

at least 72 hours at each data point. Over 400 hours were spent below the alleged decomposition temperature of 700 °C. Finally the sample was exposed to a hydrous atmosphere by means of steam introduced into the furnace for over 120 hours, the sample itself being at 580 °C.

Fig. 1 does not reveal any tendency for the åkermanite to decompose into wollastonite and monticellite. Fig. 2, which is a plot of the atomic spacing of the 211 plane at various temperatures, also does not indicate any tendency for åkermanite to break up (if it did, a significant change in the slope would be expected).

The above data tend to indicate that åkermanite, at least in an anhydrous atmosphere, does not, even over a prolonged period of time, decompose into other compounds, but is apparently stable from its melting point down to room temperature. That the åkermanite did not decompose at 580 °C in the increased humidity environment caused by the introduction of steam is of some interest.

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Pyrrhotine and the origin of terrestrial diamonds

HYPOTHESES on the origin of the diamond usually begin with graphite, iron carbide, or free carbon. This seems appropriate in considering the origin of meteoritic diamonds. However, terrestrial carbon-bearing abyssal magmas, which have surfaced as kimberlite diamond pipes, are rare. Only one in twenty kimberlite pipes or fissures contains diamonds (Shand, 1952). Where diamond does occur, special conditions seem required.

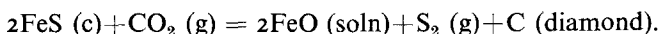
Quite possibly, a carbon or diamond phase originated from the reduction of carbon dioxide, a common mantle constituent (Hearn, 1968; Kennedy and Nordlie, 1968). The reduction could be centered around a specific reducing agent, where its absence in abyssal magmas could mean the absence of diamond as well. Pyrrhotine could fill this role. It is a common syngenetic inclusion in South African diamonds (Sharp,

1966). And troilite, another ferrous sulfide mineral, is well known for its close association with meteoritic graphite and diamonds (Lipschutz and Anders, 1961).

At some depth in the earth, diamond will be the thermodynamically stable form of carbon. This depth, and the corresponding pressure-temperature conditions, can be determined from the phase diagram for carbon (Bundy *et al.*, 1961) and pressure-depth and temperature-depth curves for the earth (Clark and Ringwood, 1964). The geotherms of Clark and Ringwood place the minimum formation temperature between 1050° and 1350 °C. The corresponding pressures are 43 and 51 kb, at depths the order of 140 and 160 km. These conditions may approximate those of actual diamond formation since graphite inclusions and black diamonds indicate that many diamonds are formed close to the graphite-diamond equilibrium line.

In this pressure-temperature interval, pyrrhotine could remain below its melting point (1195 °C at 1 atm). In a solid state reaction, however, bulk diffusion rates would be appreciable.

A possible moderate-temperature-high-pressure reaction between iron-rich pyrrhotine and carbon dioxide is:



This open system reaction would be diffusion-controlled by the carbon dioxide. The diamond phase could form directly, by-passing a graphite or carbide phase. From the composition of kimberlite (Kennedy and Nordlie, 1968) and the phase diagram for the system: MgO-FeO-SiO₂ (Nafziger and Muan, 1967), a separate wüstite or magnesiowüstite phase is unlikely. The FeO (ideal) would either combine with excess silica or dissolve in the kimberlitic silicate.

The standard Gibbs energy change for this reaction is 44.6 ± 0.6 kcal at 1050 °C and 47.2 ± 0.6 kcal at 1350 °C (from the data of Robie and Waldbaum, 1968).

The Gibbs energy change, a measure of reaction feasibility, will be determined by the standard Gibbs energy change and the actual activity or fugacity of each substance.

With an activity coefficient, γ , of 0.1, the activity of FeO at a mole fraction of 0.05 (Kennedy and Nordlie, 1968) would be 0.005. This activity coefficient is quite reasonable for a silicate solution since a partial molar heat of solution $\Delta\bar{H}$, as small as -6 kcal per mole at 1050 °C could give this value ($4.58 T \log \gamma \approx \Delta\bar{H}$). The contribution this activity makes to the Gibbs energy change is -27.7 kcal at 1050 °C and -34.0 kcal at 1350 °C.

The net effect of the prevailing pressure on the solid state activity will be determined by the reaction molal volume change. This could be as large as -9.0 cm³ (Robie and Waldbaum, 1968), neglecting mineral compressibilities and thermal expansions. The contribution to the Gibbs energy change would be -9 kcal at 1050 °C and -11 kcal at 1350 °C.

Then, assuming CO₂ and S₂ have the same fugacity coefficient, a S₂ mole fraction the order of 0.1 would be adequate for the reaction to proceed in the temperature interval 1050 to 1350 °C.

In summary, a new hypothesis is proposed for the formation of terrestrial diamonds with carbon dioxide as the source of carbon, and pyrrhotine as the reducing agent and

reaction catalyst. Kinetically, the direct conversion of carbon dioxide to diamond overcomes certain experimental problems (Kennedy and Nordlie, 1968).

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