

Preliminary evidence indicates that this seasonal temperature record may be preserved in the isotopic record of deep-sea sediments. The equation describing the ^{18}O fractionation with temperature in living foraminifera off Bermuda is nearly identical to that describing the isotopic composition of *G. ruber* analyzed from fossil assemblages of the Indian Ocean (14). In addition, *G. ruber* and *G. truncatulinoides* fossils (from regions of the Indian Ocean with a seasonal range in surface temperature equal to that off Bermuda) have an isotopic difference similar to the seasonal isotopic change in living species off Bermuda (14). We believe that these similarities between the living and fossil foraminifera are too close to be fortuitous and that, with further calibration, these relationships could be used to determine the seasonal temperature contrast and isotopic paleotemperatures of oceans in the past.

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- N. J. Shackleton and E. Vincent [*Mar. Micropaleontol.* **3**, 1 (1978)] estimate that *G. ruber* deviates from equilibrium by only -0.25 per mil.
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- Horizontal tows were taken with plankton nets (200- μm mesh) over a depth range of 0 to 10 m at a station located at 32°16'N, 64°39'W, approximately 6 km southeast of Castle Harbour, Bermuda.
- Unpublished Bermuda Biological Station hydrographic data for 1975 and 1976, analyzed at the Woods Hole Oceanographic Institution by E. Schroeder.
- The foraminiferal specimens were carefully cleaned of adhering debris with a brush, measured, and oven-dried at 50°C. Each foraminiferal sample was roasted in vacuo for 1 hour at 400°C and reacted in vacuo with concentrated phosphoric acid at 50°C. The isotopic difference between the derived sample CO_2 and the Pee Dee belemnite (PDB) standard was determined with an on-line VG micromass 602-C mass spectrometer. All values are reported as

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{PDB}}} - 1 \right] \times 10^3 \text{ per mil}$$

Duplicate analyses of the foraminiferal samples have an average standard deviation (S.D.) of ± 0.06 per mil for $\delta^{18}\text{O}$. Isotopic analyses were also made of four species of living foraminifera removed from two portions of a freshly collected plankton tow that were either frozen or preserved in 5 percent formalin solution buffered with hexamethylenetetramine. The results obtained with the specimens preserved by the two different methods indicate that formalin does not significantly affect the oxygen or carbon isotopic compositions of the calcite shells. All the isotopic differences are within the experimental error of ± 0.1 per mil (1 S.D.) (D.F.W., unpublished data).

- The complete isotopic data set will be published separately (A. W. H. Bé, D. F. Williams, R. G. Fairbanks, in preparation) and is available on request.
- The calcite (c) equilibrium line was computed using the isotopic paleotemperature (T) equation from S. Epstein, R. Buchsbaum, H. A. Lowenstam, and H. C. Urey (1).

$$T = 16.5 - 4.3 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.14 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2$$

Here $\delta^{18}\text{O}_w$ (PDB) = $0.595 - 20.68$ for water (w) relative to PDB; where S is salinity [S. Epstein and T. Mayeda, *Geochim. Cosmochim. Acta* **4**, 213 (1953); H. Craig and L. I. Gordon, in *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, E. Tongiorgi, Ed. (Consiglio Nazionale della Ricerche, Laboratorio di Geologia Nucleare, Pisa, 1965), pp. 1-22].

- Possible systematic errors in estimating calcite equilibrium include (i) calibration of laboratory reference gas BIG II to PDB, (ii) estimation of $\delta^{18}\text{O}$ of seawater near Bermuda, and (iii) accuracy

of the paleotemperature equation. None of the factors are accurate to better than ± 0.1 per mil. From these data alone we cannot resolve the question of whether planktonic foraminiferal species calcify in oxygen isotopic equilibrium. Additional analyses of planktonic foraminifera from surface tows and laboratory cultures and direct measurement of $\delta^{18}\text{O}$ of ambient seawater are in progress and should help resolve this question.

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Silicon in Carbonaceous Chondrite Metal: Relic of High-Temperature Condensation

Abstract. *Electron microprobe analyses of an extraordinarily large metal grain from the Murchison type 2 carbonaceous chondrite gave 0.24 mole percent silicon. Thermodynamic calculations show that this is a natural consequence of condensation of alloys from the solar nebular gas at a total pressure $10^{-3} \leq P_{\text{tot}} < 10^{-2}$ atmosphere, provided they failed to equilibrate with it after cooling to < 1200 kelvins.*

A wide range of oxidation states is represented in chondritic meteorites (1). In fact, so variable is the oxidation state that it is used as the basis for the broad classification of chondrites. Carbonaceous chondrites are the most oxidized, the majority containing only trace amounts of metallic nickel-iron. Most of the iron in these meteorites is present as FeO dissolved in silicates and even Fe_2O_3 dissolved in the mineral magnetite, Fe_3O_4 . Enstatite chondrites are the most reduced, containing virtually no oxidized iron in solid solution in silicates. Their iron occurs principally as the metal and sulfide. These meteorites are so reduced that elements normally combined with oxygen are present as sulfides (Ca, Mn), nitrides (Ti), and metal [Si dissolved in the nickel-iron phase in concentrations of 1.0 to 3.7 percent by weight (2)]. We report here the discovery of Si in the metal phase of a normal carbonaceous chondrite. We offer an explanation in terms of condensation processes from a nebular gas of solar composition.

