



Shreibersite and growth of life on Earth

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Abstract. A careful SEM analysis of a number of iron meteorites have shown a generalized presence of reduced P as schreibersite. The schreibersite is the only P compound able to decompose in water forming P-C and P-P linkages required by biological metabolism. This work supports the hypothesis that a main source of biological P was the big rain of cosmic material on the primordial Earth, during the Late Heavy Bombardement

1. Introduction

It is well known that some kinds of meteorites (Carbonaceous Chondrites) contain the building blocks of proteins (terrestrial and non terrestrial amino-acids) and of nucleic acids (sugars and nucleic bases) and that comets contain a large amount of molecules from which these blocks can naturally arise (HCN to give nucleic bases and HCHO to give sugars).

But the natural formation of nucleic acids (DNA/RNA) needs almost another main element, the P (Phosphorous). The P is a rare element in nature: its cosmic amount is 1000 times lower than Carbon and it is almost absent in sea water, where, probably, first life forms were born.

P is present in small amount (0.13%) on the surface of the Earth, where it is released (at present as in the distant past) by volcanic-geological events: but, normally, this P is in form of phosphates, salts totally insoluble in water. Because the soluble (in water) P was quite absent in the primordial oceans of the Earth, a major problem arises: understanding how sugars (more exactly the ribose) were able to form a number of linkages P-C (Phosphorus-

Carbon) indispensable as support to nucleic bases.

The fact that Earth can't produce endogen P able to form P-C linkages is very disturbing to understand the origin of life (on the Earth and elsewhere). This situation encouraged, in the last years, the alternative hypothesis that this fundamental kind of P could come from outside the Earth, that's from the space.

P is certainly present, in different forms, inside the meteorites. Inside the rocky meteorites (ordinary chondrites) the P is often present as phosphate, a form once again unsuitable for the biological synthesis. The case of iron meteorites (siderites, containing up to 20% of Nickel) is different: here P is present in a very distinctive form, named Schreibersite $[(Fe, Ni)_3P]$, in which the linkages with the metallic matrix are very weak and easy to be broken in presence of water Schreibersite, discovered in 1848, by the Austrian geologist Karl Franz Anton von Schreibers in an iron meteorite found in Slovakia, is always present inside iron meteorites with Ni content > 5% and it is characterised by a substantial increase of the Ni/Fe ratio compared to the rest of the matrix

In 2007 the S. Lauretta Group (Arizona Univ.) discovered that Schreibersite easily decomposes in presence of water [M. Pasek et al, 2007], giving rise to oxidized compounds of P able to easily react with organic Carbon to produce Phosphonates (compounds in which P is linked at the same time with Oxygen and Carbon).

In order to understand if and how Schreibersite is widespread inside iron meteorites, we made a systematic SEM (Scanning Electron Microscope) study of a number of iron meteorites of the Museum of Natural History of Milan [Folco L. et al., 2002]. We used the SEM Jeol JMS-5610LV located near the Mineralogy Section of the Museum, equipped with a cooled EDS probe for compositional analyses.

2. Siderites

Siderites (from the Greek "*sideros*" iron) are differentiated meteorites coming from the nucleus of an M type asteroid destroyed by the collision with an other cosmic object.

Siderites are about 7% of all known meteorite as number but (because their high specific weight) their total weight nears 90% of total meteorites. The surface of many siderites is sometime eroded by well visible cavities (named *regmaglipsis*), generated by very hot whirlwinds during the crossing of the atmosphere.

The most of the mass of siderites (up to 95%) consists of Iron, Nickel, and (max 1%) Cobalt. A very small amount of Germanium, Indium, Iridium could be often present. The value of the ratio between Nickel and these metals is a parameters used for the classification of siderites in 13 chemical classes.

But, for practical purposes, the reference to the % of Ni compared to Fe is preferred.

A melted mixture of Fe and Ni, under cooling can results in two alloys of different composition: Ni content not exceeding 4-7% (Kamacite) and Ni content reaching 20-65% (Taenite).

Inside the progenitor body, the pure taenite dominate when temperature is high, and the

Komacite begins to form gradually during the cooling.

To resume, the matrix of a siderite will be composed above all of crystals of Kamacite, if Ni percentage is <7%, while will consist of a mixture of Taenite and Kamacite if Ni percentage is much higher.

Siderites composed of kamacite (Ni<6%) are named hexahedrites, because of their cubic crystals. If Nickel content is 7-17%, siderites enclose crystals of Komacite entangled with crystals of Taenite and are named octahedrites.

