CHEMICAL DISEQUILIBRIUM IN CARBONATE MINERALS OF MARTIAN METEORITE ALH 84001: INCONSISTENT WITH HIGH FORMATION TEMPERATURE. A.H. Treiman, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058 (treiman@lpi.jsc.nasa.gov)

The origin of ellipsoids and patches of carbonate minerals in ALH 84001 is controversial *(1-5)* and important because they may contain traces of ancient martian life *(6)*. Estimated formation temperatures of >650°C *(3,4)* seem inimical to life, but are based on assumptions of chemical equilibria among various carbonate compositions and/or the surrounding silicate minerals *(3)*. However, the carbonate minerals were not in chemical equilibria among themselves, and were not in chemical equilibria with the surrounding silicate minerals. Thus, these arguments for a high temperature origin are invalid.

Disequilibrium Carbonate Compositions. Carbonate mineral deposits in ALH 84001 are strongly zoned in their chemical compositions *(1-6)*, from calcite on their interiors through dolomite(ss) to magnesite(ss) on their exteriors (Fig 1). The chemical variations appear completely gradual, without sharp compositional boundaries except at dark bands rich in magnetite and iron sulfide. This gradual chemical zoning is *prima facie* evidence that the compositions of the carbonate minerals do not represent chemical equilibria among themselves *(7)*. Zoning in the ALH 84001 carbonates was almost certainly established while the crystals grew, because the outlines of original crystal faces are preserved near the magnetite-rich bands *(1,2,5,6)*.

High Temperature? Harvey and McSween *(3)* presented four arguments that ALH 84001's carbonate formed at high temperatures, >550°C: magnesite(ss) - dolomite(ss) thermometry, equilibrium among three carbonate phases, calcite - dolomite(ss) thermometry, and equilibria among magnesite, enstatite, olivine, and silica. All of these arguments assume chemical equilibria among carbonate minerals or among carbonate and silicate minerals.

MAGNESITE-DOLOMITE. Mittlefehldt *(1)* and Harvey and McSween *(3,4)* inferred that the carbonates formed near 700°C because many magnesite(ss) compositions fall near the magnesit-dolomite solvus for that T (B on Fig. 1). However, the solvus curve is inapplicable because almost none of the magnesite(ss) is associated with equilibrium dolomite(ss); only the most ferroan magnesite(ss) could possibly be in Fe/Mg equilibrium with the dolomite(ss) (A on Fig. 1) *(9)*. Ca-rich magnesite (B of Fig. 1) without equilibrium dolomite <u>can</u> form and persist indefinitely outside the spinode surface (Fig. 2); a magnesite(ss) composition at a T between the spinode and solvus spinode is not thermodynamically stable, but will <u>not</u> transform spontaneously to equilibrium dolomite and magnesite *(7,11,12)*. The ALH 84001 magnesite(ss) closest to the $CaCO_3$–$MgCO_3$ join fall between the solvus and spinode for 100°C < T < 700°C and so could have formed and persisted at these temperatures.

Thus, only the most Fe-rich magnesite(ss) could be used for solvus thermometry (A of Fig. 1). But it is so variable in its Ca content that a unique formation T cannot be chosen. The Ca contents of these Fe-rich magnesite(ss) ranges from ~20% to ~30% $CaCO_3$ component, and there is no clue of which composition could have been in equilibrium with dolomite(ss). Magnesite(ss) compositions suggest solvus temperatures from ~800°C to well over 1000°C *(3,9)*, but these compositions are probably mixtures of dolomite(ss) and magnesite(ss), represent upper limits to the formation temperature, and actually only restrict formation to <~800°C.

THREE COESIXTING CARBONATES. Harvey and McSween inferred that the carbonates formed at >550°C from the inference that calcite, dolomite(ss) and magnesite(ss) in the carbonate globules were in chemical equilibrium *(3)*. However, these three carbonates in equilibrium cannot have the compositions as analyzed in ALH 8400. At equilibrium among the three carbonates, magnesite(ss) always has a molar Fe/Mg ratio > 4 and dolomite(ss) always has Fe/Mg > 2 *(9)*. In ALH 84001, the ferroan magnesite(ss) and dolomite(ss) have Fe/Mg near unity *(3)*, and so cannot represent equilibrium with calcite. Thus, the three carbonate association in ALH 84001 has no thermometric significance.

CALCITE-DOLOMITE. Harvey and McSween calculated a carbonate formation temperature of ~680ºC from compositions of calcite and dolomite(ss) in the carbonate ellipsoids and the position of the calcite-dolomite(ss) solvus *(3,9)*. As with the magnesite(ss) above, however, the range of calcite compositions makes it difficult to accept that they represent chemical equilibrium.

CARBONATE-SILICATE EQUILIBRIA. Harvey and McSween inferred that magnesite in ALH 84001 formed by reaction between the meteorite's olivine and enstatite and CO_2; at equilbrium, these formation reactions must represent high temperature, > 525-625°C, and high partial pressures of CO_2 gas for normal crustal pressures of 2-5 kbars *(3,10)*. Further, they suggested that the growing front of the carbonate ellipsoids was in continuous equilibrium with the silicate minerals, and that the radial changes in carbonate compositions

reflect decreasing temperatures of equilibration and carbonate growth *(3)*.

