

**A THERMODYNAMIC STUDY OF INVERSION OF MgO AND SiO<sub>2</sub> RELATIVE FUGACITY AT CAI EVAPORATION.** S. I. Shornikov<sup>1</sup>, O. I. Yakovlev<sup>1</sup>, M. A. Ivanova<sup>1,2</sup>. <sup>1</sup>Vernadsky Institute of Geochemistry & Analytical Chemistry of RAS, Kosygin st., 19, Moscow, 119991, Russia; e-mail: [sergey.shornikov@gmail.com](mailto:sergey.shornikov@gmail.com). <sup>2</sup>Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC, 20560.

In the framework of the developed semi-empirical thermodynamic model of the evaporation of oxides from refractory melts [1], we studied the changes of the residual melt compositions of Ca–Al–inclusions in the chondrite (CAIs) and Krymka ordinary chondrite at 2300 K. The used thermodynamic model was based on the theory of ideal associated solutions and the experimental data of oxide activities in melts of the CaO–MgO–FeO–Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>–SiO<sub>2</sub> system found by Knudsen mass-spectrometric effusion method in the temperature range of 1600–2500 K. The accuracy of the approach was confirmed earlier [2] by the experimental data on two different samples. The first of them was a sample of lunar alumina basalt whose evaporation was studied by the mass spectrometric method using Knudsen tungsten effusion cells at 1577–2502 K [3]. The second sample was a synthetic oxide material with a solar composition whose vacuum evaporation was studied using graphite crucible at 1673–2273 K [4].

As shown in Fig. 1a, despite the differences in the considered initial compositions – CAIs, 5aN, AOA, FAN, Krymka ordinary chondrite [5–8] there is a definite similarity in the change of the ratio of the most refractory melt components – CaO and Al<sub>2</sub>O<sub>3</sub> at evaporation. This change is accompanied by inversion of MgO / SiO<sub>2</sub> relative volatility typical for most compositions that is the MgO predominant evaporation (Fig. 1b). However, evaporation of the 5aN composition is the opposite – the ratio is increasing.

Fig. 2 shows the melt composition change at evaporation of the AOA-52E and the 5aN compositions, and the oxide activities  $a_i$  in the melts at 2300 K. The initial melt compositions of the AOA-52E and the 5aN are in [6]. It is possible to notice the MgO predominance (as compared to SiO<sub>2</sub>) in the initial composition of AOA-52E and conversely the SiO<sub>2</sub> predominance (as compared to MgO) in the initial composition of 5aN. The inversion of the ratios of MgO / SiO<sub>2</sub> occurs at evaporation. It correlates with the inversion of the oxide activities (oxide volatilities).

To explain these observations, we consider the oxide activities in the CaO–MgO–SiO<sub>2</sub> and MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> ternary systems at 2300 K and at the typical molar ratio of MgO / SiO<sub>2</sub> = 2 / 3 (Fig. 3). Fig. 3a shows that the increase of the CaO content in the CaO–MgO–SiO<sub>2</sub> system leads to a decrease in SiO<sub>2</sub> activity (and therefore volatility) and increases the MgO activity (volatility). In the case of the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system (Fig.

3b) the increase in the Al<sub>2</sub>O<sub>3</sub> content leads to a much lesser extent reduces SiO<sub>2</sub> activity (volatility) (compared to the CaO–MgO–SiO<sub>2</sub> system), and significantly reduces MgO activity (volatility) (compared with CaO–MgO–SiO<sub>2</sub> system). In particular, for the CaO–MgO–SiO<sub>2</sub> system containing 50 mol. % CaO  $a(\text{SiO}_2) = 0.0032$  and  $a(\text{MgO}) = 0.61$  (Fig. 3a), and for the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system containing 50 mol. % Al<sub>2</sub>O<sub>3</sub>  $a(\text{SiO}_2) = 0.11$  and  $a(\text{MgO}) = 0.066$  (Fig. 3b).

Thus, the Al<sub>2</sub>O<sub>3</sub> predominance (compared to CaO) in the 5aN composition (Fig. 1) shows the ordinary ratio of MgO / SiO<sub>2</sub> relative volatility as for the case of simple oxides – MgO and SiO<sub>2</sub> (Fig. 2c, d). In the case of low Al<sub>2</sub>O<sub>3</sub> content (compared to CaO) we observe inversion of MgO / SiO<sub>2</sub> relative volatility leading to the MgO preferential evaporation (compared to SiO<sub>2</sub>) from other presented melts (Fig. 2a, b).