When a section of an octahedrite is eroded by nitric acid, the so called Widmanstätten patterns are formed (after Alois von Beckh-Widmanstätten, 1808), consisting of a fine interleaving of kamacite and taenite bands called lamellae.

If the Nickel % exceeds 17% , the siderite matrix is totally composed of very small crystals of Taenite: Widmanstätten patterns can't be produced and this kind of siderite is named ataxite. The heaviest iron meteorite so far found (Hoba West, 60 ton, 1920, Namibia) falls in this category. The majority of octahedrites contain small amount of Sulfur (S= 0.02-5%), Carbon (C=0.05-2%) and Phosphorus (P=0.1-1%), of course in reduced or elemental form, because of the original conditions lacking in water and Oxygen.

Sulfur forms with Fe a ferrous sulphide (Troilite of formula FeS). C forms a Carbide with Iron-Nickel-Cobalt (Cohenite of formula (Fe,Ni,Co)₃ C). P forms a phosphide with Fe-Ni of formula (Fe,Ni)₃P, named Schreibersite: this is the subject we carefully studied in this work.

3. Experimental part

Schreibersite inclusions were looked for inside these seven iron meteorites of Museum of Natural History of Milan: Canyon Diablo (Octahedrite, USA 1861), Bendego (octahedrite, Brasil 1874), Odessa (octahedrite USA, 1922), Gibeon (octahedrite, Namibia 1936), Sikhote Alin (octahedrite, Russia, 1947), Seymchan (octahedrite, Russia 1967), Kamil (Ataxite, Egypt, 2010).

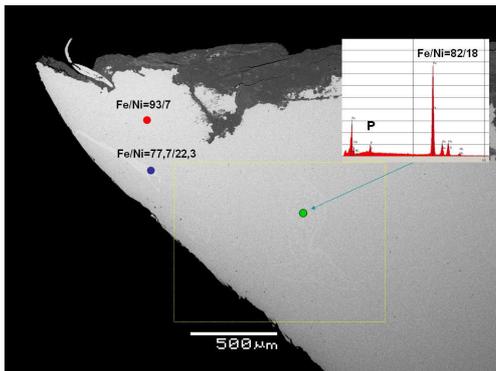


Fig. 1. A SEM-BSE picture of a section of the Canyon Diablo siderite, in which some EDS measures of composition are enclosed.

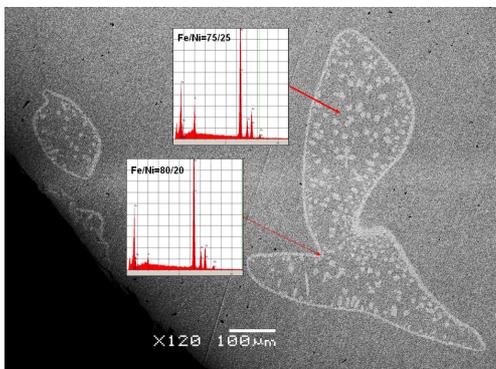


Fig. 2. A Schreibersite inclusion of the Canyon Diablo siderite, with EDS analyses in regions showing different BSE reflectivity.

We took a sample of few millimetres from the internal matrix of each siderite (a procedure to be made with great care, because of the hardness of involved materials) and we embed it in a small (3x3 cm) cylinder of thermosetting resin (Araldite) to make easy the polishing of the surface requested by SEM exploration.

The polishing was made manually using rotating discs of abrasive paper, under continuous water flow. The polishing was completed by a rotating disc of felt, over which a suspension in nujol of powder of diamond (0.5 micron) was placed.

Each section was carefully explored by the SEM-BSE detector (Backscattering electrons,

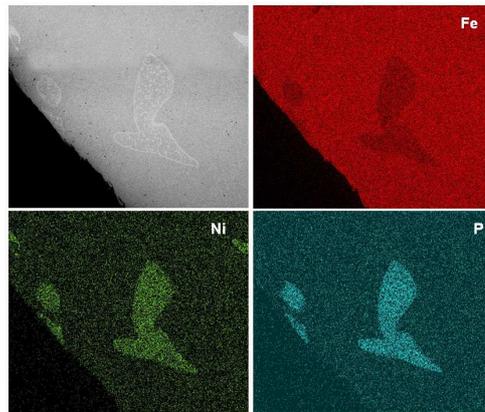


Fig. 3. EDS maps of some parts of the Canyon Diablo siderite : high amount of P proves the presence of Schreibersite.

more sensitive to the composition) to obtain global pictures, and by SEM-EDS probe to check for the local composition in some interesting points.

