Development of an R-based wrapper code for the computation of hydrochemical predominance diagrams based on PHREEQC modeling outputs

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When investigating stability relations in aquatic solutions or rock-water interactions, the number of dissolved species and mineral phases involved can be overwhelming. To facilitate an overview about equilibrium relationships and how chemical elements are distributed between different aqueous ions, complexes, and solids, predominance diagrams are a widely used tool in aquatic chemistry. In the simplest approach, the predominance field boundaries can be calculated based on a set of mass action equations and log K values for the reactions between different species. Example given, for the popular redox diagram (pe-pH diagram), half cell reactions according to Nernst's equation can be used (Garrels & Christ 1965). In such case, boundaries between different species are "equal-activity" lines. However, for boundaries between solids and dissolved species a specific concentration needs to be stipulated, and the same applies if other components than those displayed in the diagram are involved in the possible reactions. In such case, the predominance field boundaries depend on the actual concentration values chosen.

An alternative approach can be the computation of predominance diagrams using the full speciation obtained from a geochemical speciation program, which then needs to be coupled with an external wrapper code for appropriate control and data pre- and post-processing. In this way, the distribution of different species can be based on the consideration of complete chemical analysis obtained from laboratory investigations.

We present the results of a student semester-project that aimed to develop and test an external wrapper program for the computation of pe-pH diagrams based on modeling outputs obtained with PHREEQC (Parkhurst & Appelo 1999). We have chosen PHREEQC for this core task as a geochemical calculation module, because of its capabilities to simulate a wide range of equilibrium reactions between water and minerals. Due to the intended final users, a free and extensible simulation platform was considered important. The wrapper program was created in the R environment which is freely available under the GNU General Public License (R Development Core Team 2011).

The wrapper reads in analytical data in the standard PHREEQC input file format and then iterates over a systematic selection of pe and pH values. These data are transferred to PHREEQC for the calculation of a corresponding set of hydrochemical speciations based on thermodynamic equilibrium. The results of the PHREEQC simulations are subsequently analyzed by a postprocessor function in order to derive a two-dimensional representation of the dominant aquatic species in the pe-pH plane. In this step, the most abundant species at each grid point is identified as the predominant one. To investigate the utility of the program, differences in the speciation of iron were calculated from chemical compositions of water samples from one of our current field sites (Gardermoen / Øvre Romerike aquifer in S-Norway).

References:

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R Development Core Team (2011): R: A language and environment for statistical computing. http://www.R-project.org/