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Proxies for the evolution of acidulous iron-rich springs in Carinthia (Austria)

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Natural CO_2-rich Muri springs in Carinthia arise from palaeozoic shale close to the Periadriadic Lineament. The solutions are less mineralized but contain elevated Fe content. Some are used for health purposes. The aim of this study is to evaluate the subsurface evolution of the solutions and secondary effects by specific chemical and isotopic proxies.

Water sampling was carried out at two springs and the adjacent creek, in which the springs drain. At one spring the emerging solution was sampled along a distinct flow channel of about 4 m.

Analyzed oxygen, hydrogen and tritium isotope distribution indicate that the solutions are of local meteoric origin with subsurface resident times of only several years. Low concentrations of Na^+, K^+ and Cl^- ([Na+K+Cl] $<$ 0.43 mmol L^{-1}) correspond to negligible mixing with high concentrated salt solutions from deep underground areas which are accessible from wells nearby. However, access of gaseous $CO_2$from deep horizons to the solutions is verified by high internal CO_2 partial pressures close to 1 atm. $\delta^{13}C_{DIC}$-values of dissolved inorganic carbon between -5 and -8 $^o/_{oo}$(V-PDB) reflect CO_2 from igneous or mantle origin. $^3He/^4He$-isotope distribution argues for mantle origin of higher age (>2Myr) or crustal source. Mg/Ca ratios close to one, less Ca ([Ca] $<$ 1.3 mmol L^{-1}), and less $Si(OH)_4$ content may reflect preferential dissolution of magnesium-rich carbonates like dolomite or ankerite. Latter may be in accordance with about 0.7 mmol $L^{-1}$of aqueous Fe which exclusively occurs in divalent form.

As the solution enters the Earth‘s surface pH increases from 5.5 to 5.8 due to degassing of CO_2. This can be directly followed by an increase of $\delta^{13}C_{DIC}$-values along the flow course caused by $^{13}CO_2$ discrimination during degassing. On the other hand, O_2 is absorbed into the solution and aqueous Fe is significantly reduced by iron oxides precipitation. The precipitate mainly consists of ferrihydrite, goethite, and haematite. Significant amounts of REE are co-precipitated with the iron oxides changing the original “fingerprint”. Fractionation process will be discussed in comparison to REE content of the precipitates.