By the EDS probe, we made also maps of some wider parts, to look for Fe, Ni, P, O, possibly Co. Surprisingly, we realized that inclusions of Schreibersite were always present, with amount and morphology always different. As a further surprise, inside Schreibersite the ratio Ni/Fe was always higher than the mean value of the matrix. In other words: where an EDS map showed a higher concentration of Ni, here P was almost always present.

Here are some of the most interesting analytical results.

In **Canyon Diablo** (Fig1,2,3), the ratio Ni/Fe in the matrix is about 93/7. But Ni (compared to Fe) increases 3-4 times inside some "islands" where there is presence of P in absence of O: a clear indication of the presence of Schreibersite.

Very interesting (and difficult to be explained) is the 3D structure of islands of Schreibersite inside the Canyon Diablo. A darker primary matrix (at SEM-BSE) with higher content of P (Fe/Ni=75/25) is littered with lighter inclusions with lower content of P (Fe/Ni=80/20). A lighter skin, of the same composition of the inclusion, encloses each single island.

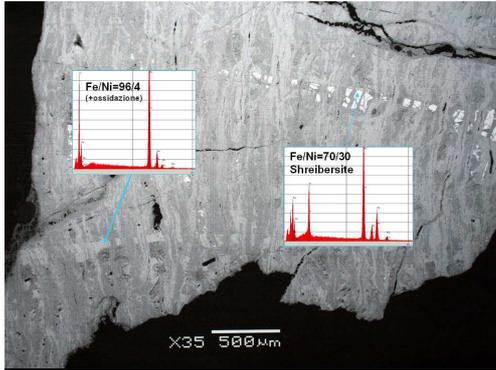


Fig. 4. A SEM-BSE picture of a section of the Bendego siderite, in which some EDS measures of composition are enclosed.

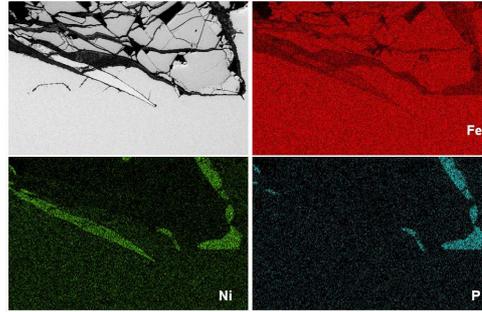


Fig. 7. EDS maps of some parts of the Bendego siderite, in which high Ni amount matches only partially the presence of P (and so of Schreibersite).

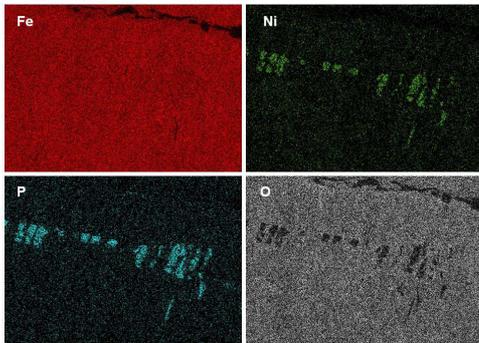


Fig. 5. EDS maps of some parts of the Bendego siderite, in which an high amount of P proves the presence of Schreibersite.

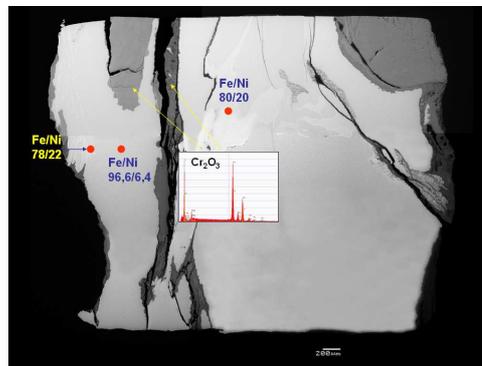


Fig. 8. A SEM-BSE picture of a section of Seymchan siderite, in which some EDS measures of composition are enclosed

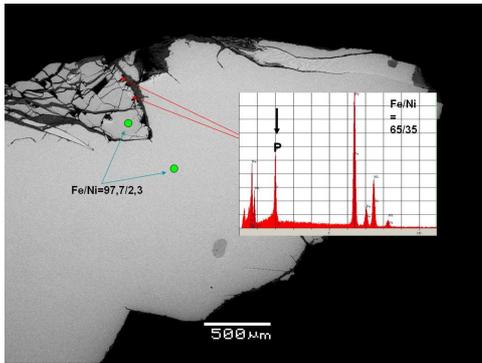


Fig. 6. A SEM-BSE picture of a section of the Odessa siderite, in which some EDS measures of composition are enclosed.

