COMPARATIVE CHEMISTRY OF P-RICH OPAQUE PHASES IN CM CHONDRITES.

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P-rich sulfide, P-Cr-rich sulfide, barringerite, and schreibersite have been described [1-5] as characteristic accessories in some CM chondrites. The phases are supposed to be of nebular origin and to be responsible for the fractionation of some moderately volatile elements in the solar nebula gas. However, the chemical composition of these phases was investigated in detail only in the Mighei chondrite and in CM clasts of the Erevan howardite [3-5]. The goal of this work was to study the chemistry of the P-rich opaques in the Murray and Boriskino chondrites, which are typical representatives of CM chondrites. Our results provide new evidence for a significant abundance of P-rich opaque phases in CM chondrites. The chemistry of these phases is highly diverse and should depend very sensitively on the conditions pevailing during condensation from the solar nebula gas.

Results. Murray and Boriskino polished thin sections were studied for P-rich opaque phases using standard ASEM and EMP techniques. Both meteorites contain numerous grains of such phases, which are usually less than 10 μm in size and comprise P-rich sulfides, Cr-P-rich sulfides, schreibersite, and barringerite. The grains are associated mainly with primary forsterite and enstatite objects, which are usually enveloped by accretionary dust mantles. Commonly, the P-rich opaques occur within the pore space between the high temperature silicate grains. The relative proportion (by number) of the phases in Murray is: 55 % P-rich sulfide, 25% Cr-P-rich sulfide, and 20 % schreibersite. Only one barringerite grain was found in the Murray section. Occasionally, the Murray schreibersite contains minute (~2-3 μm) crystals of escolaite. The most common P-bearing phase in the Boriskino chondrite is P-rich sulfide (62%), followed by barringerite (21%), and Cr-P-rich sulfide (17%). No schreibersite grains were found in our Boriskino section.

The P-rich and P-Cr-rich sulfides in the Murray chondrite have a narrow compositional range (Figs.1-3), in contrast to those from the Boriskino and Mighei chondrites [5]. Of all such phases analyzed so far, they are the lowest in the Fe/Ni, (Fe+Ni)/P, and S/P ratios, and have the highest K content (~1 wt.%). The sulfides from the Boriskino chondrite have the highest above mentioned ratios and are depleted in K. The sulfides from the Mighei chondrite are of intermediate composition (Fig.1-3). The Fe/Ni ratios of the phosphides in the investigated meteorites follow an opposite trend to that of the sulfides (Fig.4). The following order of decreasing Fe/Ni ratio is found: Murray > Mighei >Boriskino.

Schreibersite associated with barringerite has a lower Fe/Ni ratio than the latter. Similar to barringerites described from the Mighei chondrite [5], the Boriskino barringerites are rich in Ca and Na. Barringerites from the Boriskino chondrite contain 1.5 wt.% Co, whereas those from the Mighei chondrite contain only 0.2 wt. % Co [5]. The low Co content in the Mighei barringerites can be understood because Co_2P and $(Fe,Ni)_2P$ have different crystal structures. Therefore, the high-Co barringerite in the Boriskino chondrite could be a new, so far unknown phase, with a distinct crystal structure.

Discussion. Our study confirms the suggestion made previously [4,5], that P-rich sulfides, barringerite and schreibersite are characteristic accessories of CM chondrites that are very likely of nebular origin. The presence of 2 % of P-rich sulfide or 0.5 % of barringerite could account for the total P content in these chondrites. This means that these phases are probably a main carrier for P in CM chondrite matter. The high K content (up to 1,5 wt.%) in P-rich sulfides suggests also that a significant amount of K in CM chondrites could be related to these phases. Thus, both P and K are possibly be condensed as chalcophile elements during a certain stage of the nebular condensation. The same can be supposed for some other moderately volatile elements (e.g., Cr).

