

RARE EARTH ELEMENT AND YTTRIUM FRACTIONATION CAUSED BY FLUID MIGRATION

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Based on the work of V. M. Goldschmidt, fractionation of elements is considered to be a function of ionic size and charge differences. Isovalent elements of very similar size should not be fractionated. Besides these prime parameters, the structure of the electron shell can not be neglected because the interaction of the outer electrons form the base of the chemical bonds between two or more ions. These systematic changes in bonding energies lead to only small or sometimes negligible fractionation under closed system conditions. Significant fractionation of elements results from small to large differences in chemical reactions such as formation of hard chemical complexation in both solution and at mineral surfaces, or significant differences in binding energies in solids that control exsolution or dissolution.

In open systems the situation is different in that the chemical equilibrium is continuously disturbed, and the migrating fluid always meets an environment with which it is not in equilibrium. Hence, small fractionation during one equilibrium step is multiplied and might lead to considerable effects, the degree of which depends on the number of theoretical steps of equilibration.

Trivalent rare earth elements including yttrium (REY) with ionic radii ranging from 0.130 (La^{VIII}) to 0.112 (Lu^{VIII}) is the best group of elements to study the influence of ionic size and systematically changing electronic structure at constant charge in natural systems. Here, fluid flow is fundamental in order to transport the metals to sites of their accumulation. Besides that the fractionation of REY occurs.

The LREE/HREE: fractionation is largely controlled by the size of the trivalent ions resulting from the relativistic effects leading to the well-known lanthanide contraction. The formation constants of fluoro-, phosphoro-, carbonato-, and hydroxo-complexes increase from La to Lu. Carbonato-complexes have high constants that slightly decrease from La to Lu. Similarly, many surface complexes also prefer the smaller heavy REE which indicates that solution and surface complexation often competes with each other.

Yttrium can be considered as a pseudo-lanthanide which lacks the *4f* electrons that are characteristic of the lanthanides. Its crystallographic size is, depending on the co-ordination number in solids, within the range of the heavy REE. Yttrium is often enriched in migrating fluids.

In detailed studies it could be shown that the empty, half-filled and filled *4f* shells show deviation from the extrapolated trend of the neighbouring REE. This indicates the influence of the electronic structure on the formation of complexes.

In dynamic systems, i.e., migrating fluids, small differences in reaction rates and positions of equilibria of the individual REY are multiplied depending on the length of pathways of fluids and flow velocity. The higher the differences are, the higher is the final fractionation. If the formation constants of chemical complexes are systematically changing, fluid movement might lead to strong effects over short distances. If the water-rock interaction is characterized by high water/rock ratios, then even the remaining rock carries a highly modified REE pattern. This is typical for highly evolved granites and their greisens. Here the REE patterns often split into four sections, which is called the tetrad effect.

Much more pronounced effects are achieved if REE occur in different oxidation states, such as Eu and Ce. In particular, Eu is easily reduced to divalent species, which move faster through pores than the trivalent species. Under these conditions it depends on whether REE in the pores are present at a higher or lower concentration than in the intruding fluid. The resulting Eu anomaly is either positive or negative. This phenomenon is probably responsible for very high positive Eu anomalies such as in black smoker fluids. It is worth noting that only hot fluids with temperatures above about 250 °C develop such extreme anomaly, whereas cooler fluids exhibit a much lower anomaly, possibly inherited from the source rock.