

Development of an aqueous activity model for geothermal conditions

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Geochemical and reactive transport modeling of fluid-rock interaction in enhanced geothermal systems is a challenging task because of the high temperatures, pressures, and sometimes extreme fluid salinities. For such systems, extended thermodynamic databases and activity models are needed to accurately predict fluid-mineral equilibrium reactions. Typically, the Pitzer activity model is used for high salinity fluids. We tested the EUNIQAC local composition model [2] as an alternative, because it needs substantially fewer fitting parameters to describe species interactions and temperature dependence. However, tailoring the model parameters of EUNIQAC to geothermal applications requires re-fitting and extending the existing parameter space.

We developed a new tool named GEMSFIT that allows generic fitting of activity models (for aqueous electrolyte and non-electrolyte solutions) and equations of state implemented in our geochemical equilibrium solver GEM-Selektor (<http://gems.web.psi.ch>). GEMSFIT combines a PostgreSQL database for storing and managing the datasets with experimental measurements and interaction parameters, the parallelized genetic algorithm toolbox of MATLAB[®] for the parameter fitting, and an interface to the GEMS3K code (kernel of GEM-Selektor) to access activity models and perform chemical equilibrium calculations.

Our comparison revealed that the original EUNIQAC model is less accurate than the Pitzer model. Hence, we modified the EUNIQAC model in order to enhance its accuracy and retain its advantages. The new model called ELVIS combines an electrostatic framework developed by Helgeson and coworkers [1] with non-electrostatic concepts derived from the EUNIQAC model [2].

ELVIS has significantly less fitting parameters than the Pitzer approach, but is comparable in terms of quality of the fit to experimental data. We believe that with the ELVIS approach, it will be possible to derive correlations and predictions for the model parameters, which is very difficult in the Pitzer framework.

[1] Helgeson, H. H., Kirkham, D. H., Flowers, G. C. (1981), *Am. J. Sc.* (281), 1249-1516. [2] Thomsen, K., Rasmussen, P., Gani, R. (1996), *Chem. Eng. Sc.* 51, 3675-3683.

Rare earth elements of Precambrian-Cambrian phosphorites from the Yangtze Platform (S. China)

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The Precambrian to early Cambrian transition comprises an episode of major environmental changes which are believed to be relevant for the most prominent bioradiation in Earth's history: from an ocean in which algae and microbes were the dominant form of life to one in which significant skeleton-forming higher life spread. Concomitant with these global changes is the onset of biomineralization and widespread calcium phosphate deposition. However, so far, neither the source of phosphate for massive phosphorite, nor the formational mechanisms are known with certainty.

The investigation of the rare earth element (REE) content in phosphorites constitutes a powerful tool to obtain important information on depositional conditions, detrital influence and post-depositional alteration. The authigenic nature of most sedimentary apatites moreover helps in understanding the palaeochemistry of the primary marine environment.

Here, we present rare-earth elements of Precambrian Cambrian phosphorites from different sediment successions on the Yangtze Platform, representing the known facies belts from shelf to basinal environments. The total REE contents of all phosphorites investigated cover a wide range (37 - 1154 ppm), with two samples recording > 700 ppm, which is lower than the averages reported for geologically old phosphorites. PAAS (= Post-Archaean Average Shale) normalized REE patterns are characterized by LREE depletion and MREE enrichment. Low detrital input is indicated by low concentrations of Zr, the lacking correlation of HREE vs. Zr, and low Sc/La ratios. All phosphorites investigated yield negative Ce-anomalies, which is typical of seawater, indicating the palaeoceanic redox conditions of the primary water body. Unlike Ce, Eu does not show any marked anomaly. A positive Eu anomaly can only be reported for one phosphorite concretion, which is likely linked to the high barium content in this phosphorite. This suggests strongly reducing conditions at the time of phosphorite formation, increasing the mobility of Eu as Eu²⁺. The high Ba content can furthermore be indicative for an increased palaeo-productivity.