Isotopic compositions of sulphur and nitrogen in rains of Guiyang, China

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Introduction

Variations of isotopic composition of sulphur and nitrogen in rains of Guiyang, a rainy city, have been studied to discriminate between different sources of atmospheric nitrogen and sulphur, since sources of nitrogen and sulphur in precipitation are most important for the understanding of atmospheric acidity because sulphur and nitrogen are major components of acidity and their concentrations are increasing rapidly in the atmosphere due to anthropogenic activities such as the burning of coal and petroleum products.

Results and Discussion

A significant difference in mean sulphur isotopic composition was found between samples collected from flurries (-4.90±2.76‰) and storms (+4.58±5.02‰), indicating that sulphur in the two types of rains is of different sources. Since no obvious air masses came from other areas, sulfate in the flurries was only controlled by atmosphere over Guiyang city. Negative $\delta^{34}S$ values of sulfate in flurries are attributed to mixing of local sulfur sources (particulate sulphur, -2.32‰; SO_2, -15.06‰; biogenic sulphur, -10.02‰). During the storm periods, however, there were larger air masses transported from Pacific Ocean. The average of $\delta^{34}S$ values in storms is close to that of sea spray sources (+20‰, Pichlmayer et al., 1998), indicating they are of maritime origin.

Nitrogen isotopic composition of ammonium changes in different rain events. $\delta^{15}N$ values of ammonium in flurries vary with change of ammonium concentrations. The lower values in the range of $\delta^{15}NH_4^+$ (-1.7‰ ~ -22.0‰) are due to the less incorporation of ^{15}N by cloud water, which probably has a $\delta^{15}N$ value of about –28.6‰. According to the relationship between $\delta^{15}N$ value and ammonium concentration, we can estimate high $\delta^{15}N$ values for ammonium in flurries if concentrations increase. The high concentrations (averaged 1.25 mg l^{-1}) and the low$\delta^{15}N$ values (averaged -12.2±6.7‰) indicate that sources of ammonium are widespread agricultural use of excretory wastes and the release of NH_3 from soils.

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Fluid/rock interactions in UHP metamorphic rocks from drill holes in Donghai, Sulu, China: Preliminary results

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The Chinese Continental Scientific Drilling Program (CCSD) is carried out at Donghai in the Sulu ultrahigh-pressure (UHP) terrain. Using a combined study of fluid inclusions and oxygen isotopes on UHP metamorphic rocks from pre-pilot holes of the CCSD, we aim to determine the nature and extent of fluid/rock interactions during metamorphic evolution of these rocks, and to provide information about possible changes of fluid compositions with depths.

The investigated samples were collected from the pre-pilot holes PP2 and ZK703. ZK703 penetrated 558 m and consists mainly of eclogites, whereas PP2 penetrated to depths of 1000m with only minor eclogite. Our investigations focus on eclogites.

Different types of fluid inclusions were identified and were related to various metamorphic stages: Ca-rich brines in kyanite and omphacite probably contain relic metamorphic fluids during peak metamorphism; primary Na^+-bearing low-salinity inclusions in quartz from eclogite, and primary K^+-bearing low salinity inclusions in quartz from gneiss appear to be trapped during the retrograde symplectite-forming stage; the latest generation of fluid inclusions is represented by secondary pure water inclusions in quartz. These features are comparable with the UHP metamorphic rocks in the Dabie Shan aera, (Xiao et al., 2000, 2001, 2002). Final melting temperatures of primary inclusions from various depths are slightly different, but secondary fluid inclusions in quartzes have more or less the same final melting temperatures. This indicates that the fluid phase during early retrograde metamorphism was controlled by the host rock, whereas the rocks interacted with another fluid at a later retrograde metamorphic stage.

Three important observations can be drawn from the oxygen isotope data: i) All the investigated samples have $\delta^{18}O$ values lower than normal metamorphic rocks, indicating meteoric water/rock interactions and provide support for structural coherence of the geothermal system throughout subduction and exhumation (Rumble & Yui, 1998). ii) Eclogite and gneiss in sharp contact have more or less the same $\delta^{18}O$ values, suggesting that the rocks have already obtained the depleted isotope values before subduction. iii) UHP eclogites from different depths in ZK703 have similar whole-rock $\delta^{18}O$ values between 2 and 3‰, implying that the meteoric water/rock interactions were homogeneous on a kilometer-scale in a vertical-sequence.

