THERMODYNAMIC STUDY OF DOUBLE INVERSION OF MgO AND SiO₂ RELATIVE FUGACITY AT CAIs EVAPORATION. S. I. Shornikov and O. I. Yakovlev, Vernadsky Institute of Geochemistry & Analytical Chemistry of RAS, Kosygin st., 19, Moscow, 119991, Russia; e-mail: sergey.shornikov@gmail.com.

In the framework of the developed semi-empirical thermodynamic model of silicate melt evaporation [1], we studied the changes of the residual melt compositions of Ca–Al–inclusions in the chondrite (CAIs) at 2173 K. The 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_2O_3–TiO_2–SiO_2 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 sample of lunar alumina basalt whose evaporation was studied by the mass spectrometric method using Knudsen tungsten effusion cells at 1577–2502 K [3] and the synthetic oxide material with a solar composition whose vacuum evaporation was studied using graphite crucible at 1673–2273 K [4].

The model describes satisfactorily the CAIs composition evaporation – *5aN-3* [5, 6], *CAI4* [7] and Type B CAI (*CAI B*) [8] (Fig. 1). Their initial composition is given in Table 1.

Table 1. The CAIs initial composition (mol %).

Sample	CaO	MgO	Al_2O_3	SiO_2
5aN-L	11.17	25.00	23.83	40.00
5aN-3	14.43	25.60	23.83	36.14
5aN-H	17.03	27.98	23.23	31.76
CAI4	24.10	24.32	15.52	36.06
CAI B	26.76	17.05	11.41	44.78

Despite the differences in the considered CAIs initial compositions there is a definite similarity in the changes in residual melts at evaporation (Fig. 1, 2). This change is accompanied by inversion of MgO / SiO_2 relative volatility typical for most compositions that is the MgO predominant evaporation (Fig. 2). However, evaporation of the *5aN-3* composition is the opposite – the ratio is increasing and then is decreasing.

We have studied the evaporation of two compositions with a few low *(5aN-L)* and a few high (*5aN-H*) amounts of CaO in the melt to explain this phenomenon (Table 1).

The variations of amount of CaO in the melt led to the SiO_2 preferential evaporation in the *5aN-L* melt, and to the MgO preferential evaporation in the *5aN-H* melt (Fig. 3). Moreover, the initial amount of MgO in the *5aN-H* melt was larger than in the *5aN-L* melt (Table 1).

There is the double inversion in the MgO / SiO_2 ratio of in the case of the *5aN-3* composition: the first (about 35 mol % Al_2O_3) is leading to the MgO predominance in the melt and the second (about 60 mol % Al_2O_3) is leading to the SiO_2 predominance in the melt (Fig. 3, 4).
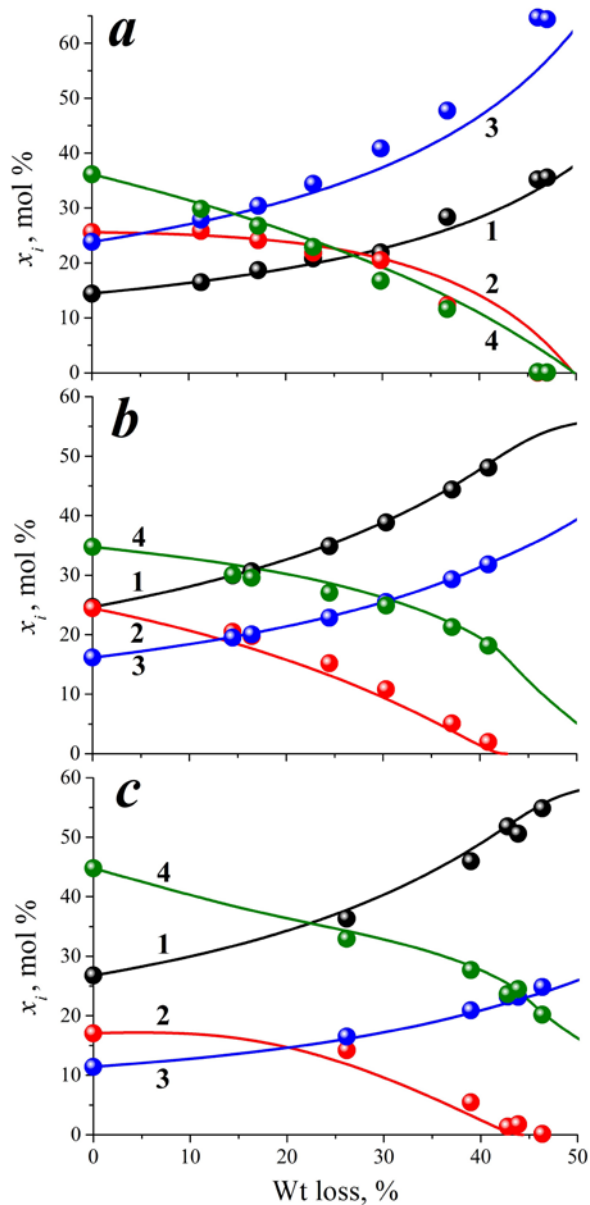

