Si-rich Fe–Ni grains in highly unequilibrated chondrites

Ermanno R. Rambaldi, Derek W. Sears
& John T. Wasson*

Institute of Geophysics and Planetary Physics, and Department of Chemistry, and * Department of Earth and Space Sciences, University of California, Los Angeles, California 90024

Some Fe–Ni grains in the Bishunpur L3 chondrite have Si contents in the range 1.3–4.5 mg per g (mole fractions of 0.003–0.009); the only previous report of Si in ordinary chondrite metal is a lower limit of 0.7 mg per g for metal in the Leighton H4 chondrite[1]. The Bishunpur Si contents are 1.1–4 times that found in a large metal grain in the Murchison CM2 chondrite[2]. As whole-rock systems both meteorites have high degrees of oxidation and consist of unequilibrated, essentially unmetamorphosed mineral assemblages. Thus the Si was not introduced into the metal during metamorphic reheating, but rather during nebular condensation[2]. Grossman *et al.*[2] calculated that the Si mole fraction of 0.0024 in the Murchison grain required a total nebular pressure $\geqslant 10^{-5}$ atm, which is higher than that generally inferred for the CM formation location. We show here that improvements in the Si activity coefficients and plausible constraints on the nucleation of mafic silicate condensates allow Si mole fractions of 0.003 at nebular pressures of $<10^{-6}$ atm. Thus such chondrites could have formed over a wide range of distances from the Sun.

Bishunpur is one of the three most unequilibrated chondrites[3-5] (Krymka and Semarkona are the others), and thus best preserves the record of processes occurring in the portion of the primitive solar nebula where the ordinary chondrites formed. Our data were obtained by electron microprobe; experimental details and Bishunpur's opaque phases are reported elsewhere[6]. All observations were made on polished thin sections 2359–1, 2359–2, and 2359–3 loaned by the Smithsonian Institution. Contrary to previous suggestions[2], we did not find that fluores-cence of Si in adjacent silicates was a problem: (1) Si was below our detection limit of 0.4 mg per g in all metal grains except those listed in Table 1 and in two others having variable Si contents apparently reflecting the presence of Si-rich inclusions; (2) the problem is least where it is expected to be greatest, as regions of the Si-bearing metal that abut silicates have Si contents below our detection limit.

Figure 1 shows photomicrographs of three of our eight Si-bearing metal grains. Figure 1a, using transmitted light and partially crossed polars, shows an FeS–metal aggregate which is embedded in an olivine grain in the matrix (no. 39 in Table 1). The olivine grain, possibly a fragment of a chondrule, contains numerous opaque inclusions and it also displays undulatory extinction indicating distortion by shock. Not resolvable in this photomicrograph is a Ca–Al-rich glass having low Na and Fe concentrations. Such glass enriched in refractories is relatively common adjacent to Si-bearing metal, indicating that refractory materials are preserved within these chondrules. The large opaque inclusion is shown by reflected light in Fig. 1b. Its outer region is FeS and other minor phases and the interior is metal with a Ni content in the kamacite range. The sulphide gives the impression of having formed by corrosion of a metal grain.

