PHOSPHORIAN SULFIDES FROM THE ALH 84029, ALH 85013, EET 96029, AND Y 82042 CM CARBONACEOUS CHONDRITES.

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Introduction: It has previously been demonstrated that phosphorian Fe,Ni sulfide is a characteristic accessory phase of CM chondrites [e.g., 1,2]. The unusual sulfides could be of extrasolar origin or at least contain presolar relics of nucleosynthetic processes [3]. Chemistry of the sulfides is highly diverse in CM chondrites and reflects probably condensation and accretion conditions [1,2,4]. The goal of this work was to continue the search for and explore the compositional range of the these sulfides in CM chondrites. Here we report on phosphorian (P-rich) sulfides and phosphides in some Antarctic CM chondrites (ALH 84029, ALH 85013, EET 96029 and Y 82042) and summarize the data on the chemistry of these P-rich phases collected by our group up to date.

Occurence: All CM chondrites studied this time contain P-rich sulfides. Their occurrences and mineral associations are similar to those described earlier [e.g., 1,2]. In ALH 84029 a simple P-rich sulfide and barringerite were found only. ALH 85013 contains simple P-rich sulfide, Cr,P-rich sulfide, and barringerite. The relative proportion (by grain number) of the phases in the meteorite is: 74%, 16% and 10%, respectively. Only one schreibersite grain was found. In the abundance pattern of P-rich phases, ALH 84029 resembles Boriskino that contains only minor schreibersite whereas ALH 85013 is similar to Mighei containing both schreibersite and barringerite [1,2]. The same P-rich opaque phases are present in EET 96029. However, their proportion (48% P-rich sulfide, 30% Cr,P-rich sulfide, 10% barringerite) points to a higher abundance of Cr,P-rich sulfide in this meteorite. This is the characteristic feature of Murchison and Murray [1,2]. However, in contrast to these chondrites containing abundant schreibersite, no grains of this phosphide were identified in EET 96029. Y 82042, classified as a CM1/2 unusual chondrite [5], is anomalous in the abundance pattern of P-rich sulfides and phosphides. The meteorite contains only simple P-rich sulfide. No Cr,P-rich sulfide or phosphide is present.

Mineral Chemistry: All P-rich sulfides analyzed from the Antarctic CM chondrites plot very well to the main stream of the S/P-(Fe+Ni)/P-Fe/Ni atomic relationships established earlier [e.g., 1,2] in P-rich sulfides of CM chondrites (Fig. 1,2). P-rich sulfides of **EET 96029** have low S/P and (Fe+Ni)/P ratios, which are in a narrow range. In these parameters the sulfides are most close to those of Banten (Table). However, the EET 96029 sulfides display a relatively high Fe/Ni ratio (Fig. 2, Table). On average, P-rich sulfides of ALH 84029, and Y 82042 are very high in the S/P, (Fe+Ni)/P and Fe/Ni ratios, and compositionally similar to those of Boriskino (Table), but the compositional range of the Boriskino sulfides is much higher, so that ALH 84029, and Y 82042 sulfide compositions are located in a middle part of the whole variance of S/P and (Fe+Ni)/P ratio values (Fig. 1,2). The most distinct feature of ALH 84029 and Y 82042 sulfides is the high Fe/Ni ratio (Fig.2; Table). P-rich sulfides of ALH 85013 have generally higher in S/P and (Fe+Ni)/P ratios than those of EET 96029 and have lower ratios compared to those of ALH 84029, and Y 82042 (Fig. 1). The ALH 85013 sulfides are closest in composition to P-rich sulfides of Cold Bokkeveld and Nogoya (Table). Barringerites of EET 96029 and ALH 84029 are lowest in the Fe/Ni ratio(Fig. 3). ALH 85013 contains barringerite and schreibersite which do not differ in Fe/Ni ratio from phosphides of the main group of CM chondrites (Fig. 3).

