

AN ANALYSIS OF THE SOLVUS IN THE CaS-MnS SYSTEM. R. A. Fogel, Department of Earth and Planetary Science, American Museum of Natural History, West 79th Street @ Central Park West, New York, NY 10024; bobby@amnh.org.

Introduction: The cubic sulfides oldhamite (CaS), niningerite (MgS) and alabandite (MnS) are essential components of the enstatite (E) chondrite and aubrite meteorites. The CaS-MgS-MnS-FeS-Fe system describes the thermodynamic behavior of these minerals in the enstatite meteorites. The work of [1] describes the behavior of the sulfides in this system between the temperatures (T) of 500°C and 1000°C. For the past 30 years, the interpretation of enstatite meteorite CaS and MnS sulfides has largely been confined to this ground-breaking study [1]. Unfortunately, the work of [1] is restricted to the subsolidus region; thus, studies attempting to interpret or model the igneous origin of aubrites and E chondrite components (i.e., chondrules) have had few tools available for interpreting the chemistry of supersolidus cubic sulfides. In an attempt to address this absence of data and to open up new insights on the formation of the E meteorites, a systematic study of low and high temperature regions of the CaS-MgS-MnS-FeS-Fe system has been initiated.

As a first step at understanding the phase equilibrium behavior of the larger cubic sulfide system, thermodynamic modeling has been undertaken. A literature search has revealed important studies on the binaries of the cubic sulfide system that have gone largely or totally unnoticed by the geochemical community. These studies come from the materials and metals research communities where an understanding of the physical and electrical properties of cubic sulfides is crucial to materials performance. Additionally, new experiments on the crucial binaries of greater sulfide system have begun.

System CaS-MnS: The current report focuses on a subset of the larger cubic sulfide system: the CaS-MnS binary. [1] showed that at $T < 500^\circ\text{C}$ no appreciable solid solution exists between CaS and MnS. At $T > 600^\circ\text{C}$ solid solutions of MnS in $\text{CaS}_{(\text{oldh})}$ and CaS in $\text{MnS}_{(\text{alab})}$ exist creating an asymmetric binary solvus. Oldhamite accommodates only half as much MnS as alabandite accommodates CaS. For example, at 800°C oldhamite can dissolve up to 5.8 mole % MnS whereas alabandite can dissolve up to 12 mole% CaS.

A study that extends this system up to 1300°C was extant at the time of [1] and went unnoticed by these authors and the greater geochemical community. The work of [2] explores the nature of the CaS-MnS solvus between 1000°C and 1300°C . [2] found that above 1000°C the solvus closes rapidly such that at 1300°C there is a complete solid solution between CaS and

MnS. At 1100°C the solvus extends from $\text{Ol}_{55}\text{Al}_{45}$ to $\text{Al}_{58}\text{Ol}_{42}$ where Al and Ol are acronyms for oldhamite and alabandite, respectively.

The data for the CaS-MnS binary is given in Fig.1.

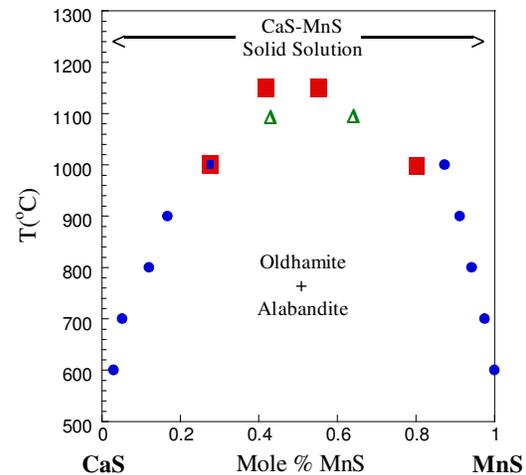


Figure 1: The CaS-MnS binary system. The experimental work of [1] is given by the glue dots and the experimental work of [2] ▲▲ is given by the orange squares.

It is immediately obvious that the data of [1] and [2] conflict with each other at 1000°C . While there is precise agreement between the two studies on the composition of the oldhamite at this temperature, the alabandite of [1] is much poorer in CaS (Ol_{13}) than that of [2] (Ol_{20}). If the data of [1] (blue dots) were extrapolated to higher T, the critical temperature (T_{crit}), representing the closure of the solvus, would occur at temperatures considerably higher than 1200°C . Moreover, the composition of T_{crit} would lie at a MnS-rich composition well to the right of the $\text{Ca}_{0.5}\text{Mn}_{0.5}\text{S}$ midpoint composition. In contrast, the data of [2] show that at 1150°C the solvus is nearly closed, so T_{crit} probably occurs somewhere near 1200°C . Furthermore, extrapolation of the data of [2] shows that the composition of T_{crit} would occur at CaS-rich compositions not far from the $\text{Ca}_{0.5}\text{Mn}_{0.5}\text{S}$ midpoint. Which data set is superior? The solution model holds the key.

