

PHOSPHIDES AND P-RICH SULFIDES IN THE MIGHEI (CM) CHONDRITE. M.A. Nazarov¹, F. Brandstaetter² and G. Kurat², ¹Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow 117975, Russia, ²Naturhistorisches Museum, A-1014 Vienna, Austria.

All chondrites are depleted in moderately volatile elements as compared to CI chondrites [1]. The distribution of such elements between minerals in chondrites could provide us with some clues to understand the reason for the depletion. Our study of CM carbonaceous clasts from the Erevan howardite [2,3] has shown that P and some other moderately volatile elements could have a chalcophilic behaviour in CM chondrites and could possibly be condensed into sulfides and phosphides. The goal of this work was to search for P-bearing phases in the Mighei chondrite, which is a typical representative of CM chondrites. As a result we show that P-rich sulfide and phosphide grains and aggregates could indeed be a main primary carrier for P and some other moderately volatile elements. A separation of such phases from the solar nebula gas could significantly alter the concentrations of these elements in the nebula and hence could provide a mechanism for the depletions observed in chondrites.

Occurrence. A Mighei section was studied with an analytical scanning electron microscope (ASEM) to search for phosphides and P-rich sulfides. Pentlandite and pyrrhotite were found to be the most abundant sulfides in the section available whereas the P-rich phases are characteristic accessories. Most common is a P-rich sulfide (83% of number of grains), followed by barringerite (9%), and a Cr-P-rich sulfide (8%). A few grains of schreibersite and a single grain of a Ca-rich oxyphosphide were also found. The P-rich phases typically are present as single small (<10 μm) grains or as rounded aggregates (10-20 μm) which are enveloped by accretionary dust mantles [4] and are closely associated with forsterite and enstatite grains. The aggregates (Fig.1) consist mainly of P-rich sulfide and rare grains of barringerite, Cr-P-rich sulfide, and diopside. There are also P-rich dust aggregates of an irregular shape (Fig.2). They consist of rounded or needle-like crystals (a few μm in length) of P-rich sulfide and barringerite which are cemented by a very fine-grained material rich in S, P, Cr, and Ca. Very thin needles of schreibersite are present as a minor component. Accessories are diopside, daubreelite, a Cr-oxide (escolaite ?), and metallic Cr (?). Aggregates of this type are covered by forsterite plates and/or enveloped by accretionary dust mantles. The P-rich grains and aggregates are never associated with metal, pentlandite, or pyrrhotite. One grain of P-rich sulfide was found in contact with magnetite. Commonly, the P-rich phases are more or less altered (oxidized) and can be completely replaced by a P-rich tochilinite-like phase. One barringerite grain was found enveloped by Fe phosphate and rimmed by iron oxides and pyrrhotite.

Table. EMP analyses of P-rich phases from Mighei (wt.%)

	1	2	3	4	5	6	7	8	9
Na	0.12			0.06		0.08	0.02		0.46
Mg	0.18	0.06	0.04	0.10	0.11	0.41	0.07		1.31
Si	0.23	0.09	0.04	0.09	0.12	0.38	0.08		1.25
Cr	0.11	0.31	0.13	0.16	0.22	0.63	4.70	0.42	0.06
Fe	27.4	29.7	32.1	33.1	40.1	36.4	36.1	54.9	33.2
Co	2.14	2.09	1.93	1.18	0.16	0.18	1.73		0.10
Ni	33.3	33.1	31.7	28.2	35.5	38.8	31.8	27.9	14.3
P	7.20	4.10	3.60	2.83	19.5	20.5	3.40	16.7	17.3
S	26.4	29.7	31.6	31.6	3.40	2.09	28.8		1.81
K	0.19	0.28	0.21	0.51			0.29		
Ca	0.03	0.12	0.01	0.07	0.09	1.22	1.04		10.9
Total	96.8	99.5	101.4	97.9	99.2	100.7	98.0	99.9	80.7

1-4 - P-rich sulfide; 5, 6 - barringerite; 7 - Cr-P-rich sulfide; 8 - schreibersite (ASEM analysis); 9 - Ca-rich oxyphosphide

Mineral chemistry. We analyzed 120 P-rich grains by ASEM but at present only 15 grains were measured with an electron microprobe (EMP). Representative EMP analyses are given in the Table. The composition of the *P-rich sulfide* is close to that of the Erevan carbonaceous clasts [2,3]. However, the sulfide in Mighei has highly variable Fe (17-32, mean: 23.9 at.%), Ni (17-27, mean: 23.1 %), S (35-48, mean: 44.1 %), and P (2-12, mean: 5.65 %) contents. Characteristic minor elements, which are often (but not always) present in the sulfide, are K (up to 0.87 at.%), Ca (up to 1 %), Cr (up to 2 %), and Co (up to 2.5 %). There is a strong

positive correlation between the S/P and cations/P (Fig.3) ratios of the sulfides and a weak positive correlation between the S/P and Fe/Ni ratios (Fig.4). Cobalt correlates positively with Ni but the Ni/Co ratio can deviate from the cosmic one (Table). *The Cr-P-rich sulfide* has a composition similar to that of the P-rich sulfide (Figs.3,4; Table), except for the very high Cr content (2-14 at.%) and the distinctly higher cations/P ratio. It

