

## Evidence of Ancient Microbial Activity in the Martian meteorite 'Tissint'

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### Abstract

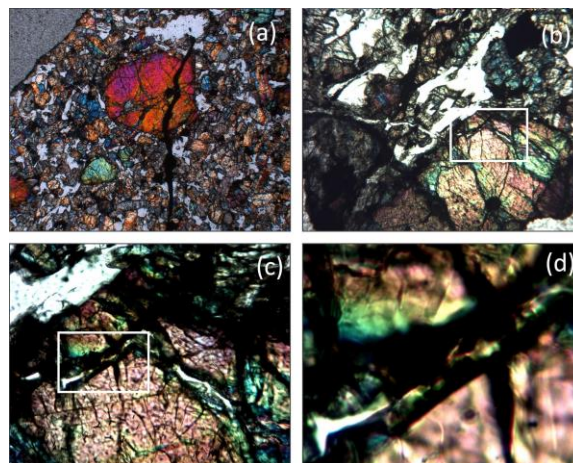
A relatively rare mineral, iron arsenate-sulphate bukovskýite  $\text{Fe}^{3+}_2(\text{As}^{5+}\text{O}_4)(\text{S}^{6+}\text{O}_4)(\text{OH}) \cdot 7(\text{H}_2\text{O})$  was found in a shock melt vein of the Tissint Martian meteorite. We hypothesise it formed within high concentrations of aqueous  $\text{H}^+$ ,  $\text{Fe(III)}$ ,  $\text{SO}_4$  and  $\text{AsO}_4$  in microenvironments created within wet subsurface Martian clays from microbial oxidation of  $\text{FeS}_2$  with concurrent release of sequestered As. This hypothesis is supported by SEM analysis of a  $15\mu\text{m}$  spherical structure comprising a carbonaceous outer coating and an inner pyrite ( $\text{FeS}_2$ ) core. The pyrite surface has morphologically distinct spherical pits and chains of pits. The pits and channels are similar to bio-mediated microstructures created by Fe- and S-oxidising microbes in the laboratory and interpreted as trace fossils resulting from the attachment of bacteria to the pyrite surfaces

### 1. Introduction

Previous studies of the Tissint Martian meteorite have focused on the carbonaceous component, whose interpretations vary from igneous and magmatic to biogenic origin [1,2,3]. In our sample, we found a number of  $5\text{-}50\mu\text{m}$  carbonaceous globules both embedded in the rough pyroxene substrate and others unbound, having been dislodged during the preparation process. SEM and EDS elemental spectra for 11 selected globules confirmed that they comprise a carbonaceous outer coating with an inner core of  $\text{FeS}_2$  (pyrite) and are characterised as immiscible globules with curved boundaries [4]. The petrographic setting of the organic carbon component showed examples of organic carbon completely occupying the cracks and cleavage around pyrite crystals, suggesting that pyrite had acted as an attractive substrate for the collection of organic material in a hydrothermal setting.

In this study we report the results of SEM, optical microscopy and Raman spectroscopy on a relatively rare secondary iron arsenate-sulphate mineral found in a shock melt vein of the meteorite. These results agree with previous interpretations of Tissint's organic carbon being precipitated from fluid [3].

