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Carbon and sulfur isotope ratios of DIC and sulfate from fresh waters - Effect of $BaCO_3$ and $BaSO_4$ coprecipitation and analytical technique

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Stable carbon isotope compositions of dissolved inorganic carbonate (DIC) and sulfate in fresh water are useful tools for modeling the evolution of aqueous solutions in natural surroundings. Moreover, $^{13}\text{C}/^{12}\text{C}$ ratio of DIC comprises a basic correction parameter for the interpretation of ^{14}C ages of for instance carbonate-bearing ground waters in hydrogeochemical studies.

Different techniques exist to prepare DIC for carbonisotope analysis. One technique is based on quantitative precipitation of DIC as $BaCO_3$ by the addition of an alkaline barium chloride solution (e.g., [1, 2]). Subsequently, precipitated $BaCO_3$ and concentrated phosphoric acid react to gaseous CO_2 which is analyzed off-line by stable isotope mass spectrometry. However, in sulfate-bearing solutions $BaSO_4$ besides $BaCO_3$ is formed. It was suggested from experimental data of [3] that isotope fractionation may occur during the reaction of co-precipitated well mixed $BaCO_3$ -BaSO $_4$ with phosphoric acid.

In the present study, the $^{13}\text{C}/^{12}\text{C}$ content of ground waters with different sulfate/DIC ratios (0.03 to 17.3) were investigated with both off-line and on-line techniques (complete combustion by C-irmMS). Additionally, $^{34}\text{S}/^{32}\text{S}$ ratios of sulfate were measured by means of C-irmMS on mixed BaCO₃-BaSO₄ coprecipitates and separately purified BaSO₄ precipitates [e.g., [1, 2]).

The results show no effect of 13 C/ 12 C analyses on sulfate/DIC ratios and no significant change of 34 S/ 32 S ratios due to varying C-content. This indicates that coprecipitation

of $BaCO_3$ and $BaSO_4$ as well as the different analytical techniques do not influence the stable isotope analyses of DIC and dissolved sulfate.

References:

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