

## Thermodynamics of crystalline iron(III) arsenates scorodite, kaňkite, and bukovskýite

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The crystalline ferric arsenates are candidates for arsenic storage at sites contaminated by this metalloid. The remediation technologies today usually involve precipitation of poorly crystalline hydrous ferric oxide which is capable of adsorbing As(V) or crystalline scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O). We seek alternatives which could be used for such processes, if found to be advantageous. To this end, we study the mineralogy and geochemistry of various sites polluted with arsenic and measure the solubility of the arsenate minerals by calorimetric techniques.

In this work, we present the formation enthalpies ( $\Delta_f H^\circ$ ) of three arsenates, scorodite, kaňkite (FeAsO<sub>4</sub>·3.5H<sub>2</sub>O), and bukovskýite (Fe<sub>2</sub>(AsO<sub>4</sub>)(SO<sub>4</sub>)(OH)·9H<sub>2</sub>O). The  $\Delta_f H^\circ$  values were determined by acid-solution calorimetry at  $T = 298$  K in 5 N HCl as the solvent, using HCl·9.96H<sub>2</sub>O,  $\gamma$ -FeOOH,  $\alpha$ -MgSO<sub>4</sub>, MgO, KCl, and KH<sub>2</sub>AsO<sub>4</sub> as the reference compounds. The resulting values for scorodite, kaňkite, and bukovskýite are  $-1508.9 \pm 2.9$ ,  $-1940.2 \pm 2.8$ , and  $-4742.2 \pm 3.8$  kJ/mol, respectively. We have also determined the  $\Delta_f H^\circ$  value for anhydrous FeAsO<sub>4</sub> (not known as a mineral) as  $-899.0 \pm 3.0$  kJ/mol.

Scorodite served as a test of our approach as many studies have been conducted on this phase (e.g. [1]). Using our  $\Delta_f H^\circ$  value and a Kopp rule estimate of entropy of 180.3 J/mol·K, we arrive at a solubility product of  $-25.4$ , in good agreement with  $-25.8$  in [1] or  $-25.4$  in [2]. Our data also predict kaňkite to be unstable with respect to scorodite, in line with the rare occurrence of kaňkite in nature.

The results presented here will be soon complemented by heat capacity measurements and entropy calculations. Once these data are secured, calculations of phase diagrams for the title and related phases will be done and presented.

[1] Langmuir, D. Mahoney, J. Rowson, J. (2006) *Geochim. Cosmochim. Acta* **70**, 2942–2956. [2] Bluteau, M.-C. Demopoulos, G.P. (2007) *Hydrometallurgy* **87**, 163–177.

## Sr and Nd isotope disequilibrium in migmatites and leucogranites, the Higo metamorphic terrane, Japan

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Sr and Nd isotope compositions of migmatites and leucogranites in the highest grade zone of the Higo low- $P$ /high- $T$  (andalusite-sillimanite type) metamorphic terrane, central Kyushu, Japan, suggest that the nebulitic migmatites (diatexite) formed due to melt infiltration into the pelitic gneisses, and the stromatic migmatites (metatexite) due to *in situ* partial melting of the pelitic gneisses. The nebulitic migmatites occur as a 3 m-thick layer and is sandwiched between 2 m-thick layers of stromatic migmatites within pelitic gneisses. Both types of migmatites are parallel to the foliation of the gneisses. The leucogranites occur as a few to ten cm-thick layer or lens within the gneisses. The nebulitic migmatites preserve a record of large magnitude Sr and Nd isotope disequilibrium with the pelitic gneisses, which show the isotope equilibrium with the stromatic migmatites. The nebulitic migmatites have higher epsilon Nd (T) values of  $-0.6$  and P<sub>2</sub>O<sub>5</sub> contents of 0.42 wt.% than those of the pelitic gneisses ( $-2.1$  and 0.18 wt.%) and stromatic migmatites ( $-3.1$  and 0.10 wt.%). The initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio,  $I_{Sr}$ , of the nebulitic migmatite, 0.70572, is lower than that of the pelitic gneisses and stromatic migmatites ranging from 0.70792 to 0.70857. Some leucogranites with high P<sub>2</sub>O<sub>5</sub> contents of 0.91 wt.% have the higher epsilon Nd (T) values of  $+3.4$  than, and similar  $I_{Sr}$  value of 0.70800 to that of the pelitic gneiss and stromatic migmatites. Based on the Sr and Nd isotope characteristics and P<sub>2</sub>O<sub>5</sub> contents, *in situ* partial melting of the pelitic gneisses could form the stromatic migmatites, but could not produce the nebulitic migmatites with the higher epsilon Nd (T) value and P<sub>2</sub>O<sub>5</sub> contents. The higher epsilon Nd (T) value and P<sub>2</sub>O<sub>5</sub> contents may imply the participation of externally derived melt during the formation of nebulitic migmatites. Dissolution of apatite into the melt under dry and high-temperature conditions might produce such a high degree of Nd isotope disequilibrium and high P<sub>2</sub>O<sub>5</sub> contents.