Another FeS–metal assemblage (no. 19 and Table 1) is embedded in an olivine pyroxene chondrule that also contains two other Si-bearing metal assemblages and numerous small, uncorroded, spherical metal grains (Fig. 1c). We cannot detect Si in the uncorroded grains and the Si content of the corroded grain drops below the detection limit at those places where there is no FeS shield (upper right corner, near the dark embayment on lower right). Both the Si-bearing metal and the surrounding FeS contain numerous inclusions too fine to analyse. Some metal grains were not free enough of inclusions to be suitable for analysis. The areas whose compositions are listed in Table 1 were uniform in Si though an occasional point showed a high Cr content, perhaps reflecting the presence of $FeCrO_4$ or $FeCrS_4$. The Si we determined is probably in solid solution in the Fe–Ni, but we cannot completely rule out the presence of uniformly distributed submicroscopic grains of Si-rich phases such as perryite, $(Fe, Ni)_2(Si, P)_5$. As such a phase would have formed by low-temperature exsolution, its presence would not complicate
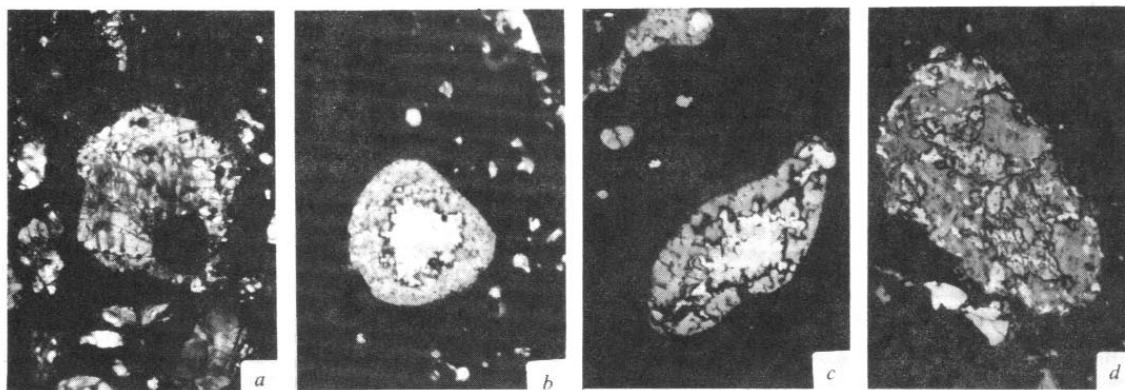

Fig. 1 Cr, Si-rich Fe–Ni grains in Bishunpur. *a*, Transmitted light photo showing a 760×950-μm olivine crystal. The olivine displays undulatory extinction, probably indicating shock, and it contains numerous glassy inclusions of variable composition, but all strongly enriched in Ca and Al. The small opaque inclusions are mainly metal; the large one (190 μm) is shown by reflected light in *b*. The white area is metal (no. 39 in Table 1) and the outer rim consists of FeS. The irregular outline of the metal suggests that the sulphide formed by corrosion of the metal. *c*, Reflected light view of a 97×310-μm metal–sulphide assemblage (no. 19 in Table 1) inside a chondrule. In the interior, the Si content is constant (3.7 mg per g) but drops below the detection limit near edges which are not coated in FeS. A fine-grained FeS-rich material, located between the metal and sulphide, is rich in Ca and P. The outer sulphide is relatively inclusion-free and contains Ca, Cr and minor P and Si. *d*, A large 320×480 μm metal–sulphide assemblage (no. 78 in Table 1) surrounded by a thin layer of matrix and sandwiched between two large porphyritic chondrules. In contrast to the other grains, the metal (white, irregular) is randomly distributed in the sulphide. The Si content drops below the detection limit at the edge of each metal grain.

Table 1   Compositions of Si-bearing metal and adjacent olivine in the Bishunpur L3 chondrite

Grain	Points	Fe (mg per g)	Co (mg per g)	Ni (mg per g)	Si (mg per g)	Cr (mg per g)	Olivine (mol % Fa)	Petrographical setting
19	5	954	4.6	38	3.7	8.6 ⎫		
20	3	933	4.5	40	1.3	10.0 ⎬	3.6	Separate grains in chondrule
27	3	941	4.2	36	2.9	6.7 ⎭		
39	5	948	8.0	40	2.0	2.0	1.4	Olivine fragment
62	6	950	6.4	36	1.6	5.2	—	Chondrule
78	6	946	6.5	36	3.4	6.2	—	Matrix

the following discussion of how the Si was originally introduced into the metal.