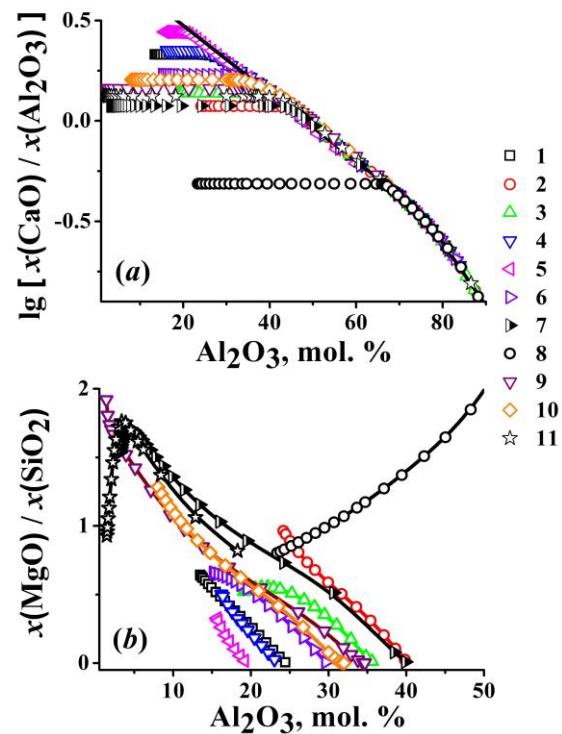


Fig. 1. The calculated ratio of CaO / Al<sub>2</sub>O<sub>3</sub> (a) and MgO / SiO<sub>2</sub> (b) in the residual melts at the evaporation at 2300 K. Designations: 1 – 3N-1, 2 – 3N-6, 3 – 3N-7, 4 – 3N-12, 5 – 3N-20, 6 – 3N-Host, 7 – AOA-52E, 8 – 5aN [5, 6]; 9 – FAN1, 10 – FAN2 [7]; 11 – Krymka ordinary chondrite [8].