Fig. 1. The experimental (points) and calculated (lines) changes in residual melts of *5aN-3* (*a*), *CAI4* (*b*) and *CAI B* (*c*) at evaporation at 2173 K. Designations: 1 – CaO, 2 – MgO, 3 – Al_2O_3, 4 – SiO_2.
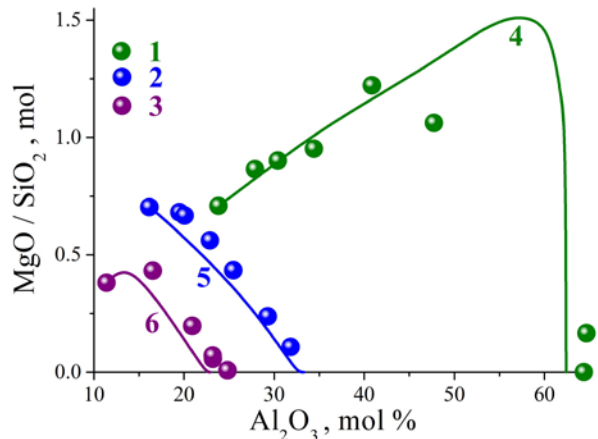
Fig. 2. The experimental (1–3) and calculated (4–6) the MgO / SiO$_2$ molar ratio changes in residual melts of *5aN-3* (1, 4), *CAI4* (2, 5) and *CAI B* (3, 6) at evaporation at 2173 K.
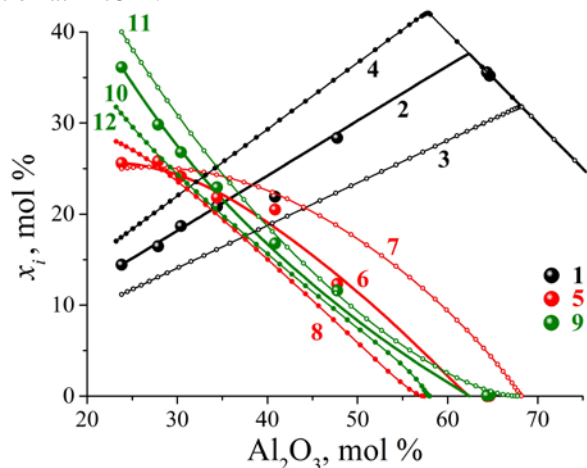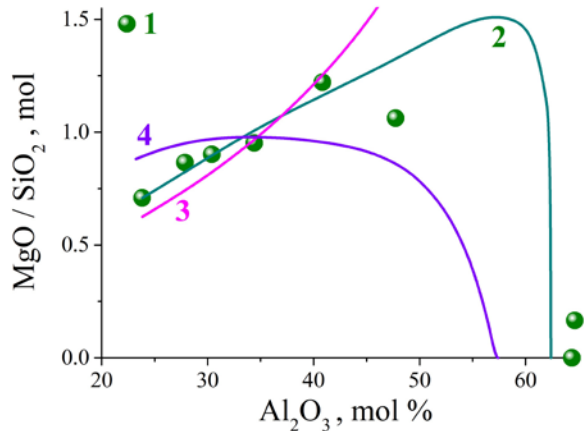

Fig. 4. The experimental (1) and calculated (2–4) MgO / SiO$_2$ molar ratio changes in residual melts of *5aN-3* (1, 2), *5aN-L* (3) and *5aN-H* (4) at evaporation at 2173 K.

Fig. 3. The experimental (1, 5, 9) and calculated (2-4, 6-8, 10-12) changes in residual melts of *5aN-3* (1, 2, 5, 6, 9, 10), *5aN-L* (3, 7, 11), *5aN-H* (4, 8, 12) at evaporation at 2173 K. Designations: 1-4 – CaO, 5-8 – MgO, 9-12 – SiO$_2$.
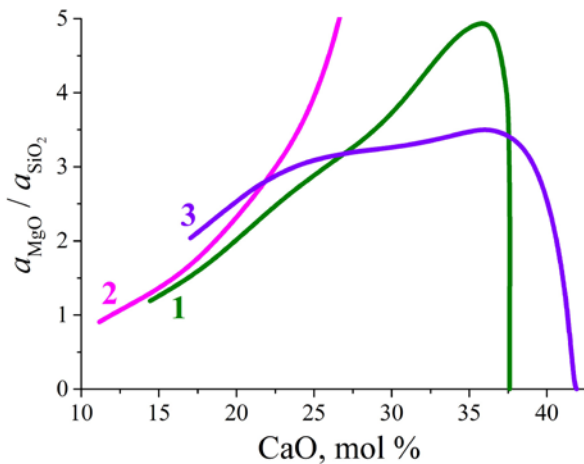

Fig. 5. The calculated MgO / SiO$_2$ activity ratio changes in residual melts of *5aN-3* (1), *5aN-L* (2) and *5aN-H* (3) at evaporation at 2173 K.

Thus, during the CAIs melts evaporate at high temperatures, the SiO$_2$ and MgO fugacities are inverted: SiO$_2$, which is more volatile than MgO, becomes less volatile when melts rich in refractory CaO and Al$_2$O$_3$ evaporate. This fugacity inversion can be realistically explained within the framework of Korzhinsky's theory of acid–base interaction between components in silicate melts [9]. According to this theory, an increase in CaO concentration in the melt increases its basicity, and this, in turn, increases the activity (and fugacity) of MgO and decreases those of SiO$_2$ (Fig. 5). In the real compositions of the CAIs in chondrites, the MgO / SiO$_2$ ratio systematically decreases with an increase in the CaO concentration under the effect of acid–base interaction (Fig. 2).

References: [1] Shornikov S. I. et al. (2017) *LPS XLVIII*, Abstract #1134. [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) *Geochem. Int.*, 24, 1559–1569. [4] Wang J. et al. (2001) *GCA*, 65, 479–494. [5] Ivanova M. A. et al. (2017) *LPS XLVIII*, Abstract #1363. [6] Ivanova M. A. et al. (2018) *LPS XLIX*. [7] Mendybaev R. A. and Richter F. M. (2016) *LPS XLVII*, Abstract #2929. [8] Richter F. M. et al. (2007) *GCA*, 71, 5544–5564. [9] Yakovlev O. I. et al. (2017) *Geochem. Int.*, 55, 251–256.