

SILICON CONCENTRATIONS IN METAL GRAINS OF CB-, CH- AND CR-CHONDRITES — IMPLICATIONS FOR THEIR FORMATION. T. W. Schoenbeck, H. Palme, *University of Cologne, Institute for Mineralogy and Geochemistry, Zuelpicher Str. 49b, 50674 Koeln, Germany (thorbjoern.schoenbeck@uni-koeln.de).*

Introduction: FeNi-metals are common in ordinary and enstatite chondrites but rare or even absent in the conventional groups of carbonaceous chondrites, except in CR-chondrites. Recently identified new groups of carbonaceous chondrites, such as CH- and CB-chondrites contain, however, abundant FeNi-metal. Whereas CV-chondrites have only about 2 vol.% metal, CH-chondrites contain up to 20 vol.% and members of the CB-chondrite grouplet as much as 60 vol.% [1]. The origin of these metals is not clearly understood. Subchondritic Fe/Ni and Fe/Co ratios in CM-, CR-, CH- and CB-chondrite metals favor the formation by condensation from a gas of solar composition [2, 3, 4]. The discovery of zoned metal grains in CH- and CB-chondrites [4, 5] provides evidence supporting the condensation origin of these metals. Zanda et al. [6] have, however, argued that the composition of metals in Renazzo is indicative of metal/silicate equilibration. The concentrations of siderophile and lithophile trace elements in carbonaceous chondrite metals should ultimately allow to resolve the question of their origin. To distinguish between these two formation processes we began a systematic study of the concentration of moderately siderophile and lithophile elements in metals from metal-rich carbonaceous chondrites. These new data, primarily on Si, and earlier literature provide the basis for distinguishing among the various modes of formation.

Analytical Procedures: All metal analyses were performed with a JEOL JXA 8900RL electron microprobe equipped with five wavelength dispersive spectrometers. The concentrations were calculated from the count rates by applying the CITZAF correction method. The accuracy of the measurements was checked by monitoring CRM standards. In order to enhance the detection limit for trace elements we applied 20 kV acceleration voltage and 200 nA beam current. Standards used for the metal analyses were BAM CRM 184-1 for Cr- and Si-calibration and San Martin hexahedrite for Ni-, Fe- and Co-calibration. To determine the detection limit and the statistical error of the measurements the background of a Si- and Cr-free standard was measured and the detection limit was set to 3 σ above the background count rate. Repeated measurements of the same sample showed that the measurement error is largely influenced by calibration standard homogeneity and instrument instabilities rather than by the statistical error of the count rate. The resulting detection limit for Si is 70 ppm, the precision of the measurement is about 5 % RSD.

Results: The results of our measurements are shown in Table 1 (Only averages are listed). The highest Ni- and Co-concentrations are found in the cores of zoned metal grains from HaH 237, reflecting their condensation origin. Concentrations of Cr and P show only comparatively small variations. The main difference in metal between the metal rich chondrites and CR-chondrites is that some CR-metals have measurable amounts of Si. Neither zoned metal grains in HaH 237 nor the larger unzoned metal grains have Si contents

above the detection limit (≤ 70 ppm). The same is true for CH-metals. These data are in good agreement with earlier analyses [2, 3], confirming that Si-rich metal grains are rare in chondritic meteorites. Even most of the high temperature Murchison metals have less than 200 ppm Si [7]. The unique grain with 7300 ppm Si listed in Table 1 is an exception.