Figure 1*d* shows the only Si-bearing metal that was not enclosed by olivine (no. 78 in Table 1). It is located in a thin layer of opaque, amorphous matrix with large porphyritic chondrules on either side. The entire assemblage is 480×320 μm, thus its area is about quadruple that of the largest of the grains embedded in olivine. The metal grains are more-or-less randomly distributed within the sulphide. They show little variation in Ni, Co, and Si, but Si drops below the detection limit at grain edges. As in the other assemblages, there is a Ca, P and Cr-rich layer between the metal and the sulphide. Unlike the grains within chondrules, this assemblage does not have a rounded outline, nor does it have the inner metal, outer sulphide configuration. Despite the differences, the compositional and petrological evidence indicates that this grain assemblage is genetically related to those found inside chondrules. It may have been freed of silicates before the chondrule melting process, or it may have been a fragment broken out of a chondrule. The preservation of reduced Si despite its siting in the matrix can probably be attributed to its large size.

Table 1 shows the compositions of the six Si-bearing Fe–Ni grains for which precise data could be obtained, and the Fe/(Fe + Mg) ratios in the host olivine. All grains are Cr-rich, but there is no correlation between Cr and Si or between these and other compositional parameters including olivine composition. One relevant observation is Cr zoning; Cr increased in concentration towards the grain edge. This implies that Cr was being reduced and diffusing into the grain before diffusion ceased. A possible interpretation is that Si was the agent reducing the Cr. All Ni concentrations are in a relatively restricted range of 34–40 mg per g, a composition that falls within the α stability field at temperatures between 550 and 1,100 K.

Summations in the FeS around the metal grains are often <980 mg per g reflecting the presence of the numerous fine inclusions mentioned above; even in areas of essentially pure FeS (Fe + S >980 mg per g), Ca, Cr, P and Si totalling 8–33 mg per g are observed.

Clearly, the FeS shell has either introduced the Si or preserved Si that entered the Fe–Ni at higher temperatures. As FeS cannot reduce silicates to Si, and because the only observed evidence for an oxidation–reduction reaction involves Si oxidation, we conclude that the latter is correct. We can think of two mechanisms by which the FeS shell could preserve the reduced state of Si during the mild metamorphism experienced by Bishunpur. It could either act as a barrier to diffusion of oxidant or Si, or it could act as a reducing buffer which consumed any oxidant (Fe^{2+}) released by the surrounding silicates. The reducing agent might have been (Fe, Ni)$_3$ P or Cr^{2+}. Diffusion at the low metamorphic temperatures experienced by Bishunpur probably limited any oxidant generation to very small amounts.

In unequilibrated chondrites the metal inside chondrules is significantly less equilibrated than the metal in the matrix[4]. Thus it is not surprising that seven of the eight Si-bearing grains that we observed are inside chondrules or inside olivine fragments that may have originated as chondrules. As the chondrules were either completely molten or high-degree partial melts, their temperatures at formation were surely ≫1,250 K, the FeS–

metal eutectic temperature, it follows that the Si-bearing metal–FeS assemblages were also molten. It therefore seems probable that the concentric geometry (FeS as an exterior shell) and corroded appearance were produced during solidification and a very brief period of annealing. As the Si was not oxidized by FeO from the silicates during this process, it follows that the chondrules cooled very rapidly following formation.

The 250×360-μm metal grain from the Murchison CM chondrite[2] contained 1.2 mg per g Si; there is no indication that it was surrounded by a sulphide shell. Considered as whole-rock chemical systems both Bishunpur and Murchison are highly oxidized. In Bishunpur ~50% of the Fe is present in the +2 state
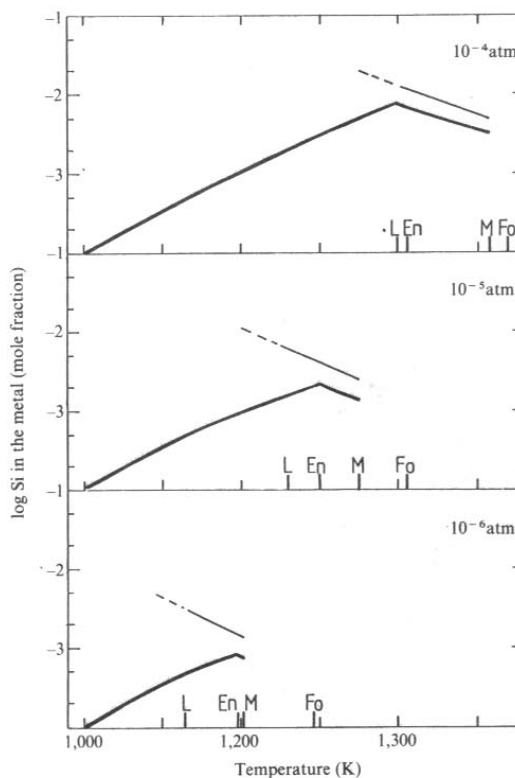