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is likely that the sulfides are chemically related and form a solid solution. However, the coexistence of separate grains of different composition points to the presence of a miscibility gap at $>2\%$ Cr. *Barringerite* from Mighei is very similar in composition to barringerite described from the Erevan carbonaceous clasts [3]. Commonly, it is enriched in S (0.5-5.3, mean: 2.3 at.%) and Ca (up to 3.4 %). Calcium and the Fe/Ni ratio are positively correlated. In contrast to the P-rich sulfide, the barringerite has a highly variable Fe/Ni ratio (Fig.4), very low Co content, and does not contain a detectable amount of K (Table). *Schreibersite* needles are too small for a precise analysis. However, it is clear that schreibersite has a distinctly higher Fe/Ni ratio than all other P-rich phases (Fig.4, Table). A single grain (5 μm in size) of *Ca-rich oxyphosphide* was found in close association with Ca carbonate. The low total (Table) could indicate the presence of O. The oxyphosphide could be the product of oxidation of Ca-rich barringerite which has similar Fe/Ni and cations/P ratios as well as S and Co contents.

Discussion. Our study demonstrates that P-rich sulfides and phosphides described by [2,3,5,6] have a significant abundance in CM chondrites. Obviously, the P-rich sulfide may be a main carrier for P in these meteorites. However, the nature of the unique sulfide phase is still poorly known. Our study shows that the sulfide is a solid solution and has variable contents of Fe, Ni, S, and P. The variations can be understood as a result of substituting Fe by Ni and of S by P. This means that P is not present as a PH_4 complex, as was suggested before [3]. The interelement correlations (Fig.3) also suggest that a thio-salt component (e.g., $(\text{Fe,Ni})_3(\text{PS}_4)_2$), as proposed by [3], can also not be present because such a composition is far away from the cations/P-S/P regression line found. Oxygen, if present in the sulfide, could be of a secondary origin because some EMP analyses show a normal total. Therefore, the phase is probably not a primary oxysulfide. At present, the best chemical model for the P-rich sulfide composition is a solid solution of a sulfide and a phosphide component. A regression of the ASEM data (Figs. 3,4) shows that these end member components are very close in composition to $(\text{Fe,Ni})\text{S}$ and $(\text{Ni,Fe})\text{P}$, and that the phosphide end member has a higher Ni/Fe ratio than the sulfide.

Our study strongly supports a nebular origin of the P-rich phases as was inferred from the study of the Erevan CM clasts [3]. Here in Mighei the phases are associated with accretionary objects. The textural features of the P-rich aggregates suggest that the grains are indeed a primary dust, probably condensed from a vapor, and we cannot see a possibility to explain their origin by processes of melting or secondary aqueous alteration. Similar to the P-rich phases in the Erevan CM clasts [3], the Mighei phases must have condensed together with forsterite, i.e., after the condensation of refractory phases (CAIs) and before the precipitation of metal and troilite. It can be suggested that the condensation of the P-rich phases took place under high sulfur fugacity. Thus, the P-rich phases should be a main pristine carrier for P and other moderately volatile elements, i.e., Fe, Ni, Co, Cr, S, and K. The very good correlation between P and S observed in chondrites [1] supports this conclusion. Hence, the distribution of P-rich aggregates in the solar nebula could significantly affect the concentrations of moderately volatile elements in chondrites. The P-rich grains and aggregates could also be the precursors of P- and S-rich objects occasionally present in chondrites [7-8].

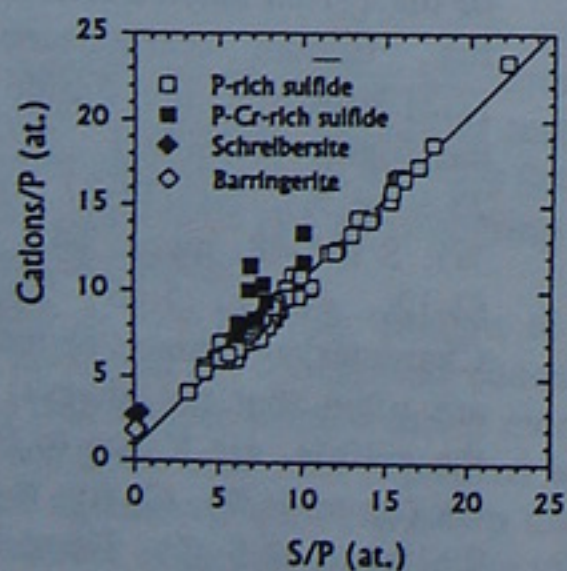


Figure : Cations/P vs S/P ratio of phosphides and P-rich sulfides from Mighei (CM).

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