Type 2 carbonaceous chondrites con-

tain a variety of coarse-grained, anhydrous silicate and oxide phases disseminated in a very fine-grained matrix of hydrated phyllosilicates. Among the anhydrous materials are whole and broken euhedral crystals of forsteritic olivine, reaching 1 mm in size. Within these are found grains of a Cr-rich nickel-iron alloy, ranging from < 1 to 10 μm in size. This is the predominant mode of occurrence of metal in type 2 carbonaceous chondrites. In previous papers (3, 4) we discussed the origin of these olivines and their inclusions in terms of condensation from a high-temperature solar nebular gas. Rarely, metal grains are found isolated in the matrix (5).

In all these occurrences, the metal is embedded in silicates. In performing electron microprobe analyses, although the beam diameter can be narrowed to less than that of some of the larger metal grains, the actual volume excited into x-ray emission is often larger than the volumes of these grains. This results in the appearance of 0.0x to 0.x percent of fictitious Si in the metal analysis because of excitation of Si x-rays in surrounding sil-

icates. For practical purposes, it is thus impossible to measure the actual Si content of most metal grains in these meteorites.

Careful binocular microscopic examination of hand specimens of the Murchison type 2 carbonaceous chondrite over a period of years serendipitously yielded in its phyllosilicate matrix a metal bead large enough to be extracted from the meteorite, cleaned of all adhering silicates, embedded in epoxy, ground down to expose a cross section of 254 by 361 μm , and polished. The grain was examined for purity by scanning electron microscope. It contains a 7- μm silicate inclusion near one end and a fracture near one edge that is filled with matrix silicates and sulfides. The central portion of the grain, 125 by 220 μm , was free of impurities and was more than sufficient to obtain a group of Si determinations by electron microprobe (6) at 23 different spots, free from the problems of spurious Si counts. The average Si content is 0.12 ± 0.02 percent by weight (0.24 ± 0.04 mole percent). The concentration range is 0.09 to 0.14 percent by weight. Individual determinations have relative uncertainties of 4.3 to 6.0 percent due to counting statistics.

Initially, the grain had been analyzed for Fe, Ni, Co, Cr, and P (7). An average of analyses of four spots gave, in percent by weight: Fe, 92.32; Ni, 6.82; Co, 0.39; Cr, 0.73; and P, 0.13; the total was 100.39. The high Ni, Co, Cr, and P contents are unusual for meteoritic metal, but fall well within the concentration ranges for these elements in the metal beads inside the olivine crystals of type 2 carbonaceous chondrites, which are, in mole percent: Ni, 4 to 8; Co, 0.2 to 0.7; Cr, 0.2 to 1.0; P, 0.3 to 6.0; and the remainder Fe (3). This is important, for it places this grain in the unique population of metal beads inside the olivine crystals, despite its different occurrence, isolated in the matrix. These grains are higher in Cr than any other meteoritic metal and usually have Ni/Fe and Co/Fe ratios greater than the cosmic ratios.

The only other report of Si in the metal phase of carbonaceous chondrites is a lower limit of 0.07 percent by weight in Renazzo (8). This occurrence is odd in that the metal is found in much larger grains (up to 1 mm) than in normal carbonaceous chondrites and in such vastly greater amounts (12 percent) than Mason and Wiik (9) classified Renazzo as intermediate between carbonaceous and enstatite chondrites. Renazzo is unusual in other ways as well. Its combination of textural and chemical properties ob-

scures its affinities to other carbonaceous chondrites (10) and its oxygen isotopic characteristics imply a different history (11). These facts, together with the anomalous Cr and P contents of Renazzo metal (3), suggest that it has a different origin from the metal in normal carbonaceous chondrites that is discussed here.

