Release of trace elements from rocks: An experimental study

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The easily accessible fraction of trace elements in rocks is derived from leaching experiments (Möller and Giese, 1996). Aliquots of rock powders are mixed with ion exchange resin and distilled water. The pH is self-adjusting to values between 3 and 4 depending on the rock's composition. After batch leaching times of 2 to 20 hours at 70°C the resin is quantitatively separated from the rock powder, and eluted with 4 *N* HNO_3. The metal contents of the leachates are determined and related to the respective contents of the whole rock. The leaching kinetics of each element is related to that of a reference element. Aluminium is most commonly chosen as a reference element because it is considered to represent the dissolution behaviour of the main rock-forming minerals. The easily accessible trace-element fraction (EAT) is given as the 'percentage of leached element at 1% Al dissolution'. These EAT values are reproducible and independent from grain size and sample/resin ratio. EAT fractions may be different due to variations in chemical composition but are independent from grain size, leaching time and sample/resin ratios. The EAT fraction can be split into two part: a fraction that is derived from rock-forming minerals by dissolution, and (2) an easily soluble fraction originating from other sources than the rock forming minerals: zonation, surface coatings, accessory minerals, etc.

In rocks, the easily accessible fraction of elements are variable and depend on the intensity of preceding alteration(s). Due to formation of alteration minerals, the EAT fraction of elements of fresh rocks are either fixed in insoluble minerals (decrease of EAT) or present in easily soluble phases (increase of EAT). They are further related to increases or decreases of total contents in the rocks. Additionally, EAT fractions correlate with changes of $\delta^{18}O$ and δD in selected rock-forming minerals.

The information obtained is more sensitive than that gained by any other analytical tool because mineral separation is not needed and the fraction accessible to fluids is measured directly under controlled conditions. In particular, the quantities that are released by desorption, ion exchange and dissolution of accessory phases are difficult to determine by other methods. However, it is still impossible to distinguish the contribution of each individual mineral. By skilful choice of reference elements, however, the type of source minerals can be inferred.

It should be pointed out that the described EAT method does not try to simulate natural alteration processes but to investigate the distribution and availability of elements in rocks as the result of crystallisation and/or subsequent alteration.

Applications

Although the leaching conditions do not correspond to the those of low temperature alteration and chemical weathering, numerous useful information can be extracted:

The leaching of a quenched, basaltic glass (MORB from East Pacific Rise) shows congruent release of all metals (Möller and Giese, 1996). If the glass is slightly crystalline, it displays heterogeneous incongruent leaching behaviour showing distinctive features of element distribution among differently soluble phases. For instance, among the rare earth elements, Eu is partly separated from its neighbours because of its divalency at high temperatures.

EAT fractions provide some insight into the distribution of metals in rocks and into the behaviour of metals during water-rock interaction. The residual quantities of soluble compounds are reported in terms of being 'more' or 'less' soluble than the associated rock-forming minerals. This knowledge is fundamental in discussing (i) the availability of metals from rocks, (ii) the changes in total metal contents of rocks, and (iii) changes in the distribution of metals in rocks and fluids. The easily soluble fractions of elements in fresh and altered rocks can be compared and trends of element distribution and related total contents can be evaluated. Thus, the action of fluids during the preceding alteration can be studied semiquantitatively.

The leaching kinetics of variably altered magmatic and metamorphic rocks provide insight into the mineralogical siting of elements and their accessibility to fluids which has significant consequences for whole rock as well as mineral dating procedures (Möller *et al.*, 1997) because the necessary 'closed system condition' can be checked.

The trace element composition of mineral and thermal waters is not yet predictable from the mineral composition of the aquifer rock(s). The leaching experiment tell us which quantity of any element is accessible to fluids at the self-adjusted pH value. Since H^+ ions play the most important role in dissolution, variation of pH allows a detailed study of the trace element distribution between solids and aqueous fluid in rocks. Although the leaching solutions are not identical in composition with natural waters, they exhibit the typical anomalies of the easily soluble mineral phases of a particular rock (Möller *et al.*, in press). Particular goals are (i) identification of the aquifer rocks that determine the chemical composition of trace elements in waters, and (ii) the approach to stationary conditions of fluid-rock interaction. Comparison of natural waters with leachates of the aquifer rocks reveal the kinetics of trace element fractionation. Under this aspect rare earth and yttrium contents and Pb isotope ratios in mineral and thermal waters from Bohemia (Möller *et al.*, in press) and Black Forest (Möller *et al.*, 1997a) will be presented.

Vanishing of Eu and Y anomalies in waters indicate the approach of stationary conditions in water-rock interaction. Differences in isotopic ratios of Pb and Sr between natural waters and leachates reflect the inhomogeneous distribution of the radioactive mother nuclides and their daughter products among the soluble phases. Leachates of rocks reveal whether or not this rock can be considered as the source of a hydrothermal fluid from which a hydrothermal mineralization formed. Here, all anomalies among the rare earth elements are of particular interest.

Mobility of elements in rocks is a prerequisite for concentration processes. To which extent, however, water-rock interactions induced changes of total contents can be determined by studying the EAT fractions as a function of changes of total contents in rocks. For instance, the rocks of KTB experienced amphibolite metamorphism without significant exchange of elements across lithologic boundaries. Retrograde greenschist metamorphism had no influence either (Möller *et al.*, 1997b). Only along fissures, some minor concentration of ore minerals occurred (Kontny *et al.*, 1997)

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