

P-RICH SULFIDE, BARRINGERITE, AND OTHER PHASES IN CARBONACEOUS CLASTS OF THE EREVAN HOWARDITE. M. A. Nazarov, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow 117975, Russia, F. Brandstätter and G. Kurat, Naturhistorisches Museum, Postfach 417, A-1014, Vienna, Austria

A Fe,Ni,Cr-bearing sulfide (Q-sulfide) was inferred to be the major carrier of carbonaceous chondrite fission xenon that may have originated by the decay of an extinct superheavy element [1]. The nature of the phase has not been identified but it has been suggested from mineralogical studies that pentlandite [2] or a Fe,Ni,Cr,P-sulfide [3] could be the Q-phase. Such a Fe,Ni,Cr,P-sulfide was found in Murchison, Murray, and carbonaceous clasts of the Jodzie howardite [3,4]. A similar but Cr-poor sulfide was identified by us in carbonaceous xenoliths from the Erevan howardite [5]. Here we report on the occurrence and chemistry of this phase in the Erevan howardite. The P-rich sulfide is associated with a high-temperature lithology consisting of forsterite, barringerite and a Cr-oxide. The P-rich sulfide most likely formed by condensation from the solar nebula gas. Condensation took place after CAIs formed but before forsterite and metal condensed. Our studies indicate that the P-rich sulfide is probably the first sulfide to form in the solar nebula. This is probably why it could be the main carrier of the anomalous xenon component.

OCCURRENCE. P-rich sulfide is a characteristic accessory phase of CM carbonaceous xenoliths in the Erevan howardite. Usually the grains are very small ($< 10 \mu\text{m}$ in size) and heavily altered. In reflected light the sulfide resembles troilite but it is slightly darker and probably isotropic. Commonly the P-rich sulfide is associated with high-temperature minerals and is enveloped by accretionary dust mantles [6]. Fig. 1 shows the phase relationship in one of the lithologies. The P-rich sulfide (light gray) occurs in the center of a large accretionary object where it is accompanied by barringerite (white), forsterite (dark gray), and minute grains of Cr-oxide (gray). The phyllo silicate matrix (gray) is rich in Ni and Cr. One forsterite contains a metal nugget (bright; 10% Ni; 1.7% P) and, perhaps, a silica inclusion. The whole object is surrounded by a normal accretionary dust mantle containing rare forsterite grains. There is no reaction zone between the barringerite and P-rich sulfide grains. A barringerite grain (Fig.2) found in another clast is not associated with P-rich sulfide. This grain is slightly enriched in S at the margins and rimmed by an unusual Fe,S-oxide. Occasionally, P-rich sulfide grains are present as clasts (up to $100 \mu\text{m}$) outside of the accretionary dust aggregates in the matrix of the carbonaceous clasts. The grains are never associated with pentlandite or pyrrhotite which are characteristic sulfides of CM matrices. Commonly these grains are enveloped or completely replaced by a P-rich tochilinite-like phase.

CHEMISTRY. All phases and matrices were analyzed with an analytical scanning electron microscope (ASEM) and with an electron microprobe (EMP). The results are given in the Table. We analyzed 13 P-rich sulfide grains from 4 different clasts by ASEM. However, only 3 of them could be analyzed with the EMP (Table). The compositions of these grains are similar and comparable to that of pentlandite, except for the P content. Characteristic minor elements are Cr, Na, and K. The sulfide has a low total which suggests the presence of oxygen and hydrogen. When compared to the P-rich sulfide described by [3,4] from Murchison, Murray and the Jodzie CM clasts, the Erevan P-rich sulfide is much poorer in Cr and contains Na. The atomic proportions of the main elements are $(\text{Fe,Ni,Co,Cr,Na,K})_{9.36}\text{S}_{7.20}\text{P}$. The alteration products of the P-rich sulfide are similar in composition to tochilinite. In contrast to ordinary tochilinite this one is always enriched in Na, Cr, Ni, and P and depleted in Fe, S, and Al (Table).

The Cr-oxide grains associated with the sulfide (Fig. 1) are too small for a precise analysis. However, they contain more than 75% Cr_2O_3 , a few percents of Mn, and are Al-free. Possibly the oxide could be esclaite. The barringerite described here is the first one found in a chondrite. The rare higher phosphide was reported previously only from the Ollague pallasite [7], the lunar meteorite Y-793274 [8], and a Cu-Ni deposit in China [9]. The Erevan barringerite is similar in composition to that from the Ollague pallasite but it has a higher Ni/Fe ratio and contains S and Na (Table). The Fe,S-oxide rimming an isolated barringerite grain (Fig. 2) could be a new tochilinite-like phase with a composition of $3[(\text{Fe,Ni})(\text{OH})_2]*\text{FeS}$. The associated forsterite (Fa 1.2) is rich in MnO (up to 0.8 wt. %) and Cr_2O_3 and poor in CaO in contrast to isolated forsterites in matrices of the other clasts which are commonly poor in MnO and rich in CaO. The phyllo-silicate matrix enveloping the sulfide - barringerite - forsterite aggregate is exceptionally rich in Cr, S and Ni (Table) and poor in Ca.