Experimental: An experiment was conducted in the CaS-MnS binary. 0.18g of MnS (99.9% pure) and

0.16g of CaS (99.9+ pure; both on metals basis) were ground in a mortar and pestal under acetone. An aliquote of this material was palletized and placed at the bottom of a sealed SiO₂ tube followed by a SiO₂ spacer and pure (99.9+%) Fe metal (method of [1]). The tube was evacuated and welded shut. The assembly was run in an 1 atm furnace for 3 hours at 1300°C (to homogenize the sample), followed by an annealing for 4 days at the run T of 1100°C. The sample was sectioned and analyzed on the AMNH-LDEO Cameca SX100 microprobe.

Solution Modeling: A solution model for the CaS-MnS binary was constructed using a three-suffix Margules model [3]. The model has two parameters, WG_1 and WG_2 , related to the excess Gibbs free energy. Each of these parameters is related to T via the equality:

$$WG = WH - T \cdot WS$$

Where WH and WS are the Margules parameters related to the excess enthalpy and entropy. WG parameters were calculated for the data of [1], [2] and the current work from 700°C to 1150°C. The 600°C data of [1] was unusable for modeling since [1] reported no solid solution of MgS in oldhamite at this T. The following table summarizes the results in calories/mole:

T°C	WG ₁	WG ₂	Source
1300	Complete Solid Solution		[2]
1150	5799	5567	[2]
1100	5242	5780	This Work
1000	5177	5975	[2]
1000	4767	6647	[1]
900	5341	6685	[1]
800	5374	6766	[1]
700	6177	7473	[1]
600	No SS in oldhamite; 3% CaS in alabandite		[1]

The results show serious inconsistencies within and between each dataset. For example, the 800°C and 900°C values for WG_1 (derived from [1]) are essentially identical. Additionally, the two WG for 1000°C, derived from [1] and [2], each differ by more than 10%. Furthermore, the WG_1 at 1150°C derived from [2] is substantially higher than the 1000°C value derived from the same work.

A plot of the Margules parameters in the table shows the seriousness of the problem (Fig. 2). The WG_2 data, including that of the current work, appear to establish a rather clear linear trend (except for the 1000°C point derived from [1]). On the other hand, the WG_1 data of [1] establishes a roughly linear decreasing trend but is highly inconsistent with the 1150°C data of [2].

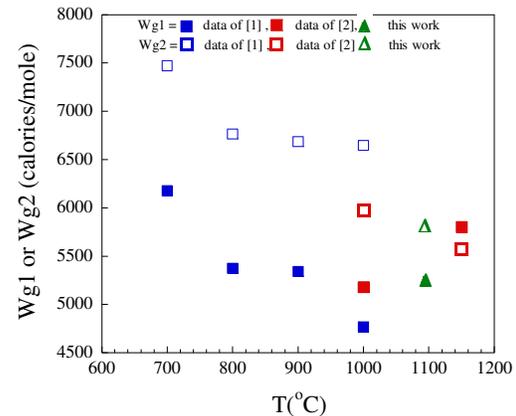


Figure 2: Margules parameters WG_1 and WG_2 . WG_1 is given by the solid squares and WG_2 is given by the open squares. The values derived from the data of [1] are coded blue and those derived from the data of [2] are coded orange.

Discussion: This analysis shows that the experimental compositions for the CaS-MnS system contain data elements that are probably flawed. The largest problems appear in the high T data above 900°C. The data of [2] appear to fit the modeling trend better than that of [1] at 1000°C. The data of [2] however, appear flawed for the 1150°C isotherm. If the solvus at 1150°C were a bit wider this would bring the Margules parameters into closer agreement with the linear trends established for the other temperatures. This being the case, the critical temperature is probably located somewhere between 1200°C and 1300°C.

Conclusions: Although the data of [1] and [2] are useful contributions to understanding the nature of the solvus in the CaS-MnS system, their data contain several serious inter- and intra- dataset inconsistencies. This calls into question the use of MnS in oldhamite and CaS in alabandite as geothermometers (as proposed by [1]) with the current dataset. A more robust dataset can only be achieved with new and more accurate experiments on this system. These experiments are being initiated.

References: [1] Skinner B. J. and Luce F. D. (1971) *Amer. Min.* 56, 1269-1296. [2] Kiessling R. and Westman C. (1970) *JISI* 208, 699-670. [3] Thompson J. B. Jr. (1967) *Researches in Geochemistry II*, 340-361.