In attempting to explain the unusual compositions of metal in normal carbonaceous chondrites, Grossman and Olsen (3) performed thermodynamic calculations to see what the composition of a metallic nickel-iron alloy would be as it condensed and equilibrated with a cooling gas of solar composition. Those calculations were based on the technique of and some results of much more extensive calculations by Grossman (12) dealing with condensation of all the abundant elements. Grossman and Olsen assumed an ideal solid solution model for the alloy and found that it would condense from a gas of solar composition at 1471 K at a total pressure (P_{tot}) of 10^{-3} atm. The initial Cr, Ni, and Co concentrations were predicted to be 0.33, 13.4, and 0.74 mole percent, respectively. With falling temperature the Ni and Co contents would decrease and the Cr content would increase if the metal grains continued to equilibrate with the gas. The condensate alloys so produced would have initial Ni/Fe and Co/Fe ratios in excess of the solar values, but these ratios would fall asymptotically to the solar ratios in the neighborhood of 1375 K. Grossman and Olsen noted that preservation of higher-than-solar Ni/Fe and Co/Fe ratios in the metal grains thus implies that they stopped equilibrating with the gas at temperatures above 1375 K, presumably by becoming physically isolated from the gas. Noting that thermodynamic calculations predict that forsteritic olivine begins to condense from a gas of solar composition at 1444 K at 10^{-3} atm and that most metal grains are contained within olivine crystals, Grossman and Olsen suggested that cessation of equilibration was caused by encapsulation of the metal grains in olivine that condensed between 1444 and 1350 K.

To see if such a model could also predict the observed Si content, we repeated the calculations, but with major improvements. Because silicates contain most of the Si in a system of solar composition at metal equilibration temperatures, the metal phase composition was calculated in a modified version of the program used by Lattimer and Grossman (13) in which the entire equilibrium condensate assemblage was computed as a

function of temperature at three different total pressures: 10^{-3} , 10^{-4} , and 10^{-5} atm. Activity coefficient data relevant to the expected temperatures and compositions were sought for Ni, Co, Cr, and Si in face-centered cubic iron alloys. Conard *et al.* (14) showed that the maximum deviation of Fe from ideality is only 2 percent and that the Ni activity coefficients are 0.5 to 0.6 in the Fe-Ni binary for the conditions expected here. We thus assumed that Fe is ideal and used an equation relating the Ni activity coefficients to Ni content and temperature in our calculations. A similar function was used for the Cr activity coefficient (15), which was close to 2 in our calculations. Dilute solutions of Co in Fe are ideal within measurement uncertainty (16) under the conditions expected here. Activity coefficients for Si in Fe are limited to body-centered cubic alloys. Two sets of calculations were done, one using a relationship computed by us between activity coefficients derived by Roberts (17), Si content, and temperature, and the other using Sakao and Elliott's (18) function based on their more recent experiments. For our conditions, both gave values of 10^{-4} to 10^{-5} , but the data from (18) are from 15 percent lower to 2.3 times higher than those from (17), depending on temperature. Effects of small amounts of Si, Cr, and Co on the activity coefficient of the solvent, Fe, were assumed negligible, as were effects of solutes on one another.

The results of these calculations are qualitatively similar to the earlier ones in that the Cr concentrations are high and increase with decreasing temperature and the Ni/Fe and Co/Fe ratios are higher than their solar values in the first condensate and decrease with falling temperature. Several quantitative differences are noteworthy. At 10^{-3} atm, the initial Ni content is now about 22 instead of 13.4 mole percent, but falls more steeply with falling temperature than in the previous work. The initial Co content is now 0.47 instead of 0.74 percent, but falls less steeply with decreasing temperature. Finally, Cr contents are always about a factor of 1.5 lower than in the previous work. These changes are relatively minor, however, in the sense that concentration ranges predicted for Ni, Co, and Cr between the alloy condensation temperature and 1375 K at 10^{-3} atm still encompass the concentration ranges for these elements in most metal grains observed within the olivine crystals and, in particular, the Ni, Co, and Cr contents of the metal grain studied here. Also as before, the equilibration temperature in-

ferred for any particular metal grain on the basis of the concentration of one of these elements is often different from that inferred from one of the other elements. This is presumably related to kinetic factors.

Regardless of the total pressure and Si activity coefficients used, the Si concentration in the metal is predicted to rise, reach a maximum, and then drop sharply as temperature falls. The maximum Si content is achieved at the temperature immediately preceding the condensation temperature of enstatite, which thereafter removes Si from the vapor quantitatively.

At 10^{-5} atm, the model predicts Si contents > 0.24 mole percent, the concentration in the metal grain, over a temperature interval of only 30 K, using the activity coefficient data of (17). Furthermore, if the Si data from (18) are used, the maximum Si content predicted falls a factor of 2.2 short of the observed value. At total pressures $< 10^{-5}$ atm, predicted Si contents are even less. We conclude that it is unlikely that the Murchison metal grain achieved its Si content by equilibrating with a gas of solar composition at or below 10^{-5} atm.