### 2. Experimental Studies

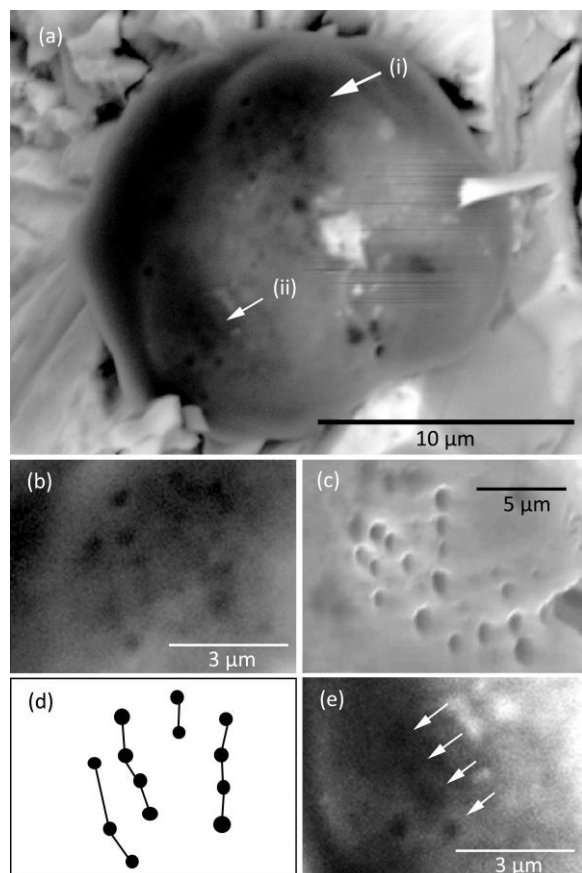


**Figure 1** images of a  $30\mu\text{m}$  thin section of Tissint in cross-polarised transmitted light. Black glass shock veins and pockets show up as black with maskelynite phases in white. (a) typical glass shock vein cutting through the pyroxene groundmass and olivine crystal (b) shock vein containing the arsenic signature with the site of interest highlighted, note also the presence of a typical olivine crystal with a melt inclusion and radiating cracks (c) enlarged image of the vein showing enclosed mineral inclusion and (d) same, in higher magnification. Field of view (a)  $2.5\text{mm}$  (b)  $1\text{mm}$  (c)  $250\mu\text{m}$  (d)  $100\mu\text{m}$

Via scanning electron microscopy, enriched arsenic domains were identified in one polished  $30\mu\text{m}$  thin section (section A) and one polished thick section (Section C) of Tissint, prepared at Cardiff University. Details of these sections are provided in Wallis *et al.*, [4]. Hi-Res Raman spectroscopy of the As-enriched domains constrained the mineral species. An As-enriched

domain was observed in EDAX elemental maps in the vicinity of a ~10 µm wide glass shock vein. Black glass melt pockets and veins are characteristic of Tissint. Figure 1 (a-d) shows an optical light montage of a typical glass shock vein.

### 3. Bacterial etch pits on pyrite



**Figure 3** (a) shows an SEM image of a pyrite grain coated with carbonaceous material. The area marked with arrow (i) in shown in higher resolution (b) where a cluster of etch pits become visible. (d) shows an overlay diagram of their position and spacing, while (e) shows a similar set of four rounded pits equally spaced in a straight line as indicated by the four white arrows. For comparison, figure 3 (c) shows a cluster of spherical etch pits in the surface of pyrite taken from the Strelley Pool Formation (SPF).

SEM was also used to identify bacterial etch pits in the surface of pyrite grains present in the meteorite, shown in Fig. 2. The similar size and sphericity of etch pits and their geometric pattern are significant since pitting and channelling of pyrite surfaces can result from the non-biological oxidation of pyrite.

### 4. Discussion

Various processes forming bukovskýite involve biological processes, notably biologically induced mineralisation. Márquez *et al.* [5] studied a two-step oxidation pre-treatment process involving a combination of bacterial and pressure oxidation of ores mined in the São Bento deposits in Brazil. Majzlan *et al.* [6] suggested clay minerals create sealed microenvironments where high concentrations of aqueous  $H^+$ ,  $Fe(III)$ ,  $SO_4$  and  $AsO_4$  are maintained for long periods of time.

Bukovskýite formation is not unambiguously associated with bio-activity. Nonetheless, the initial mobilisation of arsenic from As enriched Fe oxides, the subsequent sequestration of As by precipitating sulphides under anoxic conditions, followed by the oxidation to sulphide of sulphate species and the formation of relatively rare As secondary phases are all processes commonly associated with bacterial activity.

McKay *et al.* (1996) first suggested Fe- and S-oxidising microbes may have etched ‘biomorphs’ on pyrite surfaces in the martian ALH 84001 meteorite. Our etch pits have morphology and patterns distinct from abiotic alteration features, being comparable to biologically mediated microstructures created by Fe- and S-oxidising microbes. At present, these features are interpreted as trace fossils resulting from the attachment of bacteria to the pyrite surfaces

### References

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