Trace element and Nd-Sr isotope evidence for *REE* migration and fractionation in chloride-rich brines at elevated T and P

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Nd and Sr isotopic compositions and Rare Earth Element (*REE*) distribution patterns have been determined in Permian salts (Zechstein) adjacent to a basaltic dyke of Miocene age in two horizontal profiles. The length of the profiles are 3.0 and 3.7 meters. The salts originally essentially consisted of carnallite ($KMgCl_3 \cdot 6H_2O$) which have been transformed during basalt intrusion mainly into halite (NaCl) and sylvite (KCl) by fluids saturated in NaCl. This salt metamorphism is strongest near the basalt contact and decreases regularly with distance [1].

Sr and Nd isotopes

The Sr isotope data show that at least 200 times more fluid had penetrated the upper than the lower horizon. In the lower horizon a mixing between a salt and a more "basaltic" end-member can be observed whereas inhomogeneous fluid flow may have led to the poorer mixing observed in the upper horizon. The Rb-Sr data of the upper horizon furthermore indicate that the fluids accompanying the intrusion had a more radiogenic Sr isotopic composition than the basalt itself which could be due to the dissolution of halite in deeper stratigraphic levels.

The salt samples next to the basalt contact have almost basalt-like Nd isotopic compositions in both horizons. In the upper horizon, the ε_{Nd} values decrease only slightly with increasing distance. In contrast, the most distant samples of the lower horizon have ε_{Nd} values around -7 indicating a strong influence of salt derived Nd. This difference can be attributed to the larger fluid flow in the upper horizon which was able to transport more Nd out of the basalt.

Rare earth elements

The *REE* data document in both horizons a strong depletion of Ce, Pr, Nd, Sm and Eu with increasing distance from the basalt. The Nd isotope data show that this depletion cannot be related to a simple mixing between a basalt and a salt *REE* source. In contrast, the data indicate that the observed *LREE* depletion is due to selective solution complexation or selective surface complexation on colloidal or larger particles. A systematic comparison of the fractionated patterns with available *REE* complex stability constants for 25 °C and 1 bar suggests chloride as complexing ligand.

The most fractionated salt patterns can be used to make estimations about relative *REE* chloride complex stabilities at elevated temperatures and pressures. The results suggest that small variations occurring at surface conditions are up to 9 times magnified as temperature and pressure increase. This finding is not in agreement with *REE* complex stability estimates for comparable conditions, but the discrepancies can't be resolved until experimentally defined complex stability data covering the entire *REE* series are available.

For the *REE* and actinides leaving a leaking high level waste repository in salt rocks a similar transport as chloride complexes can be expected. In this perspective, the higher mobility of Ce, Pr, Nd, Sm and Eu with respect to the other rare earths is not only of importance for the migration behaviour of fission derived radiocative *REE*. It could also have implications for the mobility of trivalent Am and Cm which are major constituents of spent nuclear fuel and for which, owing to their almost identical ionic radii, an almost analogous behaviour in natural solutions is expected as for Sm and Nd [2, 3].

References

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