Silicon contents increase considerably with total pressure, however. At 10^{-4} atm, the Si content of the first-condensing alloy at 1371 K is predicted to be 0.16 or 0.22 mole percent and to rise to 0.24 mole percent at 1320 or 1365 K, respectively, depending on the activity coefficient data used. After reaching a maximum concentration of 0.33 or 0.62 percent at 1292 K, however, Si falls to the 0.24 percent level again at 1270 or 1212 K. Thus, the Si content of the observed metal grain could have resulted from equilibration with a solar gas in two different temperature ranges at 10^{-4} atm. The Ni/Fe and Co/Fe ratios of condensate alloys vary in the same way at 10^{-3} , 10^{-4} , and 10^{-5} atm; that is, they start off with higher-than-solar values at the condensation temperature of the alloy, decrease with falling temperature, and asymptotically approach the solar values at about 100 K below the initial condensation temperature. Thus, the metal grain would have nearly solar Ni/Fe and Co/Fe ratios if it equilibrated in the lower of the above temperature ranges and much higher ratios if it did so in the higher one. As mentioned above, most Murchison metal grains have higher-than-solar ratios, indicating equilibration near the initial condensation temperature. In particular, the one studied here has Ni/Fe and Co/Fe ratios higher than the solar values by 31 and 62 percent, re-

spectively, indicating that the higher temperature range applies to this grain.

At 10^{-3} atm, however, the first alloy to condense is already higher in Si than 0.24, containing 0.33 or 0.38 mole percent. At this pressure, condensate alloys can only contain 0.24 percent Si long after Si reaches its maximum concentration and starts to fall. Because the inferred equilibration temperature is more than 200 K below the condensation temperature of the alloy at this pressure, this Si content would be accompanied by solar Ni/Fe and Co/Fe ratios. As this is clearly the case neither for this metal grain nor for most of the others in Murchison, we feel that the total pressure in the region of the nebula where these grains formed had to be somewhat lower than 10^{-3} atm so that a Si content of 0.24 mole percent could be produced within 100 K of their initial condensation temperature.

We have thus shown that the Si content of the metal grain analyzed here is consistent with its origin by condensation from a nebular gas at $10^{-5} \leq P_{\text{tot}} < 10^{-3}$ atm. Because its Ni, Co, and Cr concentrations are in the same range as those of the metal beads inside the olivine crystals and because their compositions were determined by the same condensation process that established the Si content of the grain reported here, we believe that they too have similar Si concentrations, although this is not directly testable for the analytical reasons discussed above. Grossman and Olsen (3) attributed the preservation of the unusual compositions of the metal grains to their entrapment by condensing olivine, but this explanation cannot apply to the grain studied here because it is not contained in olivine. That model, however, is only one means of chemically isolating metal grains from the gas phase. Other mechanisms may also have operated, such as transport of grains from the site where they last equilibrated with the gas to another region just before accretion of the Murchison parent body. It is also probable that the large size of this particular grain was an important kinetic factor that prevented equilibration at lower temperatures, thus preserving a record of its high-temperature history.

Although the Si content of the metal in type 2 carbonaceous chondrites seems anomalous relative to the oxidation state of a large fraction of the material in these meteorites, it has been shown here that it is entirely consistent with the condensation model for their origin. This is because, according to this model, the metal and its associated phases last equi-

brated with a gas of solar composition at high temperatures, when the system was highly reducing, whereas the oxidized iron-bearing phases became stable at much lower temperatures, after the system had become highly oxidizing (12).

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6. This analysis was performed at 15 keV and a beam current of $1 \mu\text{A}$, using a wavelength-dispersive spectrometer. For each spot analyzed in the Murchison metal, a computer-controlled scan was made over the wavelength region of Si K α , taking 30-second accumulations of counts at each of four background positions and at the peak top. The standard used was metal from the Horse Creek iron meteorite, which contains 2.45 percent Si [V. F. Buchwald, *Handbook of Iron Meteorites* (Univ. of California Press, Berkeley, 1975), vol. 2, p. 662]. Its Si count rate was determined in the same way as the unknown. The Si content of the Murchison metal was computed from the simple ratio of its background-corrected count rate to that of the standard. Differential matrix effects between sample and standard can be assumed to be negligible compared to counting uncertainties.
7. This analysis was also performed at 15 keV and $1 \mu\text{A}$, using an energy-dispersive, Li-drifted Si crystal detector. Standards used were synthetic Fe $_3\text{O}_4$ for Fe, Ni metal for Ni, synthetic CoO for Co, synthetic Cr $_2\text{O}_3$ for Cr, and 8408 apatite for P. Correction procedure was a slightly modified version of that of S. J. B. Reed and N. G. Ware [*J. Petrol.* **16**, 499 (1975)].
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