

SIMS ANALYSIS OF MODERATELY LITHOPHILE ELEMENTS IN CR AND CB CHONDRITE METAL — CHARACTERISTIC PROPERTIES OF PRISTINE AND PROCESSED METAL. T. W. Schoenbeck, H. Palme, *University of Cologne, Zuelpicher Str. 49b, 50674 Koeln, Germany (thorbjoern.schoenbeck@uni-koeln.de)*, G. R. Huss, *Department of Geological Sciences, Arizona State University, Box 871404, Tempe, AZ 85287-1404, USA*.

Introduction CR and CB chondrites are unusual carbonaceous chondrites because of their high contents of FeNi metal grains. The origin of metal in these meteorites is still a matter of debate. Several authors claimed that all metals in CR chondrites are processed, either by metal-silicate equilibration during formation of chondrules [1], by reduction of FeO-rich silicates [2,3] and/or evaporation and recondensation [4,5] or by desulphurization of troilite [6]. On the other hand it has been proposed that at least some metal grains in CH and CB chondrites formed by condensation in a gas of solar composition and have preserved primary compositional characteristics [7,8,9]. The positive correlation of Ni with Co observed in many metal grains in CR, CH and CB chondrites is predicted by condensation calculations. Unfortunately, equilibration of metal with silicate melt at various temperatures or oxygen fugacities during chondrule formation is also capable of producing positive Ni-Co correlations [10]. Thus, further distinguishing features are needed to establish the origin of these metals.

Direct evidence for a condensation origin is provided by the occurrence of zoned metal grains in CH and CB chondrites [8,9]. The most likely explanation for the observed trace element zoning patterns is condensation in a gas of solar composition. Meibom et al. [8] concluded that metal in CH chondrites condensed at a total pressure of about 10^{-4} bar and solar oxygen fugacity. The pressure during condensation was deduced using the Si content of metal as pressure indicator. High total pressures lead to high Si concentrations in metal whereas low pressures lead to lower contents [11,12]. This is primarily the result of higher condensation temperatures at higher total pressures.

Recently we applied this method to constrain the total pressure during condensation of zoned metal grains in the CB-chondrite HaH 237. Electron microprobe analyses of Si in zoned metal grains of HaH 237 were found to be below the detection limit of 60 ppm [12] in almost all metal grains, implying that some metal grains in CB chondrites formed under different conditions than metal in CH chondrites.

To better constrain the conditions of formation of zoned metal grains in HaH 237, we used secondary ion mass spectrometry to determine the concentration of Si and other lithophile trace elements (Cr, V, Mn) in zoned and unzoned metal grains of HaH 237.

In contrast to CH and CB metal CR chondrites do not contain zoned metal grains. Many of the metal grains in CR chondrites occur inside chondrules and it is likely that they were at least partially equilibrated with silicates during chondrule formation. To determine the degree of equilibration we analyzed metal grains in chondrules of Acfer 209 (CR chondrite) to see if we are able to distinguish condensed metal from metal processed during chondrule formation [13]. In addition we address the question whether metal in chondrules

	Cr	Si	Mn	V
HaH 237 zoned grains (46 analyses)				
Avg:	1710	34.5	1.1	4.4
Min:	1165	7.1	0.7	1.1
Max:	4170	115	2.2	26.1
HaH 237 unzoned grains (30 analyses)				
Avg	2590	250	7.0	22.5
Min:	1290	12	0.8	1.3
Max:	5125	2930	32.4	77.5
Acfer 209 (71 analyses)				
Avg	3365	680	44	17.0
Min:	536	30	4.3	3.9
Max:	15310	5220	661	83.0

Table 1: Results from SIMS analysis (all data in ppm). Concentration ranges obtained by electron microprobe for Fe, Co, Ni and P can be found in [12] (HaH 237) and [13] (Acfer 209).

suffered complete re-equilibration or whether it kept compositional characteristics from primary formation.

Methods Trace element analyses were performed on 20 different zoned and unzoned metal grains in HaH 237 and 15 different chondrule metal grains in Acfer 209. Metal grains were selected from prior SEM studies. Electron microprobe analyses were performed to obtain Fe, Co, Ni, Cr, P and Si concentrations. To precisely determine Si concentrations in CB metal grains we used a high current of $2 \mu\text{A}$ and a counting time of about 150 seconds. SIMS analysis was performed using the Arizona State University Cameca ims-6f ion microprobe to confirm the electron microprobe results and to analyze additional isotopes: ^{12}C , ^{27}Al , ^{28}Si , ^{31}P , ^{51}V , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni . A primary O^- beam with 12.5 kV acceleration voltage and 10 – 20 nA probe current lead to a spot size of 10 – 40 μm . The mass resolution was set to 4400, without energy filtering. Measurement time was 20 minutes with 10 minutes presputter. For calibration, a set of 6 different certified steel alloys was used. The reference element for internal standardization was Fe, taken from subsequent electron microprobe analysis.

Results The SIMS results for high concentrations of Ni, Co, Cr, P and Si agree well with our previous electron microprobe analysis, indicating that the SIMS measurement setup is capable to measure trace elements in metal with sufficient precision and accuracy.

HaH 237: Si in zoned metal grains in HaH 237 is in most cases below 100 ppm, confirming our previous findings. Vanadium ranges between 1 ppm and 30 ppm in zoned and 1 and 77 ppm in unzoned metal grains. Mn in zoned metal grains is 1 ppm, and 7 ppm in unzoned grains.

