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Carbon isotope exchange between gaseous CO_2 and thin solution films: Artificial cave experiments and a complete diffusion-reaction model

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Abstract

Speleothem stable carbon isotope ($\delta^{13}C$) records provide important paleoclimate and paleo-environmental information. However, the interpretation of these records in terms of past climate or environmental change remains challenging because of various processes affecting the $\delta^{13}C$ signals. A process that has only been sparsely discussed so far is carbon isotope exchange between the gaseous CO_2 of the cave atmosphere and the dissolved inorganic carbon (DIC) contained in the thin solution film on the speleothem, which may be particularly important for strongly ventilated caves.

Here we present a novel, complete reaction diffusion model describing carbon isotope exchange between gaseous CO_2 and the DIC in thin solution films. The model considers all parameters affecting carbon isotope exchange, such as diffusion into, out of and within the film, the chemical reactions occurring within the film as well as the dependence of diffusion and the reaction rates on isotopic mass and temperature. To verify the model, we conducted laboratory experiments under completely controlled, cave-analogue conditions at three different temperatures (10, 20, 30 °C). We exposed thin (≈0.1 mm) films of a $NaHCO_3$ solution with four different concentrations (1, 2, 5 and 10 mmol/l, respectively) to a nitrogen atmosphere containing a specific amount of CO_2 (1000 and 3000 ppmV). The experimentally observed temporal evolution of the pH and $\delta^{13}C$ values of the DIC is in good agreement with the model predictions. The carbon isotope exchange times in our experiments range from ca. 200 to ca. 16,000 s and strongly depend on temperature, film thickness, atmospheric pCO_2 and the concentration of DIC. For low pCO_2 (between 500 and 1000 ppmV, as for strongly ventilated caves), our time constants are substantially lower than those derived in a previous study, suggesting a potentially stronger influence of carbon isotope exchange on speleothem $\delta^{13}C$ values. However, this process should only have an influence in case of very long drip intervals and slow precipitation rates.

Keywords: Speleothem; $\delta^{13}C$ values; Isotope exchange; Laboratory experiments; Modelling

1. INTRODUCTION

Speleothems have become well-established paleoclimate archives over the last decades, in particular because they can be dated very precisely with U-series disequilibrium methods (Richards and Dorale, 2003; Scholz and Hoffmann, 2008). The most frequently used paleoclimate proxies in speleothems are the stable oxygen and carbon isotope ratios ($\delta^{18}O$ and $\delta^{13}C$ values) of the speleothem calcite. These can be measured at high spatial resolution and provide long and often uninterrupted paleoclimate records.

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