## ENTHALPIES OF FORMATION OF NATURAL ZEOLITES - GISMONDINE, GARRONITE AND AMICITE

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The objects of investigation were natural zeolites with aluminosilicate framework, formed by doubly connected 4-ring chains of tetrahedra [{Al,Si}O<sub>4</sub>], such as calcium gismondine, sodium garronite and sodium-potash amicite.

The thermal behavior of studied zeolites was investigated by differential thermal (DTA) and thermogravimetric (TG and DTG) analyses in temperature range 20-1300°C.

The thermochemical study was performed on a heat-flux high-temperature Tian-Calvet microcalorimeter. To avoid zeolite decomposition at high temperature the "transposed temperature drop solution calorimetry" method was used to obtain enthalpies of formation of minerals. In each run the sample (3-10 mg) was dropped from room temperature into molten  $2PbO \cdot B_2O_3$  held at 973 K. The heat effect measured was, thus, the sum of the heat content and the enthalpy of solution of the mineral at T=973 K:  $[(H^o_{973}-H^o_{298,15})+\Delta H^o_{sol.973}]=\Delta H^o_{dropsol.}$ 

The standard enthalpies of formation from the elements were obtained using experimental and reference thermodynamic data for the constituent oxides.

The values of enthalpies of formation of gismondine, garronite and amicite of theoretical composition were estimated.

The obtained thermodynamic properties of zeolites are of considerable importance in estimating the stability fields of these minerals and associated phases and modeling of zeolites syntheses and cation exchanges processes.

## Enthalpies of formation of gismondine, garronite and amicite from the elements at T=298.15 K

| Natural gismondine  | Theoretical gismondine   |
|---|--|
| $(Ca_{0.85}Na_{0.07}K_{0.01.})[Al_{1.93}Si_{2.11}O_8] 4.32H_2O$                         | Ca[Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ]·4.5H <sub>2</sub> O                      |
| $\Delta H^{o}_{f,el} = -5542 \pm 38 \text{ kJ/mol}$                                     | $\Delta H^{o}_{f,el} = -5631 \pm 38 \text{ kJ/mol}$  |
| Natural garronite   | Theoretical garronite  |
| $(Ca_{2.66}Na_{0.54}K_{0.10}Sr_{0.02})[Al_{6.43}Si_{9.67}O_{32}]$ 12.98H <sub>2</sub> O | NaCa <sub>2.5</sub> [Al <sub>6</sub> Si <sub>10</sub> O <sub>32</sub> ]·14.0H <sub>2</sub> O |
| $\Delta H^{o}_{f,el} = -20392 \pm 42 \text{ kJ/mol}$                                    | $\Delta H^{\circ}_{f,el} = -20587 \pm 44 \text{ kJ/mol}$                                     |
| Natural amicite   | Theoretical amicite  |
| $(K_{3.88}Na_{3.84}Ca_{0.22})[Al_{8.06}Si_{7.90}Fe_{0.04}O_{32}]~9.86H_2O$              | $K_4Na_4[Si_8Al_8O_{32}]\cdot 10H_2O$  |
| $\Delta H^{o}_{f,el} = -19925 \pm 70 \text{ kJ/mol}$                                    | $\Delta H^{o}_{f,el} = -19904 \pm 70 \text{ kJ/mol}$   |