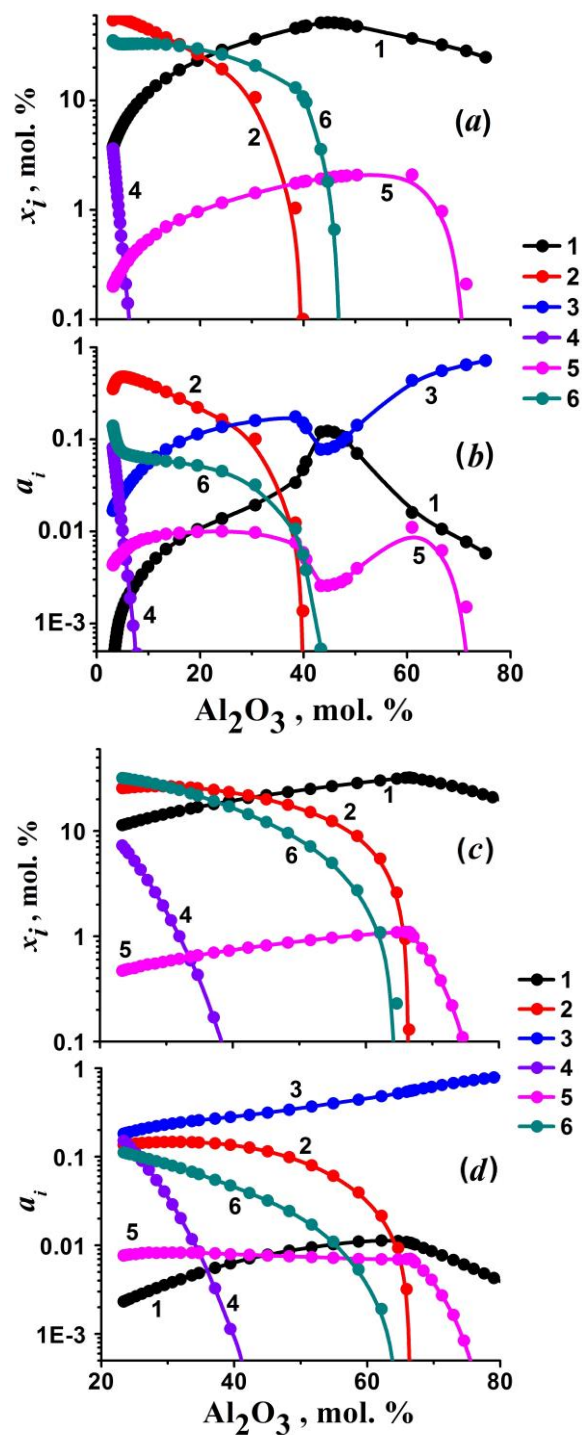


Fig. 2. The calculated change in compositions of CAIs melt (a, c) and the oxide activities (b, d) in residual melts of AOA-52E (a, b) and 5aN (c, d) at evaporation at 2300 K. Designations: 1 – CaO, 2 – MgO, 3 –  $\text{Al}_2\text{O}_3$ , 4 – FeO, 5 –  $\text{TiO}_2$ , 6 –  $\text{SiO}_2$ .

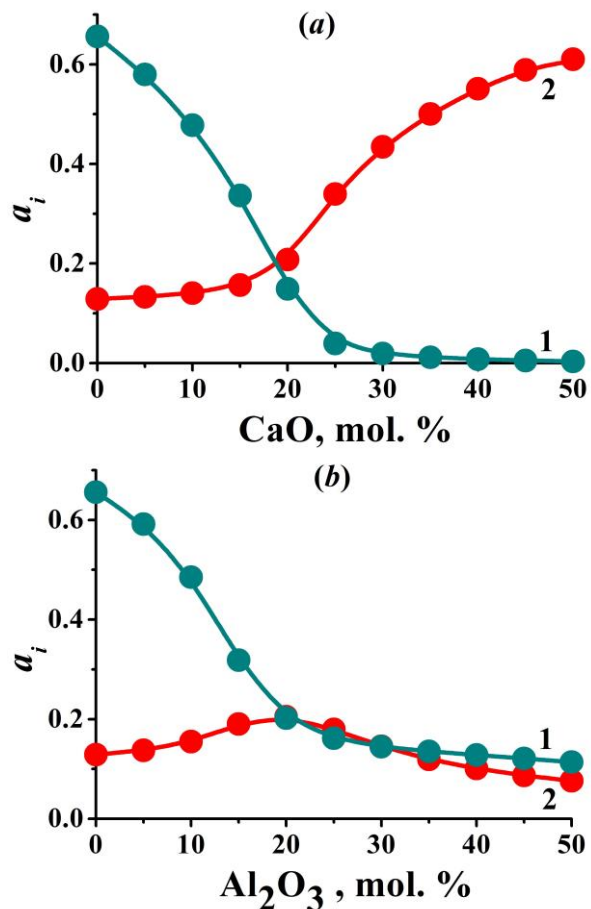


Fig. 3. The calculated values of activities of  $\text{SiO}_2$  (1) and MgO (2) vs. the CaO content in the CaO–MgO– $\text{SiO}_2$  system (a) and vs. the  $\text{Al}_2\text{O}_3$  content in the MgO– $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$  system (b) at 2300 K and at the typical molar ratio of  $\text{MgO} / \text{SiO}_2 = 2 / 3$ .

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**References:** [1] Shornikov S. I. (2009) *Herald Earth Sci. Dept. RAS*, 27, 1–4 (in Russian). [2] Shornikov S. I. (2016) *IX All-Russian Conf. on "Ceramics and composite materials"*, 446–449 (in Russian). [3] Markova O. M. et al. (1986) *Geochemistry Int.*, 24, 1559–1569. [4] Wang J. et al. (2001) *GCA*, 65, 479–494. [5] Ivanova M. A. et al. (2015) *Meteoritics & Planet. Sci.*, 50, 1512–1528. [6] Ivanova M. A. et al. (2017) *LPSC XXXXVIII*. [7] Mendybaev R. A. (2013) *GCA*, 123, 368–384. [8] Yakovlev O. I. et al. (1983) *LPS XIV*, 869–870.