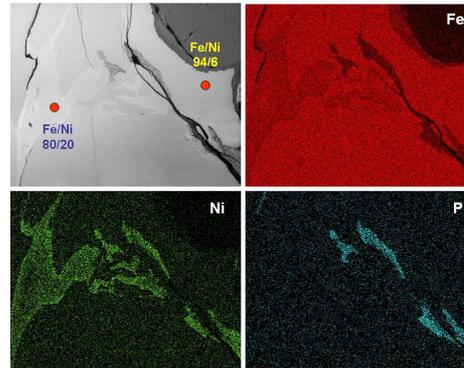


Fig. 9. EDS maps of the Seymchan siderite, in which high Ni amount match only partially the presence of P (and so of Schreibersite).

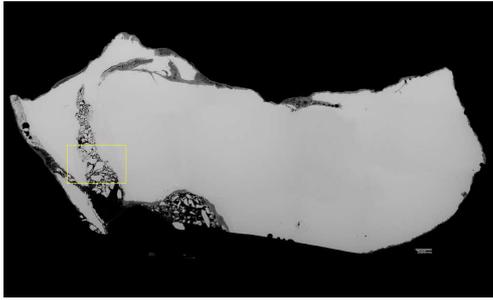


Fig. 10. A SEM-BSE picture of a section of the Kamil siderite, in which some EDS measures of composition are enclosed. Shreibersite was looked for inside some clearly brittle regions.

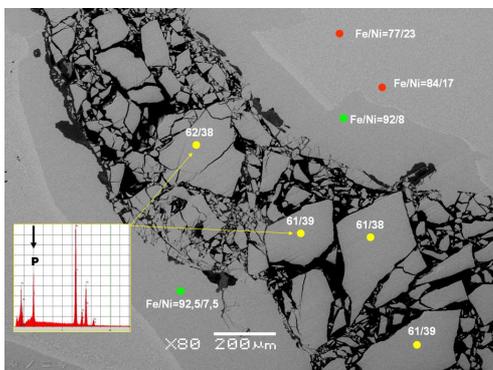


Fig. 11. This spectacular SEM-EDS picture of a section of the Kamil siderite, shows that a .river. of brittle micro-plates is composed of Schreibersite

In **Bendego** (Fig4,5) the matrix shows a ratio $Fe/Ni=95/5$ and is affected by a number of cracks and fractures that explain well the general presence of oxidized Fe (SEM-BSE dark streaks).

Ni (compared to Fe) increases 6-fold ($Fe/Ni=70/30$) in some streaks of "light zones" (to SEM-BSE) where there is clear presence of P and where the Oxygen, that is spread across most of the matrix, is quite absent: high Ni amount, presence of P and absence of O are the fingerprint of Schreibersite.

In **Odessa** (Fig6,7) the matrix shows a ratio $Fe/Ni=94/6$, a number of fractures and some brittle zones compared to the surrounding area. Here thin inclusions of Schreibersite are

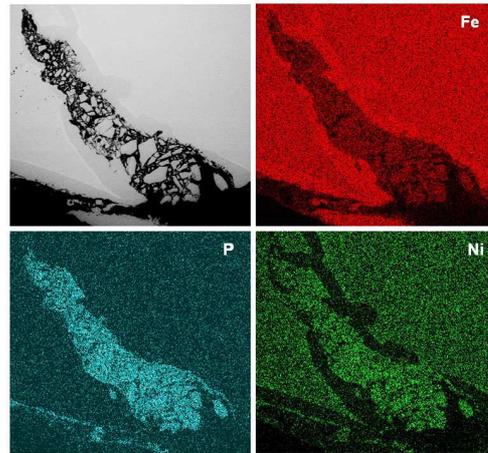


Fig. 12. This beautiful EDS map of the micro-plates river discovered inside the Kamil siderite, shows both the presence of Schreibersite (high Ni content) both edges of kamancite (Ni % tree times lower than the matrix).

present, in which the amount of Ni increases up to 7 fold compared to matrix ($Fe/Ni=60/40$): possibly the local brittleness is linked to the presence of Schreibersite.

It is interesting to note also the existence of elongated light inclusions (SEM-BSE) at high Ni content (ex. $Fe/Ni=75/35$) without presence of P, so disconnected to Schreibersite: the origin of these kind of inclusions is very difficult to understand.

Seymchan (Fig8,9) is similar (excess of Ni with and without P). The matrix shows a ratio $Fe/Ni=93/7$, and is affected by big fractures, in which Cr_2O_3 (chromite) build-ups are present. Large portions of matrix (grey to SEM-BSE) shows elongated light inclusions with high amount of Ni ($Fe/Ni=80/20$). The edges of some smaller fractures are clearly shattered in small bits similar to "icebergs": here there is high Ni content and a clear presence of P, so of Schreibersite.

