## Unusual fractionation of both odd and even Hg isotopes in precipitation

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Preliminary studies have demonstrated both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg isotopes in the environment and the potential for their application in biochemistry and geochemistry. Though atmospheric deposition is a primary pathway by which Hg enters earth surface ecosystem, little has been reported on Hg isotopes in precipitation.

In order to examine Hg isotopic composition in precipitation, rainwater and snow samples were collected in Peterborough (Ontario, Canada) in 2010. Hg isotopic compositions were determined after Hg pre-concentration using the method developed by Chen et al. (2010). All precipitation samples displayed significant MDF ( $\delta^{202}$ Hg between -0.02‰ and -1.48‰) and MIF of odd isotopes ( $\Delta^{199}$ Hg varying from -0.29‰ to 1.13‰). We reported here, for the first time, a seasonal variation of even Hg isotope MIF  $(\Delta^{200}$ Hg). Our results suggest that photo-reduction in droplets or on the surface layer of snow crystals induce odd Hg isotope anomalies determined in precipitation samples, while mass independent fractionation of even Hg isotopes is likely triggered by elemental Hg oxidation occurring on aerosol or solid surface in the tropopause. Though more research is required to fully understand the behaviour of Hg isotopes in the atmosphere, the striking seasonal variation of even Hg MIF (and with temperature) may provide useful information for meteorological research and related climate studies and help in monitoring atmospheric Hg transportation.

[1] Chen et al., (2010) JAAS 25, 1402-1409.

## The analysis of solution-ICP-MS of rare earth elements of carbonate minerals in carbonate rocks

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The trace elements of carbonate minerals in carbonate rocks, especially rare earth elements (REEs), are the best parameters to trace the redox conditions of the sedimentary environment. However, because the REE contents of carbonate minerals are much lower than that of terrigenous clays, a small quantity of clays dissolved will affect true redox implication. Therefore, to conduct an analytical method to get the true REE contents of carbonate minerals deposited in marine environment without the contamination from terrigenous clays is very important.

At the present time, the analytical methods of REEs of carbonate minerals in carbonate rocks mainly are solution-ICP-MS and LA-ICP-MS. In solution-ICP-MS method, hydrochloric acid, nitric acid and acetic acid are usually used. Hydrochloric acid and nitric acid could dissolve all carbonate minerals in carbonate rocks and also possibly parts of non-carbonate minerals, which disturb the analysis results. Although using acetic acid can avoid the interference of non-carbonate minerals, it probably could not completely dissolve the carbonate minerals in carbonate rocks, the results also could not be true. In LA-ICP-MS analysis, carbonate minerals was ablated by laser beam firstly, and then evaporation was directly carried into ICP-MS, which could be the most effective method for REE analysis of carbonate minerals without clays. But, because the diameter of laser beam is too large to avoid tiny clays which usually occur in carbonate minerals, LA-ICP-MS also has uncertainty.

Here we use 5% CH<sub>3</sub>COOH, 5% HCl, 2% and 5% HNO<sub>3</sub> to dissolve powder samples split from one carbonate rock for 0.5, 1, 2, 3, 6 and 24 hours, respectively. The XRD analysis results show that there is no calcite in insoluble residues after acid dissolution suggesting that calcite was completely dissolved. The ICP-AES analysis results of acid dissolved solution indicate that small quantities of clays were dissolved. These dissolved clays result in an increase of REE contents, but do not affect Eu/Eu\*, LaN/YbN and Gd/Gd\*. The obvious positive relation between  $Al_2O_3$  and Ce/Ce\* in acid dissolved solutions suggests that the dissolved clays did affect the Ce/Ce\* values of carbonate minerals to a certain degree.

Comparing results under different acid dissolution, we could conclude that the appropriate conditions for REE analysis of carbonate minerals in carbonate rocks is 0.5-1g samples reacting with 5% CH<sub>3</sub>COOH for 1 hour, which decrease the influence of clays on Ce/Ce\* values to the lowest. As for HNO<sub>3</sub> dissolution, the acid with concentration <2% should be used to react with 0.2g power sample for <30 min. And for 5% HCl dissolution, the reacting time should be <30 min with 0.2-1g sample. The Ce/Ce\* values obtained from HCl and HNO<sub>3</sub> dissolutions could still be used to trace sedimentary environment, but will be higher about 0.1 than that from CH<sub>3</sub>COOH dissolution.

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