

The rare earth element (REE) geochemistry of cold, high pCO₂ groundwaters was studied in springs and boreholes in the Primorye region of the Russian Far East. The gas phase in these waters is dominated by mantle-derived CO₂ (up to 2.6 atm.), being introduced to shallow groundwaters along major fault systems. The aggressive nature of these moderately acidic groundwaters has led to unusual trace element characteristics with high concentrations of relatively immobile elements such as Al, Be, heavy REEs and Zr. They are also marked by extremely high concentrations of Fe and Mn, up to 80 mg l⁻¹ and 4 mg l⁻¹, respectively. The REE patterns generally show enrichment in the middle to heavy REEs and low concentrations of the light REEs (La-Nd). Most groundwaters show relatively flat shale-normalised middle to heavy REE profiles, with the exception of Eu, which may form positive or negative anomalies depending on local mineralogy. A characteristic of many of the groundwaters is the presence of positive Sm-Eu anomalies. A range of potential ligands is present in the groundwaters and model calculations show that the dominant species are Ln³⁺, carbonate complexes (i.e., predominantly LnCO₃⁺), and LnF₂⁺. Concentrations of Cl⁻ and SO₄²⁻ are very low in most waters and nitrate and phosphate are below detection limit. The role of organic complexing is not known due to lack of data, but such complexes may be important since limited TOC data show that organic contents may be high. The middle to heavy REE enrichment found in the groundwaters is consistent with dissolution of Fe-Mn oxyhydroxides and release of adsorbed REE. Positive Eu anomalies in some groundwaters correlate with high Ca and Sr, pointing to control by plagioclase dissolution. High Y/Ho ratios and positive Y spikes on REY plots in high-F⁻ waters suggest an important control by F⁻ complexing, which is confirmed by speciation calculations. Extreme enrichments in the heavy REEs are found in two groups of mineral waters with Yb/La ratios up to 9.8. The extreme enrichments in heavy/light REEs present in these areas are too high to be simply controlled by speciation fractionation and it is suggested that a weathering phase with heavy REE enrichment is responsible. The source is suggested to be zircon, which typically displays such heavy REE enrichments. Although zircon is generally stable during low-temperature weathering, it is known to break down in acidic carbonated solutions. This is supported by high Zr concentrations (as well as high U, Be) in these groundwaters and a correlation between Zr and heavy REE enrichment.