The **Kamil** siderite (10,11,12) is absolutely outstanding. About 1.7 ton were found in February 2009 by an Italo-Egyptian expedition, led by F. Folco and M. di Martino, near a "young" crater (age < 5000 years) of 45 meter located on the border Sudan-Southern Egypt

(22°01'06"N, 26°05'15"E) and discovered some year before by V. de Michelis (ex Curator of Museum of Natural History of Milan) from a satellite pictured dated October 2005.

Kamil is an ataxite, because of a very high, even if not homogeneous, amount of Ni (we found an Fe/Ni ratio between 83/17 and 78/23).

The Kamil matrix, very compact, is strongly affected and weakened by rivers, consisting of hundreds of micro-plates of Schreibersite where the Nickel content is doubled (Fe/Ni=60/40 !) compared to the matrix. These rivers have surprising edges: here, the Ni % is more than halved (Fe/Ni=92/8) compare the matrix, taking the form of Kamacite.

4. Discussion and conclusions

This survey demonstrates that Schreibersite is almost always present in iron meteorites, even if the morphology of its inclusions is always different, possibly linked to local chemical and physical conditions (temperature, pressure, etc) of formation. A constant property of the Schreibersite is a big increase (up to two fold) of the Ni %, evidently because of a greater chemical affinity to P of Ni compared to Fe.

If Schreibersite is always present in siderites, it is possible to estimate the P amount that is delivered on Earth each year by these meteorites. The annual current flow of meteorites is evaluated about $4 \cdot 10^5$ kg/y [M. Pasek, 2005]. Given the high specific weight of iron meteorites, it is possible to estimate that their mass is almost 50% of the total weight: so their current flow is about $2 \cdot 10^5$ kg/y (2). From the study of different classes of Siderites, it is possible to estimate a P average amount of about 0.5% [Masahide Y, 1992]: this means that the current annual flow of schreibersitic P is near 10^3 Kg/y.

During the Late Heavy Bombardement (LHB) of 3.9 billions of years ago, that occurred just before first forms of life appeared, it is estimated that the flow of cosmic bodies to early Earth was, during some tens of millions of years, almost 10^5 times greater than at

present [Zahnle K, 2006]. Accordingly, the annual flow of schreibersitic P had to be about 10^8 kg/y.

In addition, assuming that the ratio ocean/ground was similar to the current (0.72), during the LHB period, about $7.2 \cdot 10^9$ kg/y ($72 \cdot 10^{11}$ gr/y = $2.3 \cdot 10^{11}$ moli/y) of biologically active P had to fall into the oceanic water.

Assuming that the early global volume of water was like the present $1.5 \cdot 10^{15}$ litres [Garrison T., 2005], there was an annual molar delivery M (mole/litre) of "active" P into the primordial oceans of about $2.3 \cdot 10^{11}$ gr/ $1.5 \cdot 10^{15}$ l = $1.54 \cdot 10^{-4}$ moli/l.

This evaluation is correct numerically, but overestimated in practice, because just a part of the schreibersitic P is biologically available: in fact, some is immediately destroyed during the impact of a meteorite, some decomposes in the ambient, some remains out of the reach inside its meteorite. It is possible to estimate [Pasek M, 2008] that not more than 5% of the original schreibersitic P is ultimately available. This means that the molar annual supply of "active" sideritic P lowers to about $7.5 \cdot 10^{-6}$ mol/l. This value can be considered a good indication of the average molar concentration of "active" P during all the LHB period, that lasted 10-100 million of years. One might wonder if a molar concentration of P in the primordial oceans of about 10^{-5} - 10^{-6} M should be enough to trigger biological processes. The reply isn't easy. Given the most recent studies [Nelson D., 2005], the lowest molar concentration of P able to trigger biological processes is located between 10^{-3} and 10^{-5} M, therefore is one or two order of magnitude greater than the schreibersitic supply of the siderites. But a couple of important observations has to be added. First at all, if the average molar concentration of P in the primordial oceans was close to 10^{-5} nothing prevents that locally this concentration could have been also much greater: this is an obvious statement taking in account the large number of big impacts during the LHB period. Secondly, we must consider that siderites were not the only source of Schreibersite. A small supply come also from the ordinary chondrites and a supply probably very important come and came in the past from IPD (Interplanetary

Dust Particle), the annual flow of which, according to certain estimations, can even be one or two orders of magnitude higher than the flow of siderites [Love S.G., 2009].

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