MINOR AND TRACE ELEMENTS IN SULFIDES IN REDUCED AND OXIDIZED CV3 CARBONACEOUS CHONDRITES: POTENTIAL RECORDERS OF NEBULAR AND PARENT BODY PROCESSES Crystal Donnelly and Adrian J. Brearley, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (e-mail: crystald@unm.edu, brearley@unm.edu).

Introduction: Of all the carbonaceous chondrite groups, the CV carbonaceous chondrites are probably the most complex. They contain a record of a wide range of early solar system processes, some of which occurred in the solar nebula and others within an asteroidal parent body. Two major groups of the CV chondrites were recognized by [1], called reduced and oxidized, based on the abundance of oxidized vs reduced Fe. More recently, [2] showed that the oxidized group can be divided into two subgroups, the Bali-like ($CV3_{oxB}$) and the Allende-like ($CV3_{oxA}$). The Bali-like subgroup has experienced extensive aqueous alteration whereas the Allende-like subgroup is dominated by secondary fayalitic olivine, nepheline and sodalite; phyllosilicates are rare. The environment where secondary alteration of these meteorites occurred is currently the subject of debate and both nebular and parent body environments have been proposed, e.g. [3], but a number of question still remain unresolved.

Although the mineralogy of CV3 chondrites is well documented, the behavior of sulfides has received remarkably little attention. Although [1] described the general sulfide mineralogy in CV3 chondrites, no systematic studies of the mineralogy and chemistry of sulfides have been undertaken, although several authors have reported electron microprobe data for sulfides in oxidized CV chondrites [1,4-7].

We have commenced a study of sulfide assemblages in the CV3 chondrites Leoville, Vigarano and Allende, spanning the range from reduced to oxidized CV3 chondrites. Vigarano is a breccia that consists of both reduced and partially oxidized material [1]. Our goal is to try and understand how sulfides in the reduced and oxidized CV chondrites differ and what these differences may tell us about the cosmochemical evolution of the two subgroups. We are especially interested in examining the minor and trace element chemistry of sulfides and how these elements may be redistributed during secondary alteration processes. The sulfides are of special importance for understanding the behavior of a number of moderately volatile elements that have chalcophile affinities and may be sensitive to thermal processing either in the nebular or on an asteroidal parent body. Our preliminary investigations have focused on petrographic characterization of different sulfide occurrences in these meteorites, building on the work on Allende by [7]. In addition, we have carried out preliminary minor and trace element analyses of sulfide minerals by electron microprobe. These studies will be followed shortly by more sensitive trace element analysis by synchrotron X-ray fluorescence microprobe (SXRF) at the National Synchrotron Light Source, Brookhaven National Laboratory. The SXRF analyses have higher sensitivity than our microprobe analyses and will allow us a cross comparison between the two techniques.

Electron microprobe analyses for minor and trace element analyses have been carried out using a JEOL 8200 electron microprobe. This instrument is equipped with 5 WDS spectrometers, including 2 high intensity spectrometers and third spectrometer with a single large area single TAP crystal. These three spectrometers achieve count rates that are 6 x higher than conventional spectrometers and are highly suited to trace element analysis. The following suite of elements was investigated: S, Fe, Cr, Ni, Co, Cu, As, Zn, Se, P and Ti, with peak counting times of up to 60 seconds for trace elements. With the exception of Se, all analyzed minor and trace elements were detectable in the sulfides. In this work, we have only determined the chemistry of the sulfides, but we also plan to examine the compositions of coexisting metallic phases as well. All the results presented below were obtained during the same extended analysis session using the same calibration and therefore should be free of errors produced from different calibrations. Although the absolute concentrations of the elements reported below need to be confirmed by SXRF analysis, the relative concentrations of the elements can be used with confidence.

General occurrence of sulfides in CV3 chondrites. One goal of our study is to understand whether different occurrences of sulfides in CV3 chondrites show systematic differences in trace element compositions that might reflect their formational history. Sulfides have many different, distinct textural occurrences in CV3 chondrites, which we simplify as follows. 1) Sulfides in chondrules (opaque nodules), 2) sulfides-rich rims around chondrules, 3) dense sulfide-bearing nodules outside chondrules 4) porous sulfide aggregates in matrices, 5) small isolated sulfide grains in the matrices. In this study, we analyzed sulfide grains in all of these different occurrences. However, in the following discussion, we focus on the general minor and trace element chemistry of sulfides in the three different meteorites, without considering the textural setting of individual sulfide mineral phases.

Vigarano and Leoville both have very simple sulfide mineral assemblages Troilite is the only phase present and is stoichiometric. In Vigarano, McSween [1] reported one high-Ni sulfide analysis out of 15, but out of 60 sulfide analyses, we did not find any Ni-rich sulfides. Allende contains both troilite and pentlandite that contains variable Ni contents. [4] reported a range of Ni contents in pentlandite from 17-23 wt% and [7] reported 16-24 wt% Ni. Our new data (16-22 wt% Ni) are consistent with these ranges.

Minor and trace element compositions The minor and trace element data for the sulfides in these three meteorites reveal some interesting behavior. The Ni contents of low Ni sulfides are somewhat different. Ni contents in Allende and Vigarano are very similar (<0.20 wt% to below detection limits), whereas Ni in Leoville is more variable and extends up to about 0.8 wt%. As reported by [4,7], pentlandite in Allende contains significant concentrations of Co, ranging from 0.8-1.5 wt%. Our new data indicate somewhat lower concentrations from 0.5 -1.0 wt%, but this could be a reflection of a more limited sample population in this study. In a previous study, we observed that Ni and Co contents of pentlandites showed a positive correlation. However, this correlation is not so obvious in our new data set, but there is an indication that there may be two separate positive trends. Additional data are needed to comfirm this suggestion. In comparison with the Allende pentlandite, troilite in all three meteorites contains much lower concentrations of Co (<0.12 wt%). However, there are notable differences between the three meteorites. Vigarano has Co concentrations ranging from 200 ppm to below detection limits (38 ppm), whereas Allende and Leoville have Co concentrations that are significantly higher (900-1200 ppm). The ranges in both meteorites overlap exactly, but there is no overlap at all with the Vigarano data, which appears to be completely distinct.

