

REEVALUATION OF THE ÅKERMANITE-GEHLENITE BINARY SYSTEM. R. A. Mendybaev^{1,2}, F. M. Richter^{1,2}, and A. M. Davis^{1,2,3}, ¹Department of the Geophysical Sciences, ²Center for Cosmochemistry, and ³Enrico Fermi Institute, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 (ramendyb@uchicago.edu).

Introduction: Melilite, a solid solution of åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), is one of the major constituents of the Ca-Al-rich inclusions (CAIs), representing the oldest material of the solar system. Therefore, knowledge of the phase and compositional relationships in the åkermanite-gehlenite binary system is very important for understanding the formation and evolution of CAIs.

The temperature-composition relationship in the åkermanite-gehlenite binary system was first determined by Ferguson and Buddington in 1920 [1]. They showed that åkermanite and gehlenite form a complete solid solution series with a minimum melting point of 1388°C (Åk_{73}). The solidus and liquidus curves were determined by identifying quenched products by optical microscopy. In 1941, Osborn and Schairer [2] used a fast quenching technique to confirm the liquidus position, but the solidus was shifted significantly to lower temperatures (e.g., from 1443°C to 1413°C for starting composition corresponding to Åk_{40}). Such a large shift in the solidus curve results in very large differences in composition of melilite crystallizing from the melt. For example, first melilite crystallizing from the melt with composition corresponding to Åk_{60} would be $\sim\text{Åk}_{45}$ according to [1] and only $\sim\text{Åk}_{30}$ according to [2]. The large discrepancy in the solidus position may be due to difficulties in quenching some glasses as was pointed out in [2], but also by lack of equilibrium between liquid and solid phases at low temperatures and slow crystallization kinetics of melilite from the melt. The latter seems to explain the difference in solidus position obtained from mostly 15 minute runs in [1] and several hours long runs in [2]. The purpose of this study was reevaluate the temperature-composition relationship in the åkermanite-gehlenite binary system by significantly increasing the run duration of the experiments and using modern techniques to analyze the quench products.

Experimental: The starting materials (Åk_{20} and Åk_{50}) were prepared by mixing (for ~ 1 hour) appropriate amounts of MgO, SiO₂, Al₂O₃ and CaCO₃ followed by melting at 1600°C for at least 3 hours in air. Quenched glasses were ground under ethanol in an agate mortar for one hour and 20-30 mg of the resulting powder mixed with polyvinyl alcohol were loaded into 2.5 mm Pt wire loops. The samples were placed into a Deltech vertical furnace, sintered at 1000°C in air, heated for 3-4 hours at $\sim 1230^\circ\text{C}$ in order to create melilite nucleation sites, and finally brought to a tem-

perature of interest. After heating a sample at fixed temperature for 10 to 20 hours it was quenched into water. Quenched products, in the form of pure glass from the experiments conducted above the liquidus, pure melilite from experiments below the solidus or coexisting glass and melilite at intermediate temperatures were examined by a JEOL JSM-5800LV scanning electron microscope with an Oxford/Link ISIS-300 x-ray microanalysis system.

Results and discussion: Quenched glass was chemically homogeneous in all our experiments. This reflects the fact that cation diffusion in CMAS melts is quite fast ($\sim 10^{-5}$ – 10^{-6} cm² s⁻¹ at 1500°, e.g. [3, 4]) resulting in relatively short (tens of minutes) homogenization times within the molten droplets.

Melilite crystals in quenched run products were slightly normally zoned (few mol. %) which is typical for materials crystallizing from a CMAS melt under oxidizing conditions (e.g., [4]). Normally zoned melilite usually forms due to change in melt composition caused by crystallization of melilite such that each new melilite layer would have slightly different composition unless the homogenization time of melilite is very short. Using experimentally measured interdiffusion coefficients in melilite from [5] and extrapolating them to slightly higher temperatures we estimate that the homogenization time of a 10 μm melilite grain with composition of Åk_{20} would be days at 1450°C and hours at 1550°C which is much longer than run durations used in [1] and [2], and somewhat longer than the run durations we used.

The data collected in [1] and [2] along with our results are summarized in Fig. 1. It clearly shows that the liquidus position obtained from our experiments is the same as that from the previous studies. The position of the solidus from our experiments, however, is significantly lower than that obtained in [1] and agrees quite well with results of Osborn and Schairer for åkermanitic compositions. For gehlenitic (Åk_5 to $\sim\text{Åk}_{25}$) compositions, however, solidus position from our experiments is shifted by as much as 20°C to lower temperatures. Such shift would result in composition of first melilite crystallizing from the melt to be up to ~ 5 mol. % more gehlenitic than that based on classical solidus curve of [2]. It is important to note that run durations in the experiments with composition Åk_{20} in [2] was only one hour long compared to at least 10 hours in our experiments.

