

## Evolution of carbon in the karst groundwater, Zunyi, China

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The carbonate system evolves with weathering reactions driven by CO<sub>2</sub> dissolved from the soil and subsequent organic/inorganic reactions in soils and aquifers. This study focuses on the carbon evolution of karst groundwater, Zunyi, China.

The studied area is mainly characterized by karst landforms in Southwest China. The mean values of DIC in winter and summer are 4.54 and 3.82 mmol C/L respectively, reflecting the dilution effects of the heavy monsoon rains; The average δ<sup>13</sup>C<sub>DIC</sub> values of ground water are -10.3‰ in winter and -11.1‰ in summer, which suggests that soil CO<sub>2</sub> makes a larger contribution to the DIC in summer than in winter. The concentration of DOC and POC in most of ground water samples are lower than 2.00 mg C/L and 0.50 mg C/L but some contaminated waters, respectively. There is a larger range of δ<sup>13</sup>C<sub>POC</sub> in summer than that in winter. P<sub>CO2</sub> of the waters generally is higher than 10<sup>-3.5</sup>, and P<sub>CO2</sub> in ground water is generally higher than that in surface water, showing deep soil CO<sub>2</sub> makes a greater contribution to ground water. The seasonal difference of contents and isotopic composition of carbon species reflect that the carbon evolution of karst groundwater is easily affected by the monsoon rains.

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## Cu isotope signature of granites

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The Cu isotope signature of bulk earth is proposed to be homogeneous (δ<sup>65</sup>Cu≈0) based on measurements of sulphides from mafic intrusions (e.g. Larson *et al.*, 2003) and a limited numbers of mantle-driven rocks (e.g. Archer and Vance, 2004). However, it has been reported that highly evolved granite can have a Fe isotope signature remarkably different (about 0.5‰ δ<sup>57</sup>Fe) from bulk earth values (Poitrasson and Freydier, 2005). As Cu is a trace element in most common rocks, and is also multivalent, its isotopes are more likely to be fractionated by Rayleigh (magma evolution) and redox (weathering / sedimentation) processes than Fe isotopes. Here we report our preliminary work to determine baseline values of δ<sup>65</sup>Cu for various granite rocks and examine the Cu isotope homogeneity of crust.

A chemical procedure, modified from Maréchal (1999), was used to separate Cu from rock matrix. Quantitative recovery (100.9±1.2%) with a low total procedural background (2.65±0.66ng) for Cu has been achieved, allowing Cu isotopic measurements on samples with as little as 10 ppm Cu. Elution curves for peridotite, basalt and granodiorite indicate that elution of Cu is not affected by the bulk composition of rocks. Cu isotope ratios were measured with a Nu Plasma MC-ICP-MS using solution nebulisation sample introduction. Mass bias was corrected by both the sample-standard bracketing and the Ni-doping methods. The long-term external reproducibility of the measurements was 0.09‰ (2 sigma).

S-type and I-type granites from southeastern Australia have been analysed. The S-type granites have a large range of δ<sup>65</sup>Cu, varying from -0.40‰ to 0.37‰, while the δ<sup>65</sup>Cu values of I type granites are less variable (from -0.05‰ to 0.26‰), generally overlapping each other within error around zero (the bulk earth value). However, samples of the mafic end member (SiO<sub>2</sub><55wt%) of an I-type granite suite show remarkable heavy Cu isotope signatures (δ<sup>65</sup>Cu up to 1.56‰).

The distinguishable variation in Cu isotopic composition of the S-type granite may reflect isotopic heterogeneity in the sedimentary source region as a result of redox processes. However, the possibility of Cu isotope fractionation during magmatic and magmatic-hydrothermal processes cannot be ruled out.

### References

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