Discussion: The new data on the Antarctic CM chondrites strengthen the constraints reported earlier [1,2,4] on chemical constitution and compositional range of P-rich sulfides. All P-rich sulfides of CM chondrites demonstrate a certain S/P-(Fe+Ni)/P atomic ratio relationship given by the best fit line (Fig. 1), $(Fe+Ni)P=0.948*S/P+1.26$. The regression is determined now by 860 analyses. The correlation coefficient is 0.9965. The relationship suggests that the P-rich sulfide should be a mixture of two components at least. The theoretically possible end members are $(Fe,Ni)_{0.95}S$ and $(Fe,Ni)_{1.26}P$. The sulfide component should be systematically higher in the Fe/Ni ratio (Fig.2). Ocassionally, Cr and Ca contents are significant (up to 20 wt%) and, hence, some other constituents should be present in the P-rich sulfide solid solution. The chemical nature of the Cr- and Ca-rich constituents is still not clear. However, even high concentrations of Cr and Ca do not change the Fe-Ni-S-P proportions mentioned above. This suggests that the Cr and Ca enrichments should be accompanied by the presence of a light element (likely C or/and O). Cobalt, K and Na are minor but characteristic elements of P-rich sulfides. Cobalt is positively correlated with Ni. Potassium seems to be correlated positively with the Fe/Ni ratio, whereas Na appears to be slightly higher in Ni rich sulfides compared to the Ni-poor ones.

The Fe/Ni ratios of phosphides and P-rich sulfides are anticorrelated (Fig. 3). As a rule, schreibersite appears in association with P-rich sulfides if the sulfides have low S/P (<10) and Fe/Ni (<1.2) ratios. Schreibersite commonly has a higher Fe/Ni ratio than barringerite, if both are present. However, if a CM chondrite (e.g., Murray) is dominated by schreibersite, then the minor barringerite has a high Fe/Ni ratio (Fig. 3). On the other hand, if a chondrite (e.g., Boriskino) contains abundant barringerite, then a minor schreibersite has the higher Fe/Ni ratio.

CM chondrites differs in composition of their P-rich phases. Murchison, Murray, Banten and EET 96029 contain sulfides with low S/P ratios. The sulfides have a narrow compositional range (Table) and commonly contain Cr and some Na. The meteorites, except for EET 96029, contain schreibersite as a main phosphide phase. In contrast, Boriskino, ALH 84029 and Y 82042 are characterized by sulfides with high S/P ratios (Table). Boriskino sulfides exhibit the largest compositional range, whereas sulfides of ALH 84029 and Y 82042 are compositionally not so variable. The sulfides are generally enriched in K and have high Fe/Ni ratios. The dominant phosphide phase of the meteorites, except for Y82042, is barringerite. Other CM chondrites (Cochabamba, Mighei, Cold Bokkeveld, ALH 85013, Nogoya and CM clasts in Erevan) are intermediate in the sulfide chemistry (Table) and contain both schreibersite and barringerite.

Table. *Average compositional characteristics of P-rich sulfides in CM chondrites (atomic ratios).*

	S/P	(Fe+Ni)/P	Fe/Ni
Murchison	3.36 (0.84)	4.54 (0.80)	0.93 (0.22)
Murray	3.40 (0.52)	4.55 (0.59)	0.85 (0.11)
Banten	3.78 (1.28)	5.22 (1.22)	0.99 (0.25)
EET96029	4.14 (1.57)	5.62 (1.58)	1.44 (0.81)
Cochabamba	5.92 (2.43)	6.58 (2.48)	1.12 (0.19)
Erevan (CM)	6.67 (0.90)	8.15 (0.96)	1.27 (0.19)
Mighei	8.75 (3.00)	9.37 (2.92)	1.10 (0.20)
Cold Bokkev.	9.10 (4.14)	9.94 (4.06)	1.20 (0.26)
ALH85013	9.20 (6.76)	10.1 (6.65)	1.14 (0.30)
Nogoya	12.4 (6.14)	13.2 (6.01)	1.21 (0.27)
ALH84029	20.8 (2.66)	21.5 (2.67)	1.93 (0.24)
Boriskino	22.0 (13.1)	22.1 (12.3)	1.61 (0.51)
Y82042	22.8 (2.55)	25.1 (3.00)	2.07 (0.38)

Standard deviation is given in brackets.