DISCUSSION. The existence of a P-rich sulfide appears to be extraordinary from the geochemical standpoint because P is known to be either a siderophile or lithophile element without any chalcophilic

SULFIDE, BARRINGERITE FROM EREVAN: Narazrov M.H. et al.

tendency. However, it is also known [10] that S can replace O in the $(\text{PO}_4)^{3-}$ ion to give phosphorothioate compounds (e.g., Na_3PS_4 , Cu_3PS_4). Such compounds and other thio-salts commonly contain alkalis and Cr, similar to the P-rich sulfide from the Erevan howardite. Hence, it is possible that the sulfide contains $\text{P}(\text{S},\text{O})_4$ tetrahedra. On the other hand, the sulfide could also accommodate $(\text{PH}_4)^+$ ions which could replace alkalis. On the basis of the EMP data it is difficult to constrain the nature of the P-rich sulfide. Because it is probably isotropic and has a pentlandite-like chemistry with a Fe/Ni ratio closed to 1, which stabilizes the pentlandite structure [11], it is possible that the sulfide is related to pentlandite. In this case its formula could be written as $(\text{Fe},\text{Ni},\text{Co})_8(\text{Fe},\text{Ni},\text{PH}_4,\text{Cr},\text{Na},\text{K})(\text{S},\text{O})_8$ which is similar to Ag-pentlandite [12] with the octahedral sites occupied at least partly by $(\text{PH}_4)^+$ ions.

Thus, from the chemical standpoint the P-rich sulfide is not a forbidden compound and its existence in nature only points to certain formation conditions. The P-rich sulfide assemblage consists mainly of moderately volatile elements. This suggests that the assemblage was formed from the solar nebula gas after the refractory phases had condensed. If the accretionary texture does reflect a sequence of condensation, then we have to conclude that the sulfide was precipitated before barringerite and forsterite, and together with Cr-oxide, indicating a relatively high oxygen fugacity during sulfide precipitation. The lack of any sulfide reaction rims around barringerite excludes the possibility of forming the P-sulfide via sulfurization of barringerite. Thus, both the P-rich sulfide and the barringerite should be considered being direct nebular condensates under certain conditions which allowed them to escape equilibrium with earliest Ca-rich silicates and the later formed metal and sulfide phases. Actually, the P-rich sulfide could be the earliest sulfide phase in the solar nebula under normal oxidizing conditions and, therefore, it could be a carrier for the anomalous xenon component [1]. It is also important that the P-Fe-Ni-Cr-S assemblage could be a certain nebular component similar to CAIs. If modified by subsequent processes, the assemblage could be a parent for chromite-rich objects in ordinary chondrites [13], pentlandite-merrillite assemblages in Allende matrix [14], and troilite-chromite-phosphate inclusions in some irons [e.g., 15].

ACKNOWLEDGEMENTS. MAN was supported by the Russian Research Foundation (Project 93-05-9222). Support by the Austrian FWF (Project P 8125-GEO) is gratefully acknowledged.

REFERENCES. [1] Lewis R. S. et al. (1975) *Science*, 190, 1251. [2] Kerridge J. F. et al. (1979) *EPSL*, 43, 1. [3] Bunch T. E. and Chang S. (1980) *GCA*, 44, 1543. [4] Bunch T. E. et al. (1979) *GCA*, 43, 1727. [5] Nazarov M. A. et al. (1993) *LPSC*, XXIV, 1053. [6] Bunch T. E. and Chang S. (1984) *LPSC*, XV, 100. [7] Buseck P. R. (1969) *Science*, 165, 169. [8] Brandstätter F. et al. (1991) *GCA*, 55, 1173. [9] Chen K. et al. (1984) *Mineral. Abstr.*, 35, 1871. [10] Wells A. F. (1962) *Structural Inorganic Chemistry*, 3d edition. Oxford, 1055 pp. [11] Prewitt C. T. and Rajamani V. (1974) In "Sulfide Mineralogy", V.1, PR-1-41. [12] Wuensch B. J. (1974) *ibid.*, W-21-43. [13] Krot A. et al. (1993) *EPSL*, 119, 569. [14] Rubin A. E. et al. (1984) *LPSC XV*, 699. [15] Olsen E. and Fredriksson K. (1966) *GCA*, 30, 459.

Table:

Chemical compositions of some phases and matrices
(EMP analyses in wt.%)

	1	2	3	4	5	6	7	8
Na	0.92	0.71	1.42	0.32	0.15	0.40	0.06	0.09
Mg	0.16	0.12	0.12	0.15	0.05	3.3	9.1	11.5
Al	-	<0.02	-	-	-	0.34	1.10	1.07
Si	0.18	0.05	0.18	0.20	0.14	1.29	15.3	13.5
P	3.7	4.0	3.7	20.1	22.0	1.59	-	-
S	29.3	28.5	27.0	1.82	0.11	19.1	3.2	1.56
K	0.36	0.46	0.22	0.04	<0.02	0.05	<0.02	<0.02
Ca	0.08	0.09	0.30	<0.02	<0.02	0.60	0.29	1.24
Ti	-	<0.02	-	-	-	0.13	0.07	0.05
Cr	0.27	0.32	1.68	0.42	0.13	1.65	1.10	0.38
Mn	-	0.06	-	-	-	0.15	0.29	0.15
Fe	36.1	32.4	28.8	36.1	49.1	42.9	22.6	19.8
Co	0.67	1.77	2.30	0.13	0.06	0.40	-	-
Ni	24.2	28.1	30.6	39.4	29.2	10.4	3.2	1.11
Sum	95.94	96.58	96.37	98.68	100.94	82.30	56.31	50.45

1-3 - P-rich sulfide; 4,5 - barringerite; 6 - P-rich tochilinite;
7 - Cr-rich matrix; 8 - normal matrix.



↑ Figure 1 ↓ Figure 2