Mass discrimination in MC-ICP-MS: example from Cu-Zn isotopes

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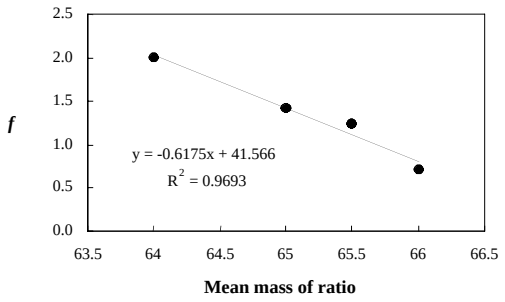
Cu and Zn isotopes in NIST976 and SpexPure Cu and Zn standard have been measured using a VG Axiom MC-ICP-MS, to investigate the mass discrimination, its stability and its dependency on sample matrices.

Based on the measurement of NIST976, a precision between 70-90 ppm can be achieved for $^{65}Cu/^{63}Cu$ ratio within an analytical session over 15 hours. This would translate into 0.09 per mil in $\delta^{65}Cu$, significantly smaller than recently reported $\delta^{65}Cu$ variations in natural samples. Thus, "sample-standard bracketing" for mass bias correction may be adequate, provided that samples are matrix matched with the standard .

NIST976 solutions spiked with various amounts of SpexPure Zn were used to measure Cu and Zn isotopes. It was found that the mass discrimination factor *f* was not constant across the Cu and Zn mass region. However, there appeared to be a correlation between *f* and mass (Fig. 1).



Similar correlation between *f* and mass has also been reported recently for Nd, Hf, and Pb-Tl isotope ratios. The correlation between *f* and Cu, Zn isotopes is independent of Zn concentration, and remains stable within an analytical session. Furthermore, data obtained from various models of MC-ICP-MS indicate that such correlations seem to be common to all currently available instruments.

These results suggest that mass bias correction by assuming equal *f* (e.g., $^{146}Nd/^{142}Nd$ for Nd isotopes, $^{205}Tl/^{203}Tl$ for Pb isotopes, and $^{68}Zn/^{64}Zn$ for $^{65}Cu/^{63}Cu$) does not fully account for the true mass bias in MC-ICP-MS. The correlation between *f* and mass can be used to further correct for mass bias, and may result in improved precision and accuracy of isotope ratio measurement in MC-ICP-MS.

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Factors influencing the vertical Pb distribution in a shooting range soil

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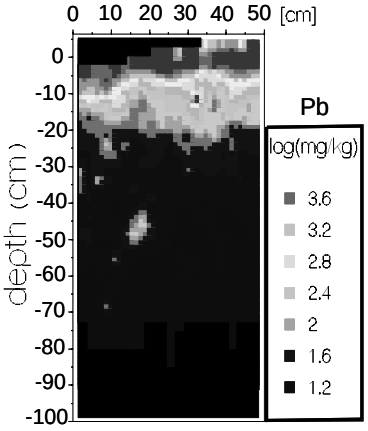
Soils in the vicinity of shooting ranges are often highly contaminated with Pb from bullets. Although metallic Pb(0) corrodes to secondary minerals with very low solubility, and dissolved Pb^{2+} is strongly sorbed by soil components, prior studies have found elevated Pb concentrations in the subsoil. A possible explanation is the transport of dissolved Pb or Pb bound to mobile colloids along preferential flow paths (PFP), i.e., bypassing the major part of reactive surfaces. To verify this mechanism, we investigated the cm-scale variation of Pb concentrations in a soil profile in relation to PFP.

A shooting range in Losone (Ticino, CH) was selected because of severe Pb contamination, strongly acidic soil (pH 3-4), and its proximity to a nature preservation area. PFP were identified by irrigating an undisturbed soil in the forest 50 m behind the stop butt with a reactive dye tracer (brilliant blue) and a conservative bromide tracer. We sampled a 50 x 100 cm^2 depth profile with 2.5-cm resolution, and measured element concentrations by X-ray fluorescence (XRF), and dye tracer concentration with a color meter. For selected samples, Pb speciation was investigated by selective sequential extractions and X-ray absorption fine structure spectroscopy (XAFS).



We found that the Pb concentration rapidly declined from >10,000 mg/kg in the upper 5 cm to background levels of 30 mg/kg at 40 cm depth. However, in one spot at about 50 cm depth (see figure below), elevated Pb concentrations of 300 mg/kg were found. This Pb spot coincided with elevated concentrations of Br and dye, suggesting transport of Pb along PFP. The distribution of Sb and Cu, two other metals deposited with gun pellets, followed a similar pattern. Thus, despite the low pH, Pb was strongly retained in the topsoil, and only a small fraction migrated down the profile. XAFS showed that Pb^{2+} was predominately bound to carboxylate groups by forming an inner-sphere sorption complex. Nevertheless, about 50% of total Pb occurred as mobile species (extractable by NH_4NO_3 and acetate).