The preferential incorporation of Co into pentlandite in Allende is mirrored by the behavior of Cu. Co and Cu are not correlated in pentlandite, but Cu is consistently present in higher concentrations than in troilite. Pentlandite Cu concentrations vary from just above detection limits to ~2000 ppm. In pyrrhotite and troilite in all three meteorites, Cu concentrations are an order of magnitude lower ranging from below detection limits (32 ppm) to 200 ppm.

The data for As and Zn are complex and indicate considerable variation in the concentrations of these elements. In Allende, Zn is below detection limits (44 ppm) in all but a few grains with concentrations that range up to ~150 ppm. The behavior of Zn in Leoville is very similar – few grains contain any detectable Zn. On the other hand, Vigarano contains a significantly higher population of sulfide grains with detectable Zn, ranging up to 200 ppm although most are <100 ppm. A plot of As vs Zn concentrations for all three meteorites shows an unusual behavior that requires more sensitive SXRF analyses to resolve. Zinc and As are present in detectable concentrations in some grains, but both elements are rarely present in the same grain. Grains with detectable Zn contain no As and visa versa. As a general observation, As is highly variable (up to 600 ppm), but is present in detectable concentrations in sulfides in more grains in Leoville and Allende than Vigarano. The reverse is true for Zn, which is much more common in sulfides in Vigarano.

Chromium data for sulfides show very different behavior in all three meteorites studied. Our data suggest that Cr is distributed very heterogeneously in sulfides in these three meteorites. Most sulfide grains contain Cr at concentrations below the detection limits of electron microprobe. This is particularly true of the Leoville data, where very few grains contain any detectable Cr. Vigarano and Allende contain a significant number of grains with concentrations that range up to as high as 0.9 wt%, but most grains contain <0.2 wt% Cr. The Vigarano data may be bimodal, with several analyses that have ~0.7 wt% Cr. In Allende, there are no obvious differences in the Cr content between pentlandite and low-Ni sulfides.

Discussion. Our electron microprobe data show that distributions of trace elements in these three CV chondrites are all somewhat different and are complex. Of particular interest is the contribution that trace elements in these phases make to the overall trace element inventory of the bulk chondrite. Compared with bulk CV chondrites, we observe the following behavior. Low-Ni sulfides in all three meteorites have concentrations of Cu that are close to 1 x bulk CV values (104 ppm) or less. In rare cases, grains with enrichments of 2 x CV values are present. Cu is clearly not behaving as a chalcophile element in these chondrites and is probably present within Fe,Nimetal. Zn shows even less chalcophile behavior, being present at 1 x CV values or less in Vigarano low-Ni sulfides. In both Leoville and Allende, low-Ni sulfides rarely contain Zn at concentrations above the detection limit of 44 ppm, indicating that Zn is highly depleted in sulfides in these two meteorites, relative to bulk CV values. Arsenic on the other hand does appear to be strongly enriched in at least some sulfide grains. The extent of this enrichment cannot be accurately assessed because our detection limits for As are relatively poor (240 ppm). Any grains with detectable As therefore have an enrichment compared with CV values (1.6 ppm) of at least 160 X ranging up to close to 400 x CV.

A key question is exactly what processes the sulfide trace elements record. Fine-grained sulfides are widely known to be susceptible to recrystallization during thermal metamorphism [9]. However, the effects of metamorphism on coarser-grained sulfide minerals is unknown. According to [10], Leoville and Vigarano are petrologic type 3.1-3.4 chondrites and Allende is a type 3.6. As well as being metamorphosed, Allende has also undergone extensive oxidation. Our data for Leoville and Vigarano indicate that if thermal metamorphism has affected the sulfides, it has not completely equilibrated the trace elements. The moderately volatile elements, Cu and As exemplify this behavior. Although most grains contain Cu and As concentrations below the detection limits of the electron microprobe, a significant number of grains contain quite variable concentrations of these elements. These data indicate that some sulfide grains have not undergone metamorphic equilibration. We are currently investigating if there is anything notable about the grains with elevated As and Cu abundances in terms of their size and/or petrographic occurrence. Although EPMA has provided some useful preliminary insights into the behavior of several elements, our planned SXRF studies will provide further constraints on the detailed trace element distributions of elements such as As, Se, Ga and Ge. These data will be essential for differentiating between primary nebular signatures vs metamorphic overprints.

References: [1] McSween, H.Y. (1977) *GCA* **41**, 1777. [2] Krot, A.N. et al. (1998) MAPS **33**, 1065. [3] Krot, A.N. et al. (1995) *Meteoritics* **30**, 748. [4] Haggerty, S and McMahon, (1979) *PLPSC* **10**, 851-870. [5] Rubin, A.E. (1991) *Am. Min.* **76**, 1356. [6] Cohen, R.E. et al. (1983) *GCA* **47**, 1739. [7] Wetteland, C. and Brearley, A.J. (2002) *LPS* 33, 1837. [8] Bonal et al. (2006) GCA [9] Grossman, J.N. and Brearley (2005) MAPS **40**, 87. [10] Bonal, L. (2006) *GCA* **70**, 1849
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