Table 1.: Composition of metal grains in Fe-rich chondrites

CB-Chondrites						
	Fe \ddagger	Ni \ddagger	Co \ddagger	Cr \ddagger	Si \ddagger	P \ddagger
Bencubbin single grain						
Ave	92.33	6.77	2770	1258	≤ 70	2978
σ	0.46	0.04	31	195		78
Gujiba n=4						
Ave	90.86	7.75	3080	2071	≤ 70	2780
σ	0.85	0.82	267	1058		446
HaH 237 — unzoned grains n=12						
Ave	91.27	7.72	3102	3841	≤ 70	3259
σ	1.35	1.19	429	607		193
HaH 237 — zoned grains n=15						
Min	84.75	3.34	1610	1112	≤ 70	400
Max	95.67	14.8	5100	2930		1520
CH-Chondrites						
Acer 207 n=6						
Ave	89.74	7.29	2926	1999	≤ 70	2164
σ	0.94	0.97	260	845		563
Murchison (CM2)						
Ave	92.32	6.82	3900	7300	1200	1300
CR-Chondrites						
Acer 209 — Si containig grains n=3						
Ave	90.98	5.67	2391	4655	350	2458
σ	0.24	0.31	118	379	187	721
Acer 209 — Si free grains n=12						
Ave	89.17	7.60	3019	3053	≤ 70	2219
σ	2.24	1.98	669	679		579
Renazzo — Si containig grains n=5						
Ave	91.97	6.59	2711	4052	242	2128
σ	0.97	0.54	196	853	185	428
Renazzo — Si free grains n=19						
Ave	92.39	6.38	2605	2604	≤ 70	2542
σ	1.66	1.26	376	990		797
Quingzhen & MAC 88136 (EH3 & EL3)						
Ave	92.7	3.57	4100	≤ 900	27200	≤ 1300
σ	0.9	0.51	300		1800	

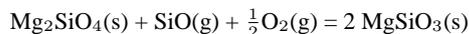
\ddagger : Wt.%, \ddagger : ppm. n: Number of analysed grains. Values for Murchison are from [2], Values for Quingzhen and MAC 88136 from [8].

Discussion: There are two possibilities for the origin of Si in meteoritic metal: (a) by condensation or (b) by metal-silicate equilibration.

(a) *Condensation.* Although the vapor pressure of Si-metal is lower than that of Fe and Ni, Si condenses as oxide, because at nebular $f(\text{O}_2)$ the fraction of Si-atoms in the nebular gas is many orders of magnitude below that of SiO. The partial pressure of Si was calculated for two regimes, (a) at

Si in CB, CH and CR-Chondrites.

temperatures above the condensation temperature of enstatite where no other Si-bearing phase is present and (b) at lower temperatures where the partial pressure of SiO is determined by the presence of forsterite and enstatite, according to the equation:



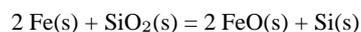
In the absence of enstatite the Si content of condensed metal increases with decreasing temperature, reaches a maximum at the condensation temperature of enstatite and drops sharply by orders of magnitude after the condensation of enstatite. The absolute Si concentration in the metal depends on the total pressure of the nebula. We calculated a maximum concentration of about 2 wt.% Si at 10^{-3} bar and 1380 K using an activity coefficient of Si in metal as given by [9], and an oxygen fugacity of the solar nebula, given by a formula from Krot et al. [10]. At 10^{-4} bar and a temperature of 1320 K we calculated 7000 ppm Si, and 2000 ppm Si at 10^{-5} bar and 1260 K, respectively. After the maximum Si content in metal is reached further cooling leads to much lower Si-concentrations. For example, the equilibrium concentration of Si at 10^{-4} bar is 7000 ppm at 1320 K and 500 ppm at 1200 K. This is in agreement with calculations from Rambaldi et al. [11].

Early condensed metals with comparatively high Ni contents formed before the onset of enstatite condensation. Thus we expect the highest Si-concentrations in Ni-rich cores of zoned metal grains. At a nebular pressure of 10^{-4} bar and a Ni content of 9.5 wt.% we calculated about 9000 ppm Si at 1330 K in the center of a zoned grain but only 150 ppm at the rim at 1150 K. However, the Si-concentration in the cores of zoned metals is in all cases below 70 ppm, although the high Ni- and Co-concentrations within the grains indicate their high-temperature origin.