The results presented here can be used to improve the thermodynamic model for melilite solid solution, and in conjunction with other data, to improve models for the temperature and composition of melilite crystallizing from CMAS liquids or condensing from nebular gases. The run products also provide melilite standards that we will use for determining matrix effects (if any) when measuring the isotopic composition of natural or synthetic melilite by laser ablation ICPMS.

References: [1] Ferguson J. B. and Buddington A. F. (1920) *Amer. J. Sci.*, **50**, 131-140. [2] Osborn E. F. and Schraier J. F. (1941) *Amer. J. Sci.*, **239**, 715-763. [3] Richer F. M, Davis A. M., and Mendybaev R. A. (2002) *LPS XXXIII*, Abstract #1901. [4] Mendybaev R. A., Richter F. M., and Davis A. M. (2006) *GCA*, in press. [5] Nagasawa H., Suzuki T, Ito M., and Morioka M. (2001) *Phys. Chem. Miner.*, **28**, 706-710.

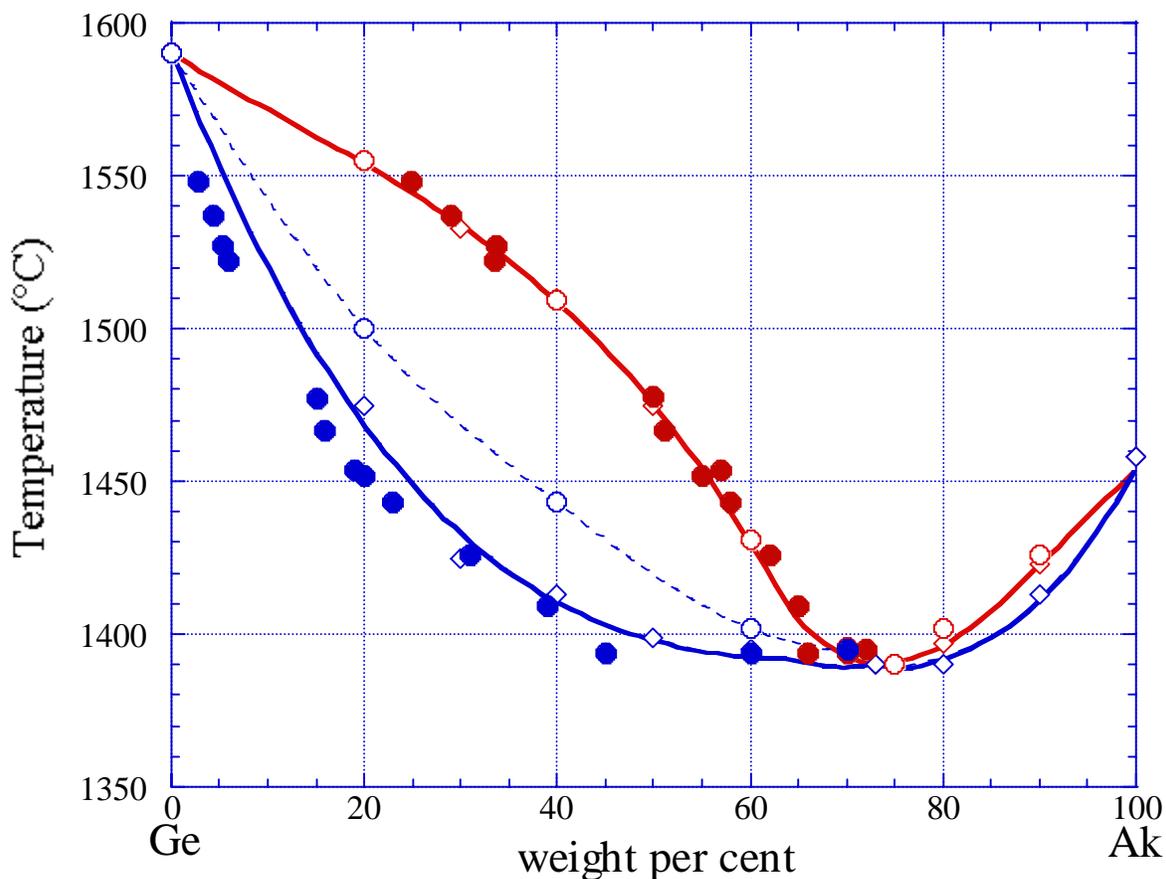


Fig.1. Temperature-composition relationship for the åkermanite-gehlenite binary system. Open symbols show the results from [1] (circles) and [2] (diamonds), filled circles show our data. The red and blue lines represent liquidus and solidus curves, respectively, from [2]. The dashed blue line represents the solidus curve from [1].