Acfer 209: Si in chondrule metal shows large variations between 30 and 5000 ppm from grain to grain. In some analyses this heterogeneity is even visible in the isotope ratios during the sputtering process on one single spot. During the run the count rates of all isotopes remain constant except for Si which varies within an order of magnitude. Mn in chondrule metal is higher than in HaH 237 with an average of 44 ppm, ranging from 4 to 600 ppm. V in chondrule metal is between 4 ppm and 80 ppm.

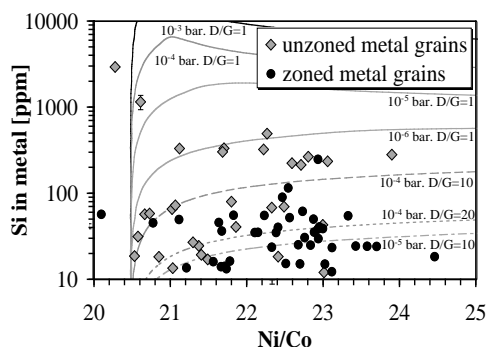


Figure 1: Ni/Co and Si content of zoned and unzoned metal grains in HaH 237. Lines in the diagram indicate calculated concentrations for condensation at different total pressures and oxygen fugacities. Details of the calculation are given in [12].

Discussion: *HaH 237:* There is little doubt that the zoning patterns in CH and CB metal were established during condensation. A comparison of metal analyses with condensation calculations is shown in Figure 1. Low pressures during condensation imply low temperatures and lead to low Si concentrations in metal. At low pressures however, growth by condensation becomes so sluggish that diffusion will erase zoning patterns [9]. The lowest pressure to maintain zoning is about 10^{-6} bar. Hence the low Si concentrations require more oxidizing conditions, i.e. higher than solar oxygen fugacities. Significant amounts of moderately lithophile elements such as Cr and P provide an upper limit to the oxygen fugacity.

The low V contents of the zoned metal grains (Figure 2) are unexpected, as V is more refractory than Cr. We assume that V condensed primarily in oxides and/or silicates before condensation of zoned metal grains. This condensation sequence is in agreement with the low pressure, postulated above.

Zoned metal grains comprising about 10 vol% of metal in HaH 237 are clearly distinguished from unzoned metals with higher V contents and a well resolved correlation of V with Cr (Figure 2). This correlation is probably the result of metal-silicate equilibration. Condensation produces an anti-correlation of V and Cr, reflecting their different volatilities.

Acfer 209: In contrast to zoned metal grains in HaH 237, metal in CR chondrites does not show pronounced zon-

ing patterns. Since most analyzed metal grains are located within chondrules, it is reasonable to assume that these metal grains were involved in a metal-silicate equilibration during chondrule formation. Further evidence for (re)equilibration is given by a significant positive correlation of V and Cr (Figure 2), and of Co and Cr. This is similar to *unzoned* metals in HaH 237, but different from *zoned* metal in HaH 237, where these elements are weakly negatively correlated. A clear exception to these positive correlations among oxidizable elements is Si. With temperature and oxygen fugacity as the only parameters controlling the amount of Si in metal during metal-silicate equilibration, one would expect correlations between Si and Mn, V, or Cr, respectively. Si in Acfer 209 chondrule metal is extremely variable, even in single grains (Table 1 and [14]), whereas Cr and P are more homogeneous. Diffusion of Si in metal is slower than of any other moderately lithophile element studied here. The obvious explanation for this variability is partial equilibration of metal with silicates so that chondrule metal preserved some of its primary properties.

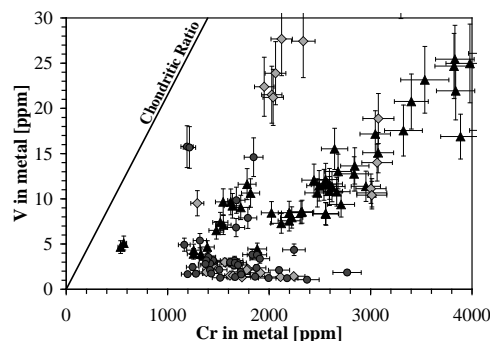


Figure 2: Cr and V concentration for metal in CB and CR chondrites. Triangles: chondrule metal in Acfer 209, circles: zoned metal grains in HaH 237, diamonds: unzoned metal in HaH 237.

References [1] Zanda B. et al. (1994) *Science* 265, 1846–1849. [2] Connolly H. C. et al. (2001) *Geochem. Cosmochem. Acta* 65/24, 4567–4588. [3] Lee M. S. et al. (1992) *Geochem. Cosmochem. Acta* 56, 2521–2533. [4] Kong P. et al. (1999) *Geochem. Cosmochem. Acta* 63, 2673 – 2652. [5] Hu-mayun M. et al. (2002) *LPSC XXXIII* #1965. [6] Zanda B. et al. (2002) *LPSC XXXIII* #1852. [7] Weisberg M. K. (1993) *Geochem. Cosmochem. Acta* 57, 1567–1586. [8] Meibom A. et al. (1999) *J. Geophys. Res.* 104, 22305–22059. [9] Campbell A. J. et al. (2001) *Geochem. Cosmochem. Acta* 65/1, 163–180. [10] Lemelle L. et al. (2001) *Am. Min.* 86, 47–54. [11] Petaev M. I. et al. (1999) *LPSC XXX* #1613. [12] Schoenbeck T. W. and Palme H. (2003) *LPSC XXXIV* #1605. [13] Schoenbeck T. W. and Palme H. (2003) *MAPS* 38 A #5233. [14] Schoenbeck T. W. and Palme H. (2004) *LPSC XXXIV* #1706.

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