



Ca isotope fractionation in a shallow groundwater system in NW Germany

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In order to evaluate the potential use of Ca isotopes in determining sources and biogeochemical processes in a shallow groundwater system, $^{44}\text{Ca}/^{40}\text{Ca}$ ratios (expressed as $\delta^{44}\text{Ca}$) of dissolved Ca^{2+} were analyzed by TIMS using a ^{42}Ca - ^{48}Ca double spike. Groundwater samples were collected from monitoring wells in the catchment area of the water works of Ristedt (NW Germany). Sampling depths ranged between 1.5 and 50 meters below surface. The aquifer is composed of unconsolidated sediments (mainly quartz sands) that were deposited during the Pleistocene glacial phases. While most of the near-surface groundwater shows a Ca^{2+} - Na^{+} - Cl^{-} and Ca^{2+} - Cl^{-} composition, the Ca^{2+} - HCO_3^{-} type prevails in deep wells. pH values increase from 4.5 in shallow wells to 7.6 at deeper levels, indicating low buffering capacities due to long-term decalcification processes in the near-surface horizons. Dissolved Ca^{2+} (7 to 51 mg/L) and HCO_3^{-} concentrations (2 to 218 mg/L) cover a wide range generally increasing with depth. Consequently, near-surface groundwater is strongly undersaturated with respect to calcite whereas deep groundwater is close to saturation with calcite. Deep groundwater and several shallow wells are characterized by anoxic conditions while in parts of the aquifer oxic conditions prevail. $\delta^{44}\text{Ca}$ values of groundwater range between 0.2 and -1.4 permil (relative to seawater), indicating changes in the sources that are contributing to the dissolved Ca^{2+} loads, and biogeochemical fractionation processes. The main sources of calcium in the groundwater include mineral weathering and atmospheric depositions. Ca isotopes may be fractionated by secondary minerals precipitation, ion-exchange processes, and biological processes. In this presentation, possible scenarios will be discussed. Acknowledgements: Thanks to Dr. P. Groth, Dr. A. Mehling and the personnel of the Harzwasserwerke GmbH, Germany.