Geochemical Evidence for Existence of Inland Foraminifera in the Nihewan Basin, China

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From the first finding in 1970s, the findings of foraminiferal fossil assemblages in inland basins have been reported until now, tend to increase in the recent years. The debates on the depositional environment of foraminiferal fossils have become the hot of researches again in China.

Based on the trace element geochemistry and SEM of shells of Quaternary foraminiferal fossils from the Xiaodukou section in the inland Nihewan basin, the original geochemical information of shells were believed to be preserved well and could be used to reveal the geochemistry of contemporaneous water, although there existed some effects of burial diagenesis on the geochemistry of shells to a certain extent. The $^{87}Sr/^{86}Sr$ ratios of well-preserved Xiaodukou foraminifera were measured, giving a range of 0.711190±25 ~ 0.712018±14 apparently higher than the value of contemporaneous seawater (0.709087 ~ 0.709147) and similar to the value of the Sangganhe river which was proven to represent the value of the ancient lacustrine water.

The hyperbolic mixing models of $^{87}Sr/^{86}Sr$-salinity and $^{87}Sr/^{86}Sr$-Sr/Ca are useful to determine the mixing relationship between seawater and fresh water (Palmer et al,1989; Ingram et al,1993). The geochemical data of Xiaodukou foraminifera indicated that depostional water of microfosslis with slightly low salinities, was near to 0‰. Furthermore, the regionally geologic field work available gives no plausible evidence to explain how the ancient Nihewan Lake 300km far from the coastal line and at 500m elevation connected with sea from the viewpoint of tectonics (Chen et al, 1988). The result implies the contemporaneous environment where Xiaodukou foraminifera inhabited was an inland lacustrine environment and there was no seawater input to the depositional environment.

So, it is reasonable to conclude that Xiaodukou foraminiferal fossil assemblages belong to non-marine foraminiferal species. The occurrence of foraminiferas may be due to the brackish water because of tectonization-climate.

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Geochemistry of dissolved and suspended loads of the Xijiang River, China: Weathering processes and erosion rates

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This study focuses on the chemistry of the Xijiang River system, one of the major rivers in China, and constitute the first geochemical investigation of both suspended and dissolved loads of this river, in order to determine both chemical and mechanical erosion rates.

Discussion

Flowing in the south of China, the Xijiang River is the second largest river in China with respect to its discharge, after the Yangtze River. As compared with the other large rivers of the world, the river is characterized by high major element concentration. The dissolved major cations average 1.17, 0.33, 0.15 and 0.04 mmol l^{-1} for Ca, Mg, Na and K, respectively, and the total cation concentrations (TZ+) vary between 2.2 and 4.4 meq l^{-1}. The high concentration of Ca and Mg, high (Ca+Mg)/(Na+K) ratio (7.9), enormous alkalinity and low dissolved SiO_2/HCO_3^- ratio (0.05) in river waters reveal the importance of carbonate weathering and erosion and relatively weak weathering and erosion of silicate over the river drainage basin.

We propose a model based on mass budget equations, that allow the proportions derived from the different sources to be calculated. As a consequence carbonate and silicate weathering rates can be estimated as well as the consumption of CO_2 by weathering of each of these lithologies. Mechanical weathering rate are also estimated according to suspended load. Dissolved elemental concentration of the river waters are corrected for rain inputs (mainle oceanic salts), they provide specific chemical erosion rates of 85-110 and 6-8.6 t/km^2/yr for carbonate and silicate, respectively. The average atmospheric CO_2 consumption results from silicate and carbonate weathering over the drainage basin are 41_10^9 and 216_10^9 mol C /yr. Mechanical erosion rate is 208 t/km^2/yr.

Conclusions

The high denudation rates are mainly attributable to high relief and heavy rainfull. Acid rain affects south China, where its frequency may exceed 50% and the pH value of rainwater may be <4.0, result from SO_2 pollution in the atmosphere (Zhao and Sun, 1986). Acid rain in the drainage basin results in the dissolution of carbonates and aluminosilicates and hence accelerates the chemical weathering rate.

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A Remarkable Climate Shift Around 1700~1500 a BP and It's Significance in The Climate Prediction of The Coming 500 Years

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A striking climate shift around 1700~1500 a BP was extracted from the proxy indicator of $\delta^{18}O$ in peat cellulose from Jinchuan (Hong et al, 2000) (NE China) and Hongyuan (Xuhai et al, in press) (SW China). Temperature was seen to arise around 1700~1500 a BP and then decrease abruptly in about 10~20 years around 1500 a BP. The humidity indictor of$\delta^{13}C$ in peat cellulose both in Hongyuan and Jinchuan indicates a decrease around 1700~1500 a BP. After this period, China suffered a 500-year cold and dry period around 1500~1000 a BP. This typical climate character has also been detected in Dunde Ice core (SW China), GISP2, North Atlantic etc. world widely.