Fig. 2   Mole fraction Si in Fe–Ni condensing in a cooling nebula of solar composition at total (pH$_2$) pressures of 10^{-4}, 10^{-5} and 10^{-6} atm. The heavy curve shows the Fe–Ni composition if both Fe–Ni(s) and Mg$_2$SiO$_4$(s) condensed according to simple thermodynamic equilibrium. The light curve shows the Si content of the metal if the metal condenses according to the equilibrium calculations but silicates condense only after 70–85 °C of supercooling. Also indicated are the nucleation temperatures of Mg$_2$SiO$_4$(Fo), Fe–Ni(M), MgSiO$_3$(En) and a silicate liquid (L).

as oxides; in Murchison about 75% is in the +2 and +3 state as oxides. At equilibrium Fe-rich silicates or magnetite will readily oxidize Si. The large amount of oxidized Fe and the highly unequilibrated nature of both chondrites are strong evidence that the Si-bearing metal did not form by reduction during metamorphism.

The more plausible mechanism for producing Si-bearing metal is to produce it during the condensation of the cooling solar nebula. In an unfractionated nebula the Si activity in Fe–Ni will be controlled by reactions of the sort

$$2MgSiO_3(s) + 2H_2(g) = Si(s) + Mg_2SiO_4(s) + 2H_2O(g) \quad (1)$$
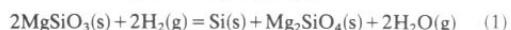
if condensed silicates are the source of the Si. If gaseous SiO is the source of the Si the appropriate reaction is

$$SiO(g) + H_2(g) = H_2O(g) + Si(s) \quad (2)$$
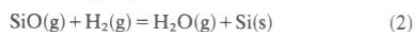
The chief hindrance to the accurate calculation of Si mole fractions during nebular condensation is the inadequacy of available activity coefficient (γSi) data[7]. Sears[8] used the function determined by Sakao and Elliott[9] at temperatures of 1,373–1,623 K:

$$\log (\gamma_{Si})\alpha = 1.19 - \frac{7{,}070}{T} - \left(6.30 - \frac{18{,}300}{T}\right)X_{Si} \quad (3)$$

A study by Sakao *et al.*[10] yielded log γ values about 0.15 more negative. Grossman *et al.*[2] used the Sakao–Elliott function and one covering the temperature range 873–1,273 K obtained by Roberts[11], we have not used the latter because it does not cover the range of condensation temperatures for Fe–Ni. The Sakao–Elliott data were obtained for Ni-free α (body centred cubic) phase. The Fe–Ni that condenses from the nebula has the γ structure (face centred cubic) and a Ni content >50 mg per g. We cannot predict the effect of Ni, but there is evidence that $(\gamma_{Si})_\gamma$ is lower than $(\gamma_{Si})_\alpha$. Wai and Wasson[12] reported that Si concentrations in the γ phase of the Tucson iron are 1.3–1.5 times higher than those in the coexisting α phase. However, equilibrium was not achieved in Tucson. (There is no definite γ phase in other highly reduced meteorites that are more equilibrated than Tucson; Keil[13] found phases having 91–98 mg per g Ni in the Fe–Ni in EH Adhi-Kot and EL Hvittis, but the low Ni content of these grains leaves doubt that they are really γ.) The observed Si_γ/Si_α distribution ratio is probably a lower limit of that prevailing at the equilibration temperature of ~1,000 K; a plausible guess is that $(\gamma_{Si})_\gamma$ is about three times lower than $(\gamma_{Si})_\alpha$ at 1,000 K. Because γ should approach unity with increasing temperature, we will assume that the Si_γ/Si_α distribution ratio drops to 2 at 1,500 K. $\log(\gamma_{Si})_\gamma - \log(\gamma_{Si})_\alpha$ usually follows an $A + B/T$ relationship over moderate temperature ranges, so that equation (3) can be written:

