powder or grains, similarly to our experiments, and leached in oxygen pressurized batch reactors.

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