Characteristics and driving factors of surface water chemistry of Wujiang watershed

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The changes of water chemistry of rivers can reflect influence of anthropogenic activities on water environment in some extent. In order to understand the relationship between the spatial distribution of eco-environment of the watershed and the characteristics of water chemistry and geochemistry of rivers, firstly, the digital Wujiang watershed was built, and then the sub-watersheds were delineated, taking the sample points as sub-watershed outlets based on GIS. Secondly, using the function of spatial analyst of GIS, the statistical features of eco-environment (such as lithology and land use/cover) of each sub-watershed were calculated according to their respective classification. Finally, the correlation between the spatial distribution of lithology of the sub-watersheds and their corresponding $^{87}Sr/^{86}Sr$ ratio of river water, the correlation between NO_3^-/HCO_3^-, Cl^-/HCO_3^-, SO_4^{2-}/HCO_3^- and anthropogenic activities respectively, and the correlation between the fraction of green vegetation of the sub-watershed and their corresponding flux of TDS (total dissolved solids) were analyzed quantitatively. The results justify that the $^{87}Sr/^{86}Sr$ ratio of river water is highly dependent on the lithologic feature of the watershed and indicate that anthropogenic activities are one of the main sources of NO_3^- and SO_4^{2-} of river waters, the output of TDS is highly dependent on the percentage of vegetation cover of the watershed.

Evaluation of kinetic effect on clumped isotope fractionation (Δ_{47}) during inorganic calcite precipitation

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To date, published Δ_{47}-temperature calibrations using different inorganic calcite precipitation and biogenic carbonates, as well as obtained by theoretical calculations, are not consistent. Here we present a set of Δ_{47} data measured from inorganic calcites grown at well-controlled experimental conditions. We show that measured Δ_{47} values are strongly influenced by pH during calcite precipitation. When pH is between 8.3 and 9.0, measured Δ_{47} values (1) generally increase with decrease of temperature, (2) are not sensitive to the change of precipitation rate, and (3) are not sensitive to variation in ionic strength. The Δ_{47}-temperature equation calibrated by our Δ_{47} values for inorganic calcite grown at pH between 8.3 and 9.0 can be written as,

$$\Delta_{47} = (0.0367 \pm 0.0033) \times 10^6/T^2 + (0.2743 \pm 0.0376)$$

where Δ_{47} values were reported in the absolute reference frame. The slope of our calibration line is very similar to theoretical line (0.0392, Schauble *et al.*, 2006; Guo *et al.*, 2009). If pH ≥10, the Δ_{47} values for calcite grown at 5ºC significantly drift from the Δ_{47}-temperature line. In this case the comparison of $\delta^{18}O$ and Δ_{47} values of calcite grown at pH ≥10 to that grown at pH≤9 indicates that every 1‰ depletion in $\delta^{18}O$ values results in 0.0155‰ enrichment in Δ_{47} values. We argue that any observed kinetic effect on carbonate clumped isotope fractionation is mainly due to isotopic non-equilibrium occurring in the solution during CO_2-H_2O (de)hydration and (de)hydroxylation.

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