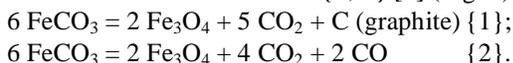


**METAMORPHIC ORIGIN OF SUB-MICRON MAGNETITE CRYSTALS IN ALH 84001: RE-EVALUATION OF EQUILIBRIA, THERMOCHEMISTRY, AND EXPERIMENTS.** A. H. Treiman<sup>1</sup> and E. J. Essene<sup>2</sup>, <sup>1</sup>Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058 <treiman#lpi.usra.edu> <sup>2</sup>Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109.

In 2003, Treiman [1] hypothesized that sub-micron magnetite grains in ALH 84001 formed by devolatilization of ferroan carbonate in the globules, and that chemical equilibrium was approached in a long-duration thermal pulse that followed a major impact event. Thomas-Keprta et al. [2] criticized several aspects of this hypothesis; their criticisms lack merit, and none disproves the hypothesis [1].

**Magnetite Formation from Siderite:** Treiman [1] calculated locations of chemical equilibria to show that the submicron magnetite grains could have formed by thermal decomposition of ferroan carbonate at reasonable P and T. Thomas-Keprta et al. [2] claimed that the calculations contain errors relating to the presence of graphite and the thermodynamics of CO. These critiques are not valid.

**Presence of Graphite.** Magnetite can form from ferroan carbonate via reactions {1, 2} [1] (Fig. 1):



Thomas-Keprta et al. [2] regarded only reaction {1} because it is thermochemically favored; Treiman [1] worked with {2} because graphite nucleates with great difficulty [3-6], and because ALH84001 was not known to contain highly polymerized C (but see [7], not cited by [2]). If the carbonate had decomposed by {1}, the hypothesis of shock-induced thermal metamorphism would remain valid – inferred equilibration T would be reduced by a few 10s of K (Fig. 1).

**Non-Ideality of CO.** Thomas-Keprta [2] located reaction {2} at higher temperature than [1] (~70 K at 200 bars; Fig. 1), and claim that the difference is a result of [1]'s failure to correct for non-ideality of CO. Actually, non-ideality of CO is insignificant at these pressures.

At high pressures, the thermodynamic fugacities ('f') of gases do not equal their partial pressures ('p'), i.e., the gases are not ideal. The fugacity coefficient, 'γ', is a measure of that non-ideality:

$$f(\text{CO}) = p(\text{CO}) \cdot \gamma(\text{CO}) \quad \{3\}.$$

In the P-T range here (500-800 K, P < 200 bars), γ(CO) is between 1.00 and 1.04, and γ(CO<sub>2</sub>) is between 0.94 and 1.02 [8].

We have re-calculated the location of {2} as did [1] (with the Thermocalc code [9]) – inclusion of measured γ(CO) [8] increases the equilibrium T of {2} by < 1 K (Fig.1). We also calculated the location of {2}

using thermochemical data of [10] and γ(CO) and γ(CO<sub>2</sub>) of [8]; that location agrees with the results of

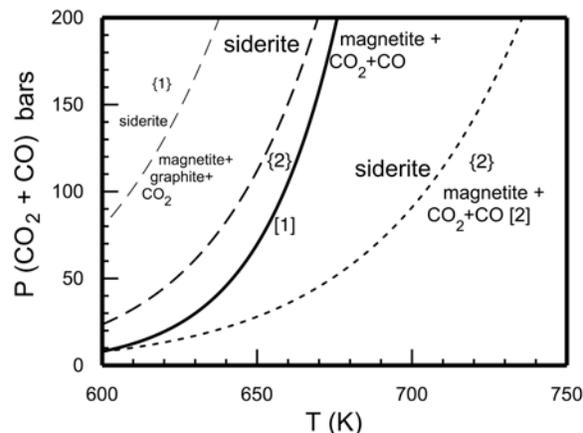


Fig. 1. P-T locations of equilibria {1} & {2}. Location of {1} as calculated by [1] and confirmed here. Locations of {2} are: solid line from [1], confirmed here, indistinguishable from calculation here including γ(CO); dashed line, as calculated here using data of [10]; and short-dash line as reported in [2].

[1], but not [2] (Fig. 1).

Thomas-Keprta et al. [2] suggested that the cause of disagreement on the location of {2} lies in treatment of γ(CO): Treiman [1] assumed it was unity; [2] derived it independently using a newly proposed equation of state (EOS). Here, we interpolate from measured values [8]. If non-ideality of CO alone caused the difference between the locations of {2} (Fig. 1), then [2] must have used a γ(CO) near 150 (for ~670 K, 200 bars) – a factor of > 120 greater than the measured value. This seems extreme.