$$\log (\gamma_{Si})_\gamma = 1.24 - \frac{7{,}600}{T} - \left(6.30 - \frac{18{,}300}{T}\right)X_{Si} \quad (4)$$

the absolute change of log γ_{Si} is assumed to be the same for γ and α metal.

Figure 1 shows the nebular condensation of Si for two models: (1) the thick curves show the metal compositions if Fe–Ni and mafic silicates condensed heterogeneously as soon as temperatures fell low enough to make the condensates stable; and (2) the thin curves show the compositions if metal condensed heterogeneously, but the mafic silicates condensed homogeneously with amounts of required undercooling[14]. The thermodynamic data set is the same as that used by Sears[8], with the exception of the Si activity coefficient.

We suggest that the second model is the more appropriate one for the low-pressure regions of the nebula in which ordinary and carbonaceous chondrites formed. Evidence[15] indicates that CM chondrites formed at solar distances ≥2 AU where nebular pressures were probably ≤10^{-5} atm, and ordinary chondrites at ~1–3 AU at pressures ≤10^{-4} atm. Although Blander and Abdel-Gawad[14] and Blander[16] argued that at low nebular pres-

sures (≤10^{-4} atm) nucleation inhibitions should result in Fe–Ni nucleating at temperatures well below those at which enstatite and forsterite condense, the opposite must have occurred for the Si-rich grains. If supersaturation of metal led to condensation of Fe as silicates or FeS, subsequently condensed metal should have had a Ni/(Fe + Ni) atom ratio well above the solar ratio of 0.054; but the Murchison ratio (0.064) is only slightly higher, the ratios in Bishunpur (0.030–0.038) distinctly lower. Moreover, there is no way to condense metal having high Si contents after Si has largely (≥99%) condensed as silicates. If the nebula had a 'solar' pH_2O/pH_2 ratio of ~5×10^{-4}, the Si concentration in subsequently condensed metal will be orders of magnitude lower than that observed in Bishunpur and Murchison. Thus, although we cannot rule out the condensation of other metal grains after silicate condensation, the evidence indicates that these Si-bearing grains condensed earlier than the bulk of the silicates. It has been proposed that refractory metal grains such as those embedded in refractory inclusions in CV chondrites could have served as condensation nuclei for Fe–Ni (ref. 17).

The carbonaceous and ordinary chondrite groups contain large quantities of Fe-rich silicates that probably either formed by direct condensation or by reaction of gaseous Fe with pre-condensed MgSiO$_3$. Direct condensation avoids the need for mass-transport of Mg out of and Fe into these silicates, and may be more likely. Direct condensation implies a high degree of supercooling both for metal and silicates, consistent with our conclusion that most of the silicate condensation occurred at temperatures well below the equilibrium condensation temperature for Fe–Ni, and not inconsistent with the condensation of a minor amount of the metal at high nebular temperatures.

