

source of CO₂ mixing with shallow water is the reason for this and that this source is similar as for other springs in the border region of Jezersko.

Stable isotope ratios and the evolution of acidulous solutions

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In the present study 35 well and spring waters were sampled in the North of Hesse (Germany) and analysed with respect to the chemical compositions and stable isotope ratios ($\delta^{13}\text{C}$, $\delta^{34}\text{S}$, δD , $\delta^{18}\text{O}$). The solutions are used as drinking water, bottled mineral water or for medical applications. Several solutions are characterized by high concentrations of dissolved components. But most conspicuous are acidulous solutions with a high content of dissolved inorganic carbon (DIC). Although, the evolution of natural solutions is extensively studied significant gaps exist with respect to such acidulous solutions. The aim of the present study is to decipher the evolution of the solutions with respect to the sources and requirements of the catchment area.

In the acidulous solutions the source of the high amounts of dissolved inorganic carbon (DIC) and great proportions of carbonic acid is mostly vague. No recent magmatic activities are observed in the study area, but Tertiary basaltic rocks appear. If Tertiary basaltic magmas might be a primary source, CO₂ has to be stored until recent times within the underlying rocks and sediments.

The results show that the evolution of the solutions is characterized by the precipitation of meteoric water, the uptake of CO₂ and a subsequent dissolution of solids of the catchment area. Three types of solutions may be distinguished according to the chemical composition:

- 1: water with low concentration of dissolved ions (LOW)
- 2: brines dominated by Na⁺ and Cl⁻ (BRI)
- 3: acidulous solutions with high concentrations of Ca²⁺, Mg²⁺, and DIC (CO₂)

The dissolution of carbonate minerals, essential calcite and dolomite, is closely related to the uptake of gaseous CO₂. The high P_{CO2}-values of the CO₂ type of about 1 atm requires a huge reservoir of CO₂-gas, which cannot be provided by soil atmospheres. From the measured $\delta^{13}\text{C}_{\text{DIC}}$ -values the ¹³C/¹²C-signatures of the primary CO₂ are obtained. The respective $\delta^{13}\text{C}_{\text{CO2}}$ -values of the CO₂ type are either in the range of about -10 ‰ or lay between 0.8 and 3.7 ‰. The values of these two groups barely depend on the boundary conditions for the dissolution of carbonate (open and closed system with respect to the CO₂-gas).

The ¹³C/¹²C-signatures of CO₂ from magmatic origin (-6 and -3 ‰) lay between the $\delta^{13}\text{C}_{\text{CO2}}$ -values of above two groups. Higher and lower values may be explained by a ¹³C/¹²C-

fractionation due to CO₂-diffusion through micropores, faults, and interfaces of solids from a CO₂-reservoir. Considering Tertiary basalts, but no recent magmatic activities in the study area, CO₂ may be referred to a subsequent liberation of CO₂-gas from respective reservoirs of the underlying rocks of the study area, which is primarily gained from Tertiary basaltic magma. An accumulation of primary magmatic CO₂ may occur in reservoir rocks such as sandstones, which are secluded e.g. by clay-rich horizons of the Röt formation (Triassic) or by storage in marine evaporites. The high CO₂ content stimulates the ascent of the solutions until the earth surface is reached by an extensive formation of a gas-solution mixture.

High concentrations of silicic acid and an excess of dissolved sodium versus that derived from the dissolution of halite exhibit an intensive weathering of silicates. This appears especially in the CO₂ type and is also documented by the occurrence of kaolinite layers at the respective sites. Dissolved sulfate is mostly obtained from the dissolution of gypsum or anhydrite of the Zechstein formation. The stable sulfur isotope ratios at low SO₄²⁻ concentrations show that sulfur is also gained by the oxidation of sulfides e.g. pyrite in shales. The presence of Sr²⁺ and Ba²⁺ reflects the dissolution of carbonate minerals, whereas iron and manganese is mostly controlled by precipitation of respective oxide/hydroxides as the solutions reach the earth surface.

The evolution of LOW and BRI type solutions is quite similar to that of the CO₂ type. However, a potential source of CO₂ for the dissolution of carbonate is mainly soil-CO₂, and the BRI type solutions contain additional amounts of dissolved marine evaporates, especially halite.

High Temperature Pyrolyses - a new field for isotope analyses

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A new method for the automated sample conversion and on-line oxygen isotope ratio ($\delta^{18}\text{O}$) determination for organic and inorganic substances was developed a few years before. The samples are pyrolytically decomposed at 1400-1450°C (HTP) in presence of a nickel/ carbon powder (mixed, 10/90).

With the presented system solid and liquid samples are measurable. Organic as well as inorganic samples such as cellulose, nitrates, sulphates and phosphates of 50 - 100 $\mu\text{g O}$ can be analyzed for their $\delta^{18}\text{O}$ values with a standard deviation of usually better than 0.3 ‰. Additionally, hydrogen isotopic ratios (standard deviation better than 3 ‰), carbon isotopic ratios of organic substances and nitrogen isotopic ratios of inorganic nitrogenous compounds are available in the same system.

References

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