Experimentally determined standard properties for $MgSO_4 \cdot 4H_2O$ (starkeyite) and $MgSO_4 \cdot 3H_2O$; A revised internally consistent thermodynamic dataset for magnesium sulfate hydrates

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A number of different hydrated forms of $MgSO_4 \cdot nH_2O$ ($1 \leq n \leq 11$) are known to exist on Earth and also on Mars. Recently, the enthalpies of formation from the elements ($\Delta_f H^0_{298}$) of kieserite (n = 1), sanderite (n = 2), hexahydrite (n = 6), and epsomite (n = 7) were measured [1]. Now, we have obtained $\Delta_f H^0_{298}$ of synthetic $MgSO_4 \cdot 3H_2O$ and $MgSO_4 \cdot 4H_2O$ (starkeyite) by solution calorimetry in water at T = 298.15 K. The resulting values are –2210.3 ± 1.3 and –2498.7 ± 1.1 $kJmol^{-1}$ for the trihydrate and starkeyite, respectively.

The standard entropy of starkeyite was derived from low-temperature heat capacity measurements using a PPMS® system [2] in the temperature range 5 K < T < 300 K resulting in S^0_{298} (starkeyite) = 254.5 ± 2.0 $J \cdot K^{-1} mol^{-1}$.

Additionally, DSC measurements with a Perkin Elmer Diamond DSC in the temperature range 280 K < T < 295 K were performed to check the reproducibility of the PPMS® measurements around ambient temperature.

All Mg sulfate hydrates change their hydration state in response to the local temperature and humidity conditions. Based on recently reported equilibrium relative humidities [3] and the new standard properties described above, the internally consistent thermodynamic database for the $MgSO_4 \cdot nH_2O$ system [1] was refined.

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Ore deposits and the SCLM

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The single largest influence on the formation of Earth's ore deposits has been the generation of the Archean subcontinental lithospheric mantle (SCLM). Geological and geochemical evidence suggests that subduction-like processes, and the progressive depletion of the convecting mantle, began at least 3.8-4.0 Ga ago, but there are few large ore deposits older than ca 3 Ga. Re-Os data suggest that the formation of the Archean cratonic SCLM began ca 3.5 Ga ago, and reached a peak around 3 Ga. This primitive SCLM was much more depleted than is commonly recognised; it was essentially a magnesian dunite, the residue after large-scale extraction of crustal material from rising plumes/mantle overturns. Since its formation it has been progressively refertilised by fluids and melts from the asthenosphere and subducting slabs. At present ≥70% of continental crust is underlain by Archean-aged SCLM. The coming of the SCLM has had major effects on the types of ore deposits and their distribution in space and time. (1) *Preservation:* The Archean SCLM is buoyant relative to the asthenosphere and resists subduction, giving its overlying crust a "life raft"; the more fertile SCLM beneath younger terrains is denser, and can be delaminated and recycled, leaving its overlying crust unprotected from the convecting mantle. Ore deposits generated in juvenile arcs, some continental arcs and rifted-margin basins thus are unlikely to survive subsequent orogenies. (2) *Lithospheric architecture*; the deep roots of old continents focus fluid flow toward their margins, and act as physical guides for plume melting. (3) *A durable metasomatic reservoir*; the refertilisation of the ancient SCLM has built up the concentrations of metals, which can be tapped by ascending magmas. There are many komatiites, but those fertile in Ni-Cu-PGEs are limited to ages <2.9 Ga, and lie along ancient craton margins. Kimberlites may be generated by low-degree melting of SCLM, but only those that intersect previously metasomatised SCLM during their ascent will carry many diamonds. (4) *New ore-forming environments*. The coming of the SCLM provided tectonic settings that did not previously exist, allowing the generation of new types of ore deposit: large foreland basins (banded iron formations), craton margins (Ni-Cu-PGE), back-arc/pericratonic basins and passive margins (granular iron formations, Pb-Zn, Mississippi Valley-type deposits).