One possible explanation for the lack of Si in the cores of zoned metal grains is the condensation at very low total pressures, as at low pressures metal condenses after enstatite, which leads to a depression of the SiO and Si partial pressures in the gas.

More oxidizing conditions, i.e. enhanced dust/gas ratio would also lead to a depletion of Si in the nebula, because the partial pressure of Si in the nebula is controlled by the oxygen fugacity. However, a depletion caused by dust enrichment would be accompanied by a depletion of Cr as well so that condensates from these regions should contain less Cr.

(b) *Equilibrium with silicate melts.* The Si content of metal can be calculated from the exchange reaction:



At nebular oxygen fugacity silicate melts will contain about 0.2 wt.% FeO independent of temperature, as the effects of decreasing oxygen fugacity and increasing equilibrium constant for the oxidation of Fe cancel out with decreasing temperature. Under these conditions we calculate 8000 ppm Si at 1400 K and correspondingly higher concentrations at higher temperatures, e.g. 5.1 wt.% Si in metal at 1500K.

The absence of high Si concentrations in metal excludes the silicate/metal equilibration at nebular oxygen fugacities.

At higher oxygen fugacities, i.e. higher FeO contents, maximum Si concentration of metals are lower. A chondrule melt with 2 wt.% FeO is in equilibrium with 270 ppm Si in metal at 1500 K. Thus observed Si concentration in some Renazzo metals may reflect metal/silicate equilibration. Metal grains with Si contents below the detection limit may either have formed by condensation or may have equilibrated with chondrule melts with FeO contents above 2 wt.%. The results of these calculations depend on the exact knowledge of the activity coefficient of Si in metal. We therefore have begun an experimental study to precisely determine the activity coefficients of Si in FeNi-alloy under conditions similar to solar nebula oxygen fugacities.

Summary: The origin of metal grains in carbonaceous chondrites cannot be uniquely defined on the basis of Si in metal. Ni-rich metals should have high Si-concentrations, if formed by condensation at nebular oxygen fugacity and total pressures of 10^{-4} bar. At lower total pressures and/or more oxidizing conditions Si contents of metals will be lower. At lower temperature when Fe is fully condensed, Si-concentrations of condensed metals are below the detection limit of the electron microprobe. High Si is expected at the center of zoned metal grains and low Si at the rim. The absence of Si in the center requires special conditions of formation.

Metal grains equilibrated in chondrule melts with FeO below 2 wt.% should have measurable Si contents. With higher FeO concentrations Si will strongly decrease. Metals equilibrated at high temperatures will have much higher Si contents (≥ 5 wt.% at temperatures ≥ 1500 K, solar $f(\text{O}_2)$). Thus Si contents of metal grains may be used to calculate the metal/silicate equilibration temperature. The variable Si-concentrations of metals in Renazzo type chondrites exclude the same origin of all metal grains.

For more precise calculations more accurate determinations of Si activity coefficients in FeNi-alloys are required.

References: [1] Weisberg M. K. et al. (2001) *MAPS*, 36, 401–418. [2] Grossman L. et al. (1979) *Science*, 206, 449–451. [3] Krot, A.N. et al. (2000) *MAPS*, 35, 1249–1258. [4] Meibom A. et al. (1999) *J. Geophys. Res.*, 104, 22305–22059. [5] Campbell A. J. et al. (2001) *GCA*, 65/1, 163–180. [6] Zanda B. et al. (1994) *Science*, 265, 1846–1849. [7] Grossman L. et al. (1974) *GCA*, 38, 173–187. [8] Lin Y. et al. (2002) *MAPS*, 37, 577–599. [9] Sakao H. et al. (1975) *Metal. Trans.*, A 6A, 1849–1851. [10] Krot A. N. et al. (1999) in: *Protostars and Planets IV*, Univ. of Arizona Press 1019–1054. [11] Rambaldi E. R. et al. (1980) *Nature*, 287, 817–820.