

# Siderophilic Phases within Iron Meteorites. Sources of Reactive Phosphorus on the Early Earth

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## Abstract

On Earth, phosphorus occurs naturally as fully oxidised orthophosphate ( $\text{PO}_4^{3-}$ ) most commonly within igneous and metamorphic rocks as the apatite family  $\text{Ca}_5(\text{PO}_4)_3(\text{X})$  [ $\text{X} = \text{Cl}, \text{F}, \text{OH}$ ]. However, the low solubility of orthophosphate salts in water coupled with low inherent chemical reactivity has raised doubts as to whether orthophosphates were Nature's first choice P-chemical *en route* to life on Earth. Gulick's proposal<sup>1</sup> that the lower oxidation state phosphorus oxyacids H-phosphonic ( $\text{H}_3\text{PO}_3$ ) & H-phosphinic ( $\text{H}_3\text{PO}_2$ ) could have been more effective phosphorylating agents than orthophosphate has been given a boost by recent discoveries by Pasek & Lauretta in Arizona<sup>2</sup> and in our own laboratory.<sup>3</sup> These studies revealed that siderophilic phosphorus (P) minerals such as schreibersite,  $(\text{Fe},\text{Ni})_3\text{P}$ , within iron meteorites (and to a less degree in CM chondrites) undergo anaerobic redox transformations in water to afford principally H-phosphonic acid under thermal and H-phosphinic acid under photochemical conditions. Here we describe some of our studies on siderophilic P-inclusions within iron meteorites such as the Seymchan pallasite, Tombigbee River, Arispe, Toluca, Sikhote Alin and Bear Creek (Figure 1). Microhardness measurements confirm the inclusions to be harder than surrounding matrix and scanning X-ray photoelectron spectroscopy studies shed light upon core energy differences between inclusion and matrix. These have been followed up by the first examples of the application of scanning electrochemical techniques such as scanning Kelvin probe (SKP) and scanning droplet cell (SDC) techniques to iron meteorite surfaces which clearly

demonstrate differences in electrochemical potential between inclusion and matrix as illustrated in Figure 2 for the Seychan pallasite. Subsequent studies have indicated that such an electrochemically differentiated material appears to undergo preferential corrosion at the grain boundaries, a process we are now studying through mapping Raman spectroscopy, a preliminary account of which will be presented. We discuss also how hydrothermal modification of siderophilic meteoritic components can lead to a variety of phosphorus species, some of which may have impacted positively on the chemical emergence of phosphate-based life on earth.

## Figures

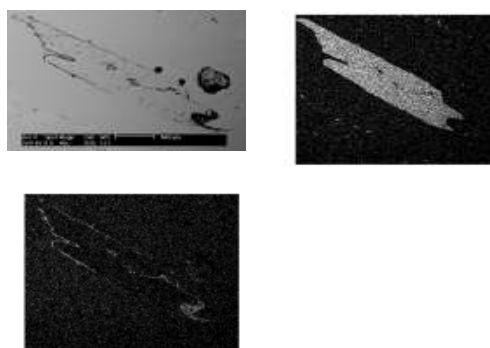


Figure 1: (*Upper Left*) SEM electron image (20 kV) of schreibersite inclusion in the type IIIB Bear Creek meteorite (dark circles are corrosion pits). (*Upper right*) EDX map at phosphorus  $K_\alpha$  (2.0137 KeV). (*Lower*) EDX map at oxygen  $K_\alpha$  (0.5249 KeV).

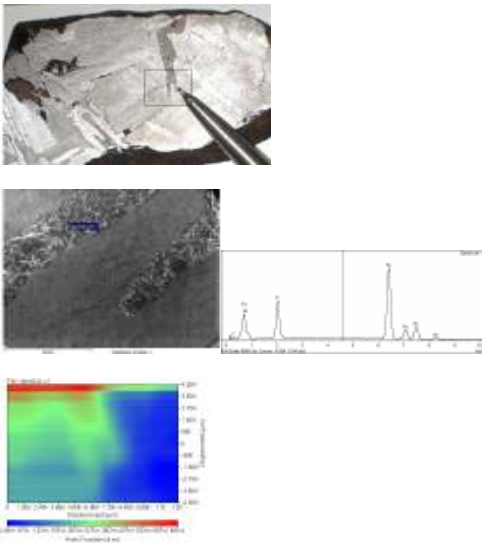


Figure 2: (*Upper*) Optical image of a “twin-fingered” Schreibersite inclusion (ringed) within a sectioned sample of the Seymchan pallasite. (*Middle*) SEM images and EDX data of one point within the inclusion. (*Bottom*) 2D-SKP map of highlighted rectangular region (12mm x 9mm) showing clearly the twin-fingered motif as a lighter colouration against a blue background (colour scale indicated beneath figure).

## References

- [1] Gulick, A., Am. Scient., 43:479. 1955.
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- [3] Bryant, D. E., Kee, T. P., Chem. Commun., 2344, 2006.