Thus, the calculations of [1] remain valid. Even if reaction {2} were located as [2] claim (Fig. 1), the hypothesis of shock-induced metamorphism [1] would remain valid, with equilibrium at a higher temperature

**Magnetite Compositions:** The submicron magnetite crystals in ALH 84001 contain little Mg and Mg – undetectable by TEM/EDS [11] – which was taken as a sign of their biological origin. Treiman [1] showed that chemical equilibrium with the ALH 84001 carbonates would yield magnetite with little Mg by calculating the location of the reactions



for his calculated P-T. Thomas-Keprta et al. [2] criticized the calculations and their use of particular ther-

mochemical data for Mg-bearing magnetite – the magnesioferrite component. However, the thermodynamics of magnesioferrite and its solid solution with magnetite are far less certain than assumed by either [1] or [2].

**Magnesioferrite Thermodynamics.** Magnesioferrite ( $\text{MgFe}_2\text{O}_4$ ) has been studied extensively but without consensus on its properties, e.g. published values of  $S_{298}^0$  range from 115.6 to 126.5 J/mol-K [12-14]. This uncertainty derives from several sources, most significant of which is variable cation disorder. Spinel (including magnesioferrite) have two types of cation sites: one tetrahedral and two octahedral sites per formula unit. Cations can be fully disordered on the three sites or ordered in two ways: ‘normal’ spinels have a divalent cation only in the tetrahedral site, whereas ‘inverse’ spinels have both one divalent and one trivalent or tetravalent cation in the octahedral sites. Cation ordering in spinels varies with T, can be slow to equilibrate below  $T_c$ , and produces an entropy contribution that is not detected in low-T calorimetry. These variations in cation ordering imply differing  $S_{298}^0$  and S at higher T up to  $T_c$ , and thus different calculated locations of reactions like {3}. To compound the uncertainties, it is not clear which ordering (and thus  $S_{298}^0$ ) is the appropriate standard state for  $\text{MgFe}_2\text{O}_4$  in highly dilute solutions with  $\text{Fe}_3\text{O}_4$  (the case for ALH 84001 magnetites).

**Magnetite-magnesioferrite Solid Solution.** Both [1] and [2] assumed that the  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  solid solution is ideal, which it is not. Calibrations are only available for much higher temperatures than [1] inferred, ~1000 K [15,16], where dilute solutions of  $\text{MgFe}_2\text{O}_4$  in  $\text{Fe}_3\text{O}_4$  show Henry’s law behavior with  $\gamma(\text{MgFe}_2\text{O}_4)$  of ~2. That  $\gamma$  should increase with decreasing T, meaning that [1]’s estimate of the Mg content of ALH 84001 magnetite is an upper limit. However, high  $\gamma$  values suggest a non-random distribution of Mg atoms, and thus affect the choice of appropriate standard state for  $\text{MgFe}_2\text{O}_4$ .

**Paths Forward.** Given these issues and uncertainties in  $\text{MgFe}_2\text{O}_4$  and in the  $\text{MgFe}_2\text{O}_4$ - $\text{Fe}_3\text{O}_4$  solid solution, other approaches may be useful. The ordering state of dilute  $\text{MgFe}_2\text{O}_4$  in  $\text{Fe}_3\text{O}_4$  solid solutions may be investigated via Landau-type models (e.g. [17]) or by e.m.f measurements. It should also be possible to derive Fe/Mg distribution isotherms from experimental and natural equilibrium assemblages, i.e. calibrating exchange reactions like



**Magnetite Formation - Experiments:** Finally, we comment on the design of “slow heating” experiments in [2], which were intended to model magnetite formation by disequilibrium decarbonation of ferroan carbonate [18]. In the design, evacuated sealed glass tubes contain two silica crucibles, one with the ferroan car-

bonate, and the other with lime (CaO). The tubes are then heated to run temperatures.

The most serious problem is the expectation ([2], p. 6635) that crucible with lime “... acts to maintain a constant oxygen fugacity ( $f(\text{O}_2)$ ).” In this apparatus, CaO will buffer  $\text{CO}_2$  via the reaction



after  $\text{CO}_2$  is produced by thermal decomposition of ferroan carbonate. Reaction {5} buffers  $p(\text{CO}_2)$  to a pressure below that of siderite decomposition (rxns. {1} & {2}), and [19] used this effect to force complete decomposition of ferroan carbonate to magnetite-rich spinel. However, reaction {5} by itself does not affect or buffer  $f(\text{O}_2)$ . If the ferroan carbonate decomposes by reaction {1},  $f(\text{O}_2)$  is fixed by the residual gas in the sealed tube. If ferroan carbonate decomposes by {2} ([2] did not report graphite as a reaction product),  $p(\text{CO})$  in the tube will increase and  $f(\text{O}_2)$  will decrease as the reaction progresses.

**Conclusion:** The hypothesis of [1] remains valid; that the magnetite grains in ALH 84001 could have formed by near-equilibrium devolatilization of ferroan carbonate in the thermal aftermath of an impact event. The criticisms of [2] are not valid, and none really addresses the hypothesis of [1] – equilibration temperatures a few 10s of K either direction can be readily accommodated within the thermal aureole of a major impact [20].

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