TRACE ELEMENT PATTERNS OF PHOSPHORIAN SULFIDES FROM THE COLD BOKKELVELD (CM) CHONDRITE.

M.A. Nazarov[1], M. Chaussidon[2] and G. Kurat[3]. [1]Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, 117975, Russia (nazarov@geokhi.ru), [2] CRPG-CNRS, BP20, 54501 Vandoeuvre les Nancy, Cedex, France, [3]Naturhistorisches Museum, Postfach 417, A-1014 Vienna, Austria.

Introduction: Phosphorian Fe,Ni-sulfides (P-rich sulfides) are characteristic accessory phases in CM chondrites [e.g.,1,2]. First trace element studies [3] have shown that the sulfide appears to be enriched in s-process elements and, therefore, could be of interstellar origin or at least have a pre-solar precursor. In this paper we report new trace element data for these sulfides from the Cold Bokkelveld (CM) chondrite as obtained by SIMS. The results confirm that phosphorian sulfides have a pre-solar trace element signature and could have originated in the reduced environment of carbon star envelopes.

Results: Trace elements were measured in four P-rich sulfide grains of the Cold Bokkelveld (CM) chondrite. All grains are associated with high-temperature forsterite-enstatite aggregates enveloped by accretionary dust mantles. Grains #9 and #10 are from the same aggregate, whereas grains #A and #17 are from two other objects. Grain #A is a simple P-rich sulfide, whereas grains #9, #10 and #17 represent Cr-rich members of the solid solution series [e.g., 1,2] The latter grains were very small and their analyses show a contamination from the surrounding silicates. Therefore, the data obtained were recalculated assuming 10 wt% of SiO_2 in the spots which were analyzed. For distinguishing pre-solar trace element signatures in the P-rich sulfide grains we consider only the abundances of s-process elements (Sr, Y, Nb, Ba, La, Ce and Nd) as compared to those of Ca, Sc, Ti and V, which should not be enriched relative to solar values. This approach has been used to identify possible sources of SiC grains in meteorites [4,5].

The measured trace element patterns are shown in Figs.1-3 and exhibit certain differences. The **grain #A** is highly enriched in Sr and Ba as compared to CI abundances (Fig.1). There is also some enrichment in V, Y, Zr and REEs, whereas Ca, Sc and Ti have practically chondritic abundances. The pattern is almost parallel to that measured for a P-rich sulfide from a carbonaceous clast found in the Erevan howardite (Fig.1) [3]. The **grains #9 and #10** have similar trace element patterns (Fig.2). They are slightly depleted in Ca, Sc and Ti, and slightly enriched in Nb, Ba and REEs relatively to their chondritic abundances. The **grain #17** (Fig.3) reveals a pattern which is complementary to that of the grain #A. In this pattern Ba and Sr are strongly depleted, whereas Y, Zr and La are distinctly enriched. Other elements are present in approximately chondritic proportions.

Discussion: It appears likely [3] that P-rich sulfides are of nebular origin and were formed by sulfurization of Fe,Ni carbides condensed under reduced conditions. Condensation calculations for such conditions [4] suggest that Ti, Nb, Zr and V carbides will condense first followed by SiC and then by sulfides of Y, Sc, REEs, Ca, Ba and Sr. Iron carbides condense after SiC and prior to the sulfides. The Fe carbides may incorporate volatiles and may dissolve refractory elements, if refractory carbide grains were removed from a gas before Fe-carbides have condensed. A trace element pattern of P-rich sulfides depends, therefore, on initial element abundances in a source gas, the gas/solid partitioning and the gas/solid fractionation during condensation and sulfurization. As a first approximation we can suggest that gas/solid partitioning is the same for the elements. This assumption appears to be correct at least for elements which form ions of the same valency (e.g., Ti and Zr, Y and Sc, Ca, Sr and Ba). If so, the ratios of elements of a similar volatility, such as Zr/Ti, Y/Sc, Ba/Ca, Sr/Ca should reflect s-process element enrichment of an initial gas, whereas the ratios of elements of a different volatility should indicate gas/solid fractionation during condensation and sulfurization.

Grain #A has distinctly elevated Sr/Ca, Ba/Ca, Zr/Ti and Y/Sc ratios as compared to those in CI chondrites (Fig.1). It means that grain #A was formed from a gas of non-solar composition which was 3-50 times enriched in s-process elements. The elemental abundance pattern of this grain suggests also that high temperature condensates of Ti, Zr, etc, were removed before formation of the P-rich sulfide, which incorporated only Ba and Sr, thus producing a relative enrichment of these elements over the more refractory elements. The pattern is very similar to that calculated for class II SiC grains condensed at 1250 K [4] (Fig.1). **Grains #9 and #10** do not show a significant s-process element enrichment. The s-process element concentrations are only 3-4 times higher than their solar abundances (Fig.2). Heavy s-process elements appear to be more enriched than the light ones. Removal of refractory condensates from the gas before formation of these grains could explain the prominent Ba enrichment. The trace element pattern of the grains matches satisfactorily that calculated for class IV SiC grains condensed between 1250 K and 1300 K (Fig.2) [4]. **Grain #17** exhibits also a low enrichment in s-process elements, 2-3 times over other refractory elements, as can be inferred from Ti/Zr and Y/Sc ratios (Fig.3). The low Zr/Y ratio suggests that refractory elements were removed from the gas before this grain was formed. In addition, the Ba and Sr depletion with respect to the other elements indicates that the grain was removed from the gas before the volatile elements condensed. A similar trace element pattern to that of grain #17 was calculated for class III SiC grains condensed between 1250 K and 1300 K (Fig.3) [4].

In summary, this study confirms the previously reached conclusion that P-rich sulfides could be of extrasolar origin or at least preserve some trace element signature of non-solar nucleogenetic processes. Sulfides occurring in different aggregates have different trace element patterns and thus likely represent condensate samples from different loci and different times of an evolving stellar atmosphere. The patterns are similar to those of different classes of SiC grains which are believed to originate from different types of carbon stars [4,5]. This suggests that the P-rich sulfides could also be related to different stars. Careful isotopic studies of P-rich sulfides need to be carried out to confirm the hypothesis.

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