The composition of P-rich sulfides from the Murray and Boriskino CM chondrites follows the S/P - (Fe+Ni)/P regression line [5] obtained for Mighei P-rich sulfides (Fig.1). However, the compositions of these sulfides as well as of the associated phosphides, are distinctly different in these different chondrites (Fig.1-3). This difference indicates that the composition of P-rich opaques is very sensitive to P, T-conditions prevailing during their formation in the solar nebula. Apparently, the Murray chondrite sampled P-rich opaques formed under narrowly defined conditions, whereas the Mighei and Boriskino chondrites collected P-rich grains condensed under widely varying conditions (Fig.1-4). Interestingly, the order Murray < Mighei < Boriskino, corresponding to increasing Fe/Ni and S/P ratios in P-rich sulfides and to decreasing Fe/Ni ratios in the phosphides (Fig.2-4), coincides with an increase in the matrix content, the volume of chondrule alteration, the bulk Na content, and with a decreasing 36Ar content of these meteorites [6-8]. Some of the parameters are widely believed to be indicators of aqueous in situ alteration [8] in the CM parent body. However, the observed correlation between the primary compositional characteristics of P-rich opaque phases and the silicate alteration indices suggests that the latter is more like the result of nebular evolution, i.e., a pre-accretionary alteration, rather than a product of parent body aqueous alteration processes. In situ alteration should not be significant in these meteorites because it would lead to a complete replacement of the small P-rich, reduced opaque phases by secondary, oxidized phases.

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References. [1] T. E. Bunch and S. Chang (1980) GCA, **44**,1543-77; [2] T. E. Bunch et al. (1979) GCA, **43**, 1727-42; [3] M. A. Nazarov et al. (1993) LPSC XX1V, 1053-54; [4] M. A. Nazarov et al. (1994) LPSC XXV, 979-80; [5] M. A. Nazarov et al (1996) LPSC XXV11, 939-40; [6] H. J. McSween (1979) GCA, **43**, 1761-70; [7] L. Schultz and H. Kruse (1989) Meteoritics, **24**, 155-72; [8] L. B. Browning et al. (1996) GCA, **60**, 2621-33.

Figures.

Figure 1: Compositional range of P-rich sulfides in Boriskino, Mighei, and Murray CM chondrites.
Figure 2: Histogram of the atomic S/P ratio of P-rich sulfides in Boriskino, Mighei, and Murray CM chondrites.
Figure 3: Histogram of the atomic Fe/Ni ratio of P-rich sulfides in Boriskino, Mighei, and Murray CM chondrites.
Figure 4: Histogram of the atomic Fe/Ni ratio of phosphides in Boriskino, Mighei, and Murray CM chondrites.