The recent 200 years (200~0 a BP) witnessed a similar climate character to that of the period of 1700~1500 a BP, with an increase in temperature and a decrease in humidity. Numerical evidences have documented the quasi-1500-yr periodicity punctuated throughout the Holocene. Climate in the period of 200~0 a BP can be recognized as a reoccurrence of that in the period of 1700~1500 a BP. To correspond the quasi-1500-yr periodicity, the coming 500 years (2000~2500 a AD) is supposed to be cold and dry similar to the climate conditions in the period of 1500~1000 a BP. Such a prediction has also been widely simulated out by thermohaline circulation (THC) models, the atmosphere general circulation models (AGCM) and so on.

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Complexation of trace metals, and origin and effects of strong ligands in Swiss Lake and river waters

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Free ionic concentrations and complexation of Cu, Zn, Cd, Co and Ni are determined by a set of indirect techniques with ligand-exchange and voltammetry in Swiss lakes and rivers, as well as in FA and HA solutions. The trace metals are mostly bound in strong organic complexes at their natural concentrations in freshwater. A class of very strong ligands (L_1) with low concentration governs the metal speciation at the ambient level of lake and river waters. Complexation of Cu, Ni, Co or Cd was stronger in productive zones, indicating that the strong ligands are linked to biological activities. The specific stronger ligands with recent biological origin are only present at low concentrations in freshwater and represent only a small fraction of DOC. Fulvic and humic acids are likely to play a role as weaker ligands and to be more important in systems with high DOC, relatively high colloidal or metal concentrations, especially if DOC mostly originates from soil or wetland. In systems with high biological productivity and relatively low DOC, such as eutrophic lakes, the specific ligands are probably more relevant. The natural ligands affect not only the metal bioavailability, but also the metal transport and transformation in natural waters, such as adsorption and sedimentation.

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The dissolution mechanisms of forsterite and enstatite: Constraints from ^{29}Si and ^{1}H MAS NMR

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Forsterite and enstatite play important roles during the weathering of ultramafic and mafic rocks. However, the aqueous dissolution mechanisms of these minerals are still controversial. We now report new ^{1}H and ^{29}Si MAS NMR, and ^{1}H-^{29}Si cross polarization (CP)-MAS NMR results that shed light on this matter.

Hydrated Mg_2SiO_4 forsterite and $MgSiO_3$ enstatite samples were prepared by immersing gently crushed synthetic minerals in deionized water at 90°C for 2 days and drying at 100°C for 20 minutes. The ^{29}Si MAS NMR spectrum for the unhydrated forsterite consists of a single, sharp peak at –61.8 ppm. The ^{29}Si MAS NMR spectrum for the unhydrated enstatite consists of two sharp peaks at –80.5 and -83.2 ppm attributable to clinoenstatite, and a third one at –84.9 ppm attributable to protoenstatite. The ^{29}Si MAS NMR spectra of the hydrated minerals are nearly identical to those of the unhydrated. The ^{1}H-^{29}Si CP-MAS NMR spectra of the hydrated forsterite and enstatite both consist of two peaks near –86 and –93 ppm that can be attributed to Q^2 and Q^3 species (SiO_4 tetrahedra sharing 2 and 3 corners with other tetrahedra), respectively. Similar spectra have been previously reported for hydrated diopside (Peck et al., 1988). The ^{1}H MAS NMR spectra of hydrated forsterite and enstatite both contain a relatively narrow peak near 0.4 ppm and a broader, asymmetric peak near 4.6 ppm. The former can be assigned to MgOH, and the latter to hydrogen-bonded SiOH and/or molecular H_2O.

The predominance of Q^2 and Q^3 peaks in the ^{1}H-^{29}Si CP-MAS NMR spectra of hydrated forsterite and enstatite suggest that the dissolution of both minerals is accompanied by the formation of a polymerized hydration layer consisting mainly of Q^2 and Q^3 units. The detection of a large amount of MgOH by ^{1}H NMR implies that the hydration layers retain a significant amount of Mg. These hydration layers could consist, in part, of biopyriboles as observed for naturally weathered enstatite (Eggleton and Boland, 1982), and may play a dominant role in determining the dissolution kinetics of these minerals.

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