This scenario is not consistent with compositions of the silicate and oxide minerals in ALH 84001, which imply with chemical equilibrium at 875±25°C *(2)*. If the silicate and carbonate minerals were in equilibrium, silicate-oxide thermometry ought to yield T≤ 525-625°C, the minimum inferred equilibrium T for the silicate-carbonate reactions *(3)*. Since the silicates and oxides equilibrated at a much higher T, the silicate and carbonate minerals could not have been in equilibrium and the reaction thermometry of *(3)* is not valid.

Conclusion. The carbonates in ALH 84001 represent a disequilibrium assemblage, and cannot be used geothermometers that assume chemical equilibrium. So, the inferences of *(1,3,4)* that the ALH 84001 carbonates formed at >550°C must be rejected. Other arguments for a high-temperature origin must be evaluated on their own merits.

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(1) D.W. Mittlefehldt *Meteoritics* **29**, 214 (1994). (2) A.H. Treiman *Meteoritics* **30**, 294 (1995). (3) R.P. Harvey and H.Y. McSween Jr. *Nature* **382**, 49 (1996). (4) R.P. Harvey and H.Y. McSween Jr. *Lunar Planet. Sci.* **XXVI**, 555 (1995). (5) C.S. Romanek, et al. *Nature* **372**, 655 (1994). (6) D.S. McKay et al. *Science* **273**, 924 (1996). (7) A.R. Philpotts *Principles of Igneous and Metamorphic Petrology*, Prentice-Hall, New Jersey (1990). (8) Essene E.J., in Mineralogical Society of America, Rev. Min. v. 10, 153 (1982). (9) L.M. Anovitz and E.J. Essene *J. Petrol.* **28**, 389 (1987). (10) V. Trommsdorff and J.A.D. Connolly, *Contrib. Min. Petrol.* **104**, 1 (1990). (11) P.L. McSwiggen, *Phys. Chem. Minerals* **20**, 42 (1993). (12) P.M. Davidson, *Am. Mineral.* **79**, 332 (1994).

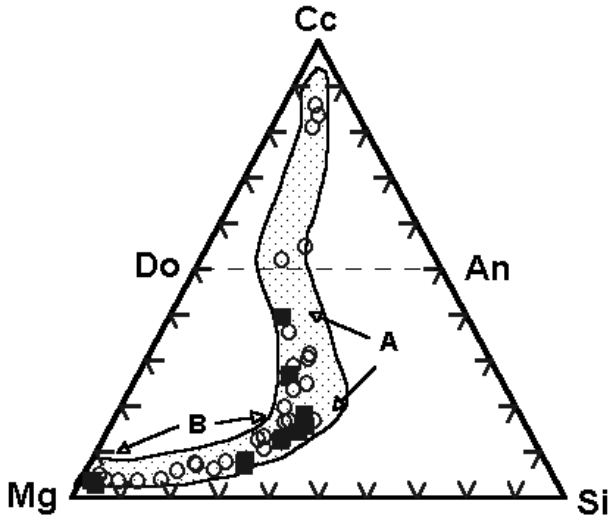

Figure 1. Electron microprobe analyses of carbonate minerals from ellipsoids in ALH 84001. Composition components are: Cc, $CaCO_3$; Mg, $MgCO_3$; and Si, $FeCO_3$. Other minerals are Do, dolomite, $CaMg(CO_3)_2$, and An, ankerite, $CaFe(CO_3)_2$. Shaded field encloses all 'semiquantitative' analyses of *(3)*; open circles are quantitative analyses here; filled circles are quantitative analyses from *(3)*. Ranges 'A' and 'B' referred to in text.

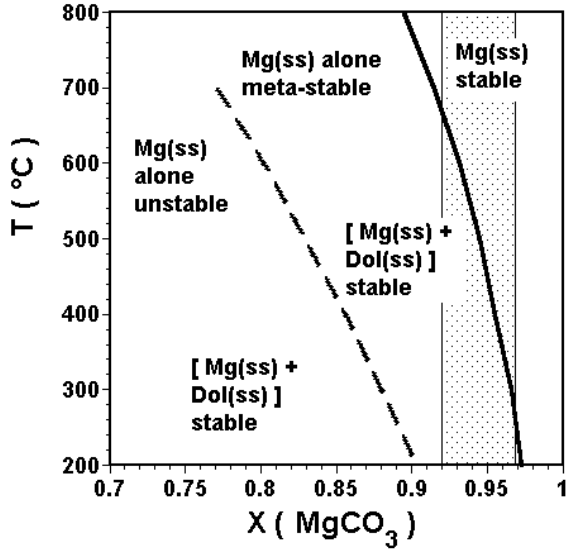

Figure 2. Locations of solvus and spinode curves in the $MgCO_3$-rich portion of in $CaCO_3$–$MgCO_3$. Shaded field is range of Fe-poor magnesite(ss) from ALH 84001 (*1,3*, Fig. 1). Solvus is solid line *(9)*, consistent with *(11,12)*; spinode is dashed line, calculated from thermochemical model of *(9)*, consistent with that of *(12)*. "Mg(ss)" denotes magnesite(ss), "Dol(ss)" denotes dolomite(ss). Unstable minerals would spontaneously decompose to compositions on the solvus. Note that the Fe-poor magnesites from ALH 84001 are all metastable below ~700ºC, but are not unstable until well below 200ºC.