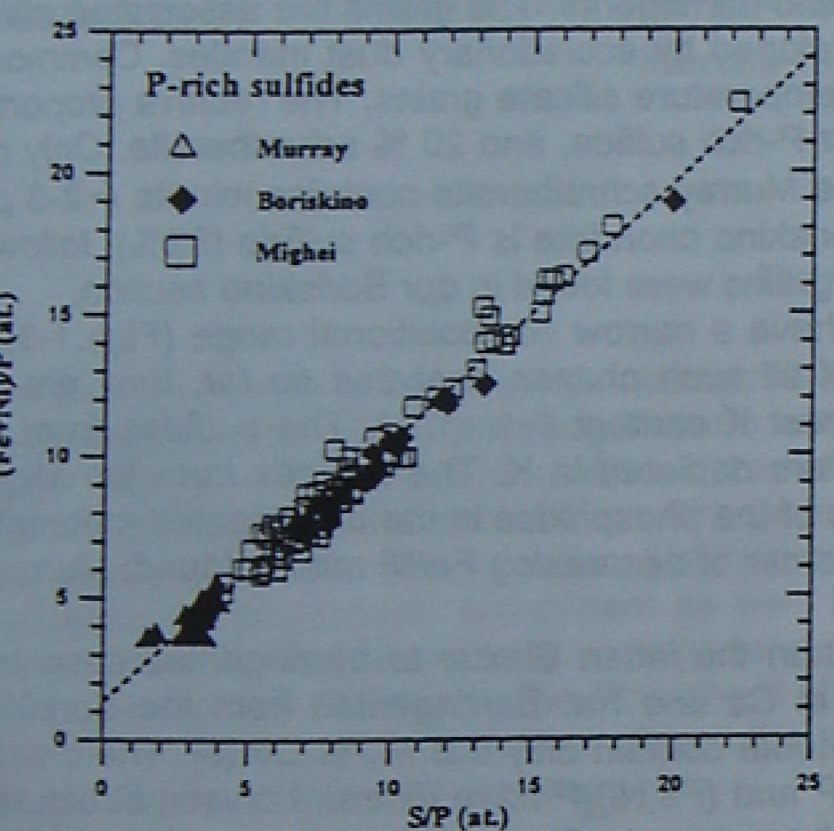

Fig. 1

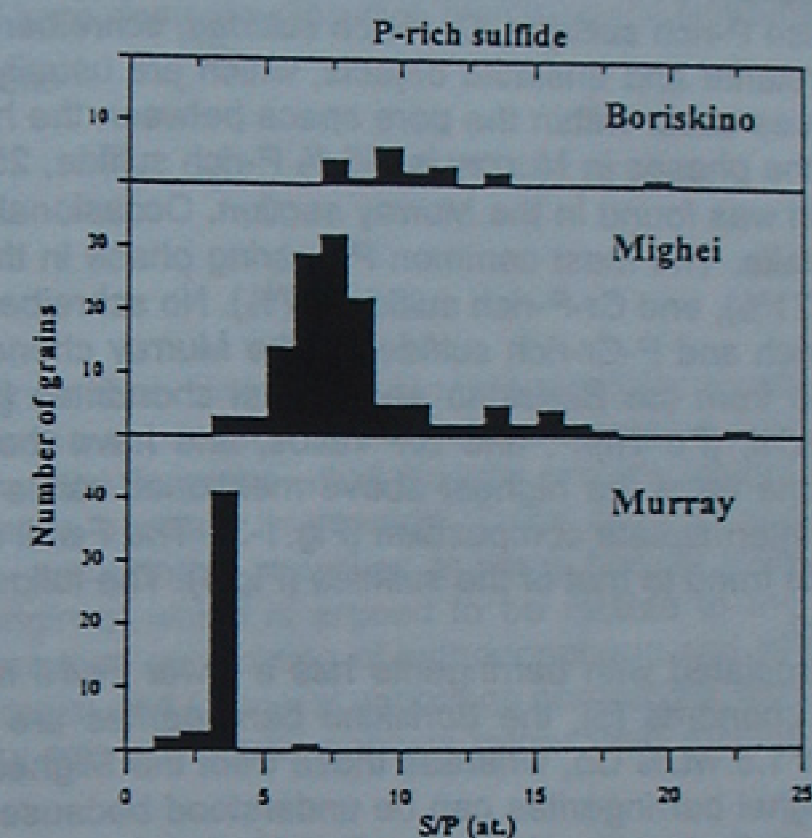

Fig. 2

