RADIUS-INDEPENDENT FRACTIONATION OF YTTRIUM AND RARE EARTHS: EXPERIMENTAL EVIDENCE

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Inductively Coupled Plasma Mass Spectrometry (ICP–MS) can provide highly accurate and precise data on concentration of yttrium and all fourteen naturally-occurring rare earths (including the monoisotopic rare earth elements, REE) for geological solid materials and, combined with proper pre-concentration and matrix-separation techniques, for natural waters. Compared to previously available data determined by INAA or IDMS, this is a major step forward, because it allows to extend REE geochemistry from discussion of radius-dependent (causing LREE–HREE fractionation) and redox-dependent fractionation (causing Ce and Eu anomalies) to interpretation of charge- and radius-*in*dependent fractionation of La, Gd, and Lu from their respective neighbours in the REE series, fractionation of the geochemical twins Y and Ho, and generation of the lanthanide tetrad effect. All of these features have been reported from natural systems, examples range from seawater and hydrothermal fluids to high-silica granites and pegmatites, chemical sediments, and hydrothermal minerals. However, over the years the discussion apparently suffered much from prejudices that occasionally misguided both defenders and opponents of the concept. Moreover, because no experimental verification has been available of at least one process that might cause this type of fractionation, the idea of radius-independent fractionation of Y and trivalent REE is still not widely accepted.

Here, I report the first experimental evidence for a natural process (interaction of dissolved Y and REE with iron-oxyhydroxides) that may induce radius-independent fractionation of Y and REE. Scavenging experiments performed at pH 4 to 7 with synthetic solutions and natural water containing dissolved Fe, Y, and REE show that rare earths and yttrium (REY) are strongly fractionated during interaction with iron-oxyhydroxides. Patterns of apparent REY distribution coefficients between iron-oxyhydroxide and solution indicate anomalous behaviour of Y, La, Gd, and Lu, the extent of which increases with increasing pH. Moreover, at pH ≥ 5, the patterns give clear evidence for the lanthanide tetrad effect, and at pH ≤ 5, there occurs oxidative scavenging of Ce from the synthetic solution. The scavenging-induced fractionation of non-redox-sensitive REY cannot be explained by differences in their ionic radii, and indicates that electron structure exerts an important control on the aqueous geochemistry of REY.

The results of the scavenging experiments are compatible with observations on the behaviour of REY during interaction with iron-oxyhydroxides in natural surface environments. Moreover, the data suggest that typical features of the REY distribution in seawater, such as positive Y, La, Gd and Lu anomalies, and also the W-type tetrad effect, are produced during mixing of seawater and river water in the low-salinity part of estuaries.