Acknowledgements: The thin sections of ALH 84029, ALH 85013 and EET 96029 were made available from the NASA Antarctic Meteorite Collection. This work was supported by the Austrian Academy of Sciences and the Austrian FWF.

References:[1] Nazarov M.A. et al. (1998) *LPSC XXIV*, #1628; [2] Nazarov M.A. et al. (1999) *LPSC XXX*, #1260. [3] Nazarov M.A. et al. (2000) *LPSC XXXI*, #1662. [4] Nazarov M.A. et al. (2000) *MAPS*, **35,** A117. [5] Grady M.M. et al. (1986), *11th NIPR Symp. Ant. Met.* 134-136

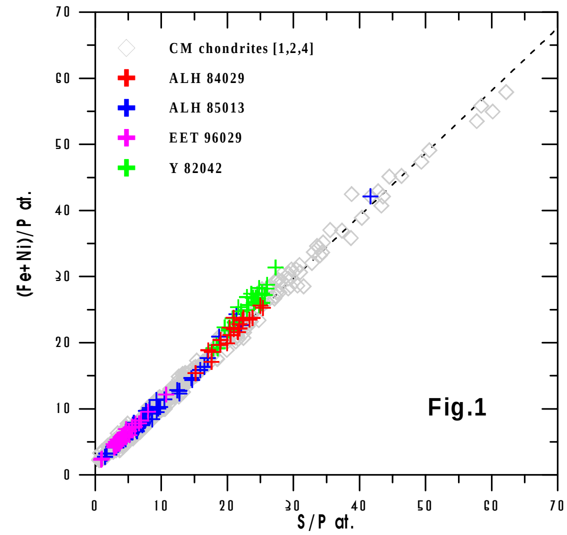

Fig.1

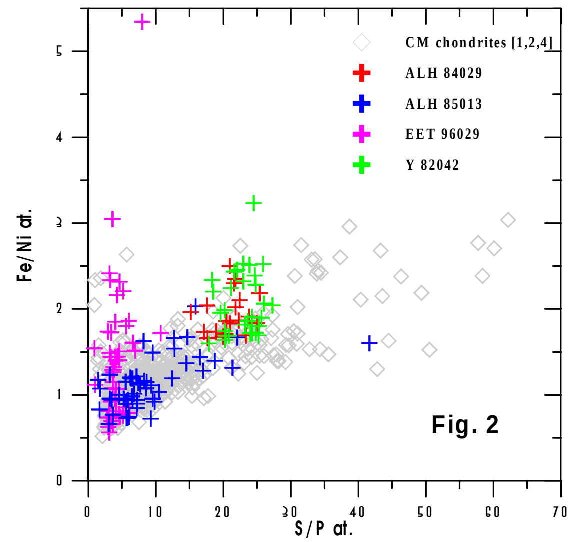

Fig. 2

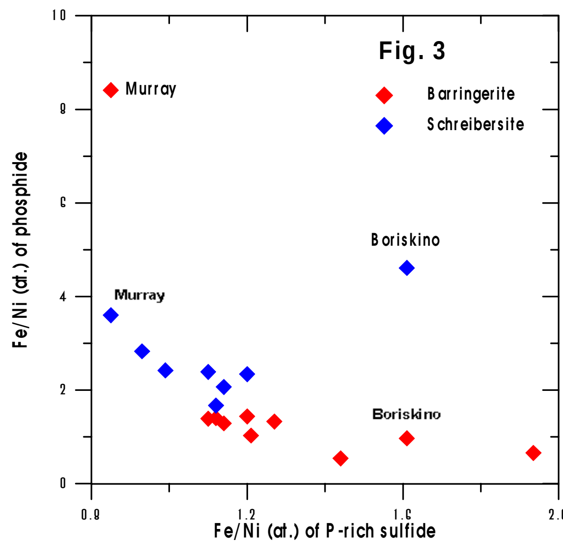

Fig. 3