Figure 2 shows mole fractions of Si in Fe–Ni at nebular pressures of 10^{-4}, 10^{-5}, and 10^{-6} atm based on these alternative models. The positions are marked where $Mg_2SiO_4(Fo)$, Fe–Ni(M), and $MgSiO_3(En)$ become stable if equilibrium holds, and the point where silicate liquid (L) becomes stable in the constrained equilibrium model of Blander and Abdel-Gawad[14]. The heavy curves depict the $Si/(Fe + Ni + Si)$ trajectories in equilibrium conditions. Maximum mole fractions reach 0.006, 0.002 and 0.001 at 10^{-4}, 10^{-5} and 10^{-6} atm, respectively. The results at 10^{-4} and 10^{-5} atm seem to agree with those of Grossman *et al.*[2]. The light curves show the Si mole fractions for metal grains condensing heterogeneously (in equilibrium conditions) while the condensation of the major silicates has not occurred because of nucleation constraints; the extensions of these curves below the estimated silicate nucleation temperatures (L) are shown dashed. If our second model is correct, then the $Si/(Fe + Ni + Si)$ ratios of 0.012, 0.007 and 0.003 are reached before silicates condense at nebular pressures of 10^{-4}, 10^{-5} and 10^{-6} atm, respectively. If this is the correct model for the formation of Si-bearing grains, the Murchison grain could have formed at nebular pressures of 10^{-6} atm or slightly lower.

Is it reasonable that high Si contents could be preserved after mafic silicates start to condense? In some cases the Si was oxidized by $H_2O(g)$ and entered silicates that nucleated on the surfaces of the metal grains. On the other hand, uncondensed SiO(g) is a more readily available source of Si, and rapid formation of silicates around a metal grain could remove the metal from contact with the gas and preserve its Si content, just as the refractory-rich metal grains are preserved in the inclusions of CV chondrites[17,18].

Studies of highly unequilibrated chondrites have taught us that if a phase can form in certain solar–nebula conditions it will probably eventually be found in these remarkable meteorites.

1. Wood, J. A. *Icarus* **6,** 1–49 (1967).
2. Grossman, L., Olsen, E. & Lattimer, J. M. *Science* **206,** 449–451 (1979).
3. Sears, D. W., Grossman, J. N., Melcher, C. L., Ross, L. M. & Mills, A. A. *Nature* **287,** 791–795 (1980).
4. Afiattalab, F. & Wasson, J. T. *Geochim. cosmochim. Acta* **44,** 431–446 (1980).

Rambaldi, E.R., Sears, D.W. and Wasson, J.T. (1980) Si-rich grains in highly   820
unequilibrated chondrites. *Nature*, **287**, 817 - 820.

5. Huss, G. R., Keil, K. & Taylor, G. J. *Meteoritics* **13,** 495–497 (1978).
6. Rambaldi, E. R. & Wasson, J. T. *Geochim. cosmochim. Acta* (submitted).
7. Baedecker, P. A. & Wasson, J. T. *Geochim. cosmochim. Acta* **39,** 735–765 (1975).
8. Sears, D. W. *Icarus* (in the press).
9. Sakao, H. & Elliott, J. F. *Metall. Trans. A* **6A,** 1849–1851 (1975).
10. Sakao, H., Kubo, A. & Ishino, Y. *Proc. int. Conf. Sci. Technol. Iron and Steel,* 449 (1971).
11. Roberts, W. *Jernkont. Annlr.* **155,** 285–287 (1971).
12. Wai, C. M. & Wasson, J. T. *Geochim. cosmochim. Acta* **33,** 1465–1471 (1969).

13. Keil, K. *J. geophys. Res.* **73,** 6945–6976 (1968).
14. Blander, M. & Abdel-Gawad, M. *Geochim. cosmochim. Acta* **33,** 701–716 (1969).
15. Wasson, J. T. in *Comets Asteroids Meteorites: Interrelations, evolution and origins* (ed. Delsemme, A. H.) 551–559 (University of Toledo Press, 1977).
16. Blander, M. in *Asteroids* (ed. Gehrels, T.) 809–821 (University of Arizona Press, 1979).
17. Palme, H. & Wlotzka, F. *Earth planet. Sci. Lett.* **33,** 45–60 (1976).
18. Blander, M., Fuchs, L. H., Horowitz, C. & Land, R. *Geochim. cosmochim. Acta* **4** 217–224 (1980).