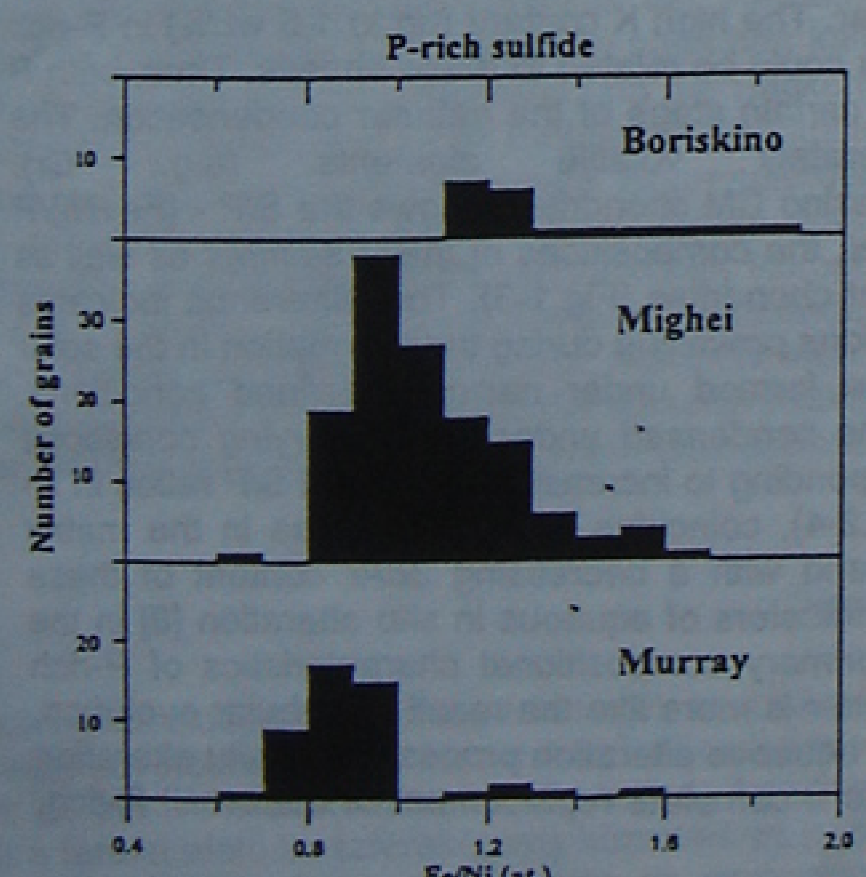

Fig. 3

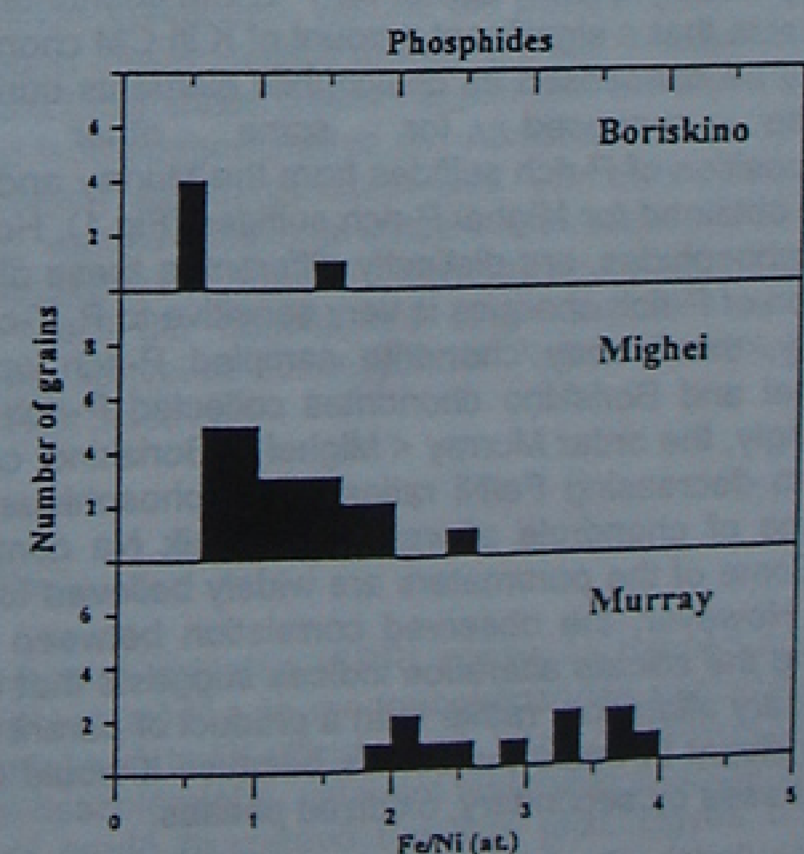

Fig. 4