



Thermodynamics of hydrothermal systems with oxalate ion

I.L. Khodakovskiy (1) and O.A. Devina (2)

(1) Dubna University, Universitetskaya, 19, 141980, Dubna, Moscow Region, Russia, (2) Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS, Kosygin str., 19, 117975, Moscow, Russia

The geochemical and industrial significance of oxalates have led to great interest in the behavior of oxalate ion in hydrothermal systems.

On the basis of a study by G.B. Naumov et al (1971) of gaseous-liquid inclusions it is shown that whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) which was found in quartz-calcite-fluorite veins in the uranium ore deposit of the Eastern Transbaikalian region was formed at temperatures about 150°C and pressure CO_2 of 600-860 atm. The isotopic composition of carbon for these hydrothermal whewellite samples was determined by Galimov et al (1975): $\Delta^{13}\text{C}$ from -1.56 to -2.22‰.

In a continuation of the study of organic-acid-water-rock interactions the thermodynamics of hydrothermal equilibria for the systems Ox-H, Ox-H-Ca, Ox-H-Mg (where Ox = $\text{C}_2\text{O}_4^{2-}$), are described up to 200°C .

The key network reactions and compounds related to the aqueous ion $\text{C}_2\text{O}_4^{2-}$ are discussed and used to define the key values. The critical evaluation of thermodynamic properties for this ion is a part of the development of the new key values system for the joint thermodynamic database in the Internet. The evaluation involves the analysis of the enthalpy changes, Gibbs energy changes, and the entropy calculations for all key substances in the key network. A consistent set of thermodynamic property values is given for $-\text{H}_2\text{C}_2\text{O}_4(\text{cr})$, $-\text{H}_2\text{C}_2\text{O}_4(\text{aq})$, $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{cr})$, $\text{CaC}_2\text{O}_4(\text{cr})$, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{cr, whewellite})$, $\text{NaC}_2\text{O}_4(\text{cr, natroxalate})$, $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}(\text{cr, glushinskite})$ and aqueous species $\text{C}_2\text{O}_4^{2-}$, HC_2O_4^- , $\text{H}_2\text{C}_2\text{O}_4^\circ$, $\text{CaC}_2\text{O}_4^\circ$.

This study was funded by Russian Foundation for Basic Research (project N 07-05-01108).