Thermodynamic properties of spessartine

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Garnet is an important rock-forming mineral and knowledge of its thermodynamic properties is imperative in order to undertake various investigations. Many thermodynamic studies on aluminosilicate garnet have been made. However, there are still gaps of knowledge concerning the various thermodynamic functions for even the garnet end-members. This is the case for spessartine.

The heat capacity of two different synthetic spessartine samples was measured on 20-30 mg-size samples in the temperature range 2 to 864 K by heat-pulse calorimetry (HPC) and differential scanning calorimetry (DSC). Samples were synthesized in two different laboratories and characterized by X-ray powder diffraction and electron-microprobe analysis. The heat capacity data show a prominent lambda transition with a peak at 6.2 K, which is interpreted to be the result of a paramagnetic-antiferromagnetic phase transition. The calorimetric standard entropy for the two samples is S° = 334.6 ± 2.7 J/mol/K and 336.0 ± 2.7 J/mol·K. The preferred standard third-law entropy for spessartine is S° = 335.3 ± 3.8 J/mol/K. The DSC data around ambient T agree well with the HPC data and can be represented by the C_p polynomial at T > 250 K as:

$$C_p^{Sps}\,(\mathrm{J/mole/K}) = 610 - 3060 \cdot T^{-0.5} - 1.45 \cdot 10^{7} \cdot T^{-2} + 1.82 \cdot 10^{9} \cdot T^{-3}.$$

The vibrational heat capacity was analyzed giving $S_{vib}^{298.15}$ = 297.7 J/mol/K at 298.15 K. The magnetic heat capacity and entropy of spessartine, S_{mag}, were also calculated. S_{mag} is 38.0 J/mol/K, which is 85% of the maximum possible magnetic entropy given by the Boltzmann relation (i. e. 3Rln6 = 44.7 J/mol/K.)

Using these new calorimetric data, together with high P-T experimental phase equlibrium data on Mn-Mg partitioning between garnet and olivine, allows calculation of the standard enthalpy of formation of spessartine. This gives $\Delta H^{\circ}_{f,\,Sps} = -5693.6 \pm 1.4$ kJ/mol, a value that is nearly 50 kJ more negative than published estimates. The Gibbs free energy of spessartine was also calculated as $\Delta G^{\circ}_{f,\,Sps} = -5364.3$ kJ/mol at 298.15 K.

Ocean oxygenation after the rise of animals

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The evolution of the Earth's biosphere is intimately linked to the redox evolution of the oceans and atmosphere [e.g. 1]. We use Mo elemental and isotopic abundances in sedimentary rocks to explore this relationship through the early stages of animal evolution.

The isotope composition of Mo in sedimentary rocks, δ^{98}Mo, depends critically on the local redox environment, with strong fractionation from seawater δ^{98}Mo in fully oxygenated deep ocean sediments, little fractionation in oxygen-poor sediments where sulfide is present near the sediment-water interface, and no fractionation in euxinic sediments deposited under a highly sulfidic water column. Seawater has a homogeneous isotope composition, δ^{98}Mo, determined by the input and proportions buried into the three major sinks. It can be used as an indicator for global oxygenation, when viewed in combination with sedimentary Mo/TOC. This is possible, due to a 100-1000 fold faster accumulation rate in sulfidic sediments than in deep oxic sediments which means seawater [Mo] and δ^{98}Mo respond differently to the expansion of each sink. We find that seawater Mo and δ^{98}Mo increased over the last 1800 Myr.

Our results indicate two episodes of oxygenation. The first occurs in the late Neoproterozoic and is coincident with the emergence of large bilaterian animals, reinforcing ideas that Earth-surface oxygenation may have enabled this evolution. The second occurs around 400 million years ago and correlates with the expansion of vascular plants, which likely contributed to increased oxygenation through the enhanced burial of organic carbon in sediments. It also correlates with an evolutionary radiation of ‘high energy’ predators [2], consistent with further oxygen-related environmental forcing of early animal evolution.

[1] Knoll (1992) *Science* **256**, 622. [2] Bambach (1999) *Geobios* **32**(2), 131–144.