

Iron Isotope Compositions of Natural River and Lake Samples in the Karst Area, Guizhou Province, Southwest China

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Abstract: To better understand the Fe isotope characteristics of natural samples in the Karst area, the Fe isotope compositions of riverine suspended particulates, lake suspended particulates, lake sediments, porewaters, phytoplanktons, and aerosols in the watersheds of Lake Aha (a mineralized water system) and Lake Hongfeng (a mesotrophic water system), which are located in the Karst area, southwest China, were investigated. The studied samples displayed a variable range between $\delta^{56}\text{Fe}=-2.03\text{‰}$ and 0.36‰ . Aerosols and phytoplanktons have similar or slightly heavier Fe isotope compositions relative to the average of igneous rocks. Fe isotope compositions of riverine Suspended Particulate Matter (SPM) were mainly affected by the types of tributaries. Suspended particulates collected from tributaries seriously contaminated with coal mine drainages displayed negative $\delta^{56}\text{Fe}$ values (-0.89‰ to -0.31‰) during summer, and there were significant increases of $\delta^{56}\text{Fe}$ values in winter, except AR2, which was polluted with both coal mine drainage and sewage effluent. Characteristics of lakes have important influences on Fe isotope compositions of suspended particulates, lake sediments, and porewaters. The epilimnetic particulate Fe of Lake Hongfeng had $\delta^{56}\text{Fe}=-0.04\text{‰}$ to 0.13‰ , while lighter Fe isotope compositions were measured for particulate Fe from Lake Aha, ranging from -0.42‰ to -0.09‰ . Sediments collected from Hou Wu (HW) station of Lake Hongfeng have an average $\delta^{56}\text{Fe}$ value of 0.09‰ and their corresponding porewaters have lighter Fe isotope compositions, ranging from -0.57‰ to -0.31‰ ; no significant variations have been observed. For the Liang Jiang Kou (LJK) station of Lake Aha, the content of reactive Fe and the concentration of sulfate were all high. Due to the reactive Fe recycling, including dissimilatory Fe reduction, adsorption, and Fe-sulfide formation, porewaters sampled near the sediment surface have been found to have a $\delta^{56}\text{Fe}$ value as low as -2.03‰ and an increase up to 0.12‰ , with a burial depth of 10 cm. In contrast, an opposite variation trend was found for LJK sediments. Sediments sampled at 1-cm depth had a value of $\delta^{56}\text{Fe}=-0.59\text{‰}$ and decrease as low as -1.75‰ with burial depth. This investigation demonstrated that significant Fe isotope fractionations occur in surface environments. Fe isotope compositions of particulate Fe were seriously affected by Fe sources, and Fe biogeochemical recycling has an important influence on Fe isotope fractionations in lake sediments, especially when there are significant amounts of reactive Fe and sulfate.

Key words: Fe isotope composition, karst, riverine particulate, lake particulate, sediment, porewater

1 Introduction

As one of the most abundant elements in the Earth's

crust, Fe occurs in a variety of rocks and minerals and is widely involved in weathering processes. Fe is also a redox-sensitive element, which is important for the delivery of other inorganic heavy metals (e.g. Davison, 1993;

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Balistreri et al., 1994). Furthermore, as one of the essential micronutrients for biota, Fe is thought to be linked with primary production in oceans (Martin, 1990) and lakes (Clasen and Bernhardt, 1974; Evans and Prepas, 1997) as well. So the biogeochemical cycling of Fe is of great importance in the near-surface environment. Previous studies indicated that significant Fe isotope fractionations occurred within a variety of processes, including biologically- or abiologically-mediated redox reactions (Beard et al., 1999; 2003; Bullen et al., 2001), Fe (III) precipitation (Balci et al., 2006), mineral dissolution with organic ligands (Brantley et al., 2001; 2004), and high-temperature processes (Zhu et al., 2001; Poitrasion et al., 2004; Weyer et al., 2005). An overall variation of $\sim 5\%$ for $\delta^{56}\text{Fe}$, relative to IRMM-014, has been reported for natural samples (Beard and Johnson, 2004; Johnson et al., 2004; 2008), while the igneous rocks have an average $\delta^{56}\text{Fe}$ of 0.09% (Beard et al., 2003). So Fe isotopes are thought to be potential tools for monitoring and quantifying the processes that Fe is involved, especially after the development of MC-ICP-MS, and the improvement of reproducibility.

Many studies have been carried out on Fe isotope fractionations during continental weathering (Fantle and DePaolo, 2004) in rivers and ocean systems (Zhu et al., 2000; Rouxel et al., 2004; Staubwasser et al., 2006; Manuela et al., 2008; Ingri et al., 2006; Bergquist et al., 2006). In China, Zhu et al. (2008) and Tang et al. (2006a; 2006b) carried out Fe isotope studies on column purification. Mass spectrometry and case studies were also performed on banded Fe formations in the Ansha-Benxi area (Li et al., 2008), whereas less work has been done in biogeochemical processes (Song et al., 2008a). In the present study, we examined the Fe isotopic compositions of natural samples, including river suspended particulates, lake particulates, aerosols, soils, phytoplanktons, macrophytes, lake sediments, and porewaters in the Karst area, southwest China. These results provide Fe isotopic compositions of possible end-members in the biogeochemical cycling of Fe in the Karst area. In addition, important processes in which Fe isotope fractionations occurred have also been implied.

2 Study Site and Sampling

The Karst terrain is widely distributed in Guizhou province, southwest China. Lake Hongfeng and Lake Aha are two artificial reservoirs located in the Karst area. Sampling was performed in these two lake watersheds (Fig. 1). Lake Hongfeng is a mesotrophic water system, while Lake Aha is a highly mineralized one. There is a watershed area of 1596 km^2 for Lake Hongfeng, and the surface area is 57.2 km^2 . The maximum depth of the water system is 45 m,

and the residence time is 0.325 a. In contrast, Lake Aha has a smaller watershed area of only 190 km^2 , and a smaller surface area of 3.4 km^2 . The average and maximum depths are 13 m and 24 m, respectively. The retention time of lake water is approximately 0.44 a. The Lake Hongfeng watershed consists mainly of Permian-Triassic carbonate rock, and approximately 80% of the area is Triassic carbonate rock. Limestone soil and yellow soil are widely distributed in the watershed. For the Lake Aha watershed, its bedrock is mainly a mixture of Permian carbonate rock and coal-bearing strata covered with silico-alumina and silico-ferric yellow soil. There are also small amounts of outcrops of Triassic carbonate rock covered with black and tan limestone soil.

There are mainly six tributaries for Lake Hongfeng and five tributaries for Lake Aha. Among these inflowing rivers, some are seriously deteriorated owing to the acid coal mine drainages, such as HR4, AR1, AR2, and AR4, while some are contaminated with sewage effluent, like AR5. Before sampling, all the bottles and tubes were carefully acid-cleaned and rinsed with Milli-Q water ($18.2\text{ M}\Omega$), with the exception of those used for the anion analyses. The bottles were prerinsed with the water samples three times. River water and lake water were collected during summer and winter. The samples used for the anion and cation analyses were filtered with a $0.45\text{-}\mu\text{m}$ membrane filter in the field, and the filtered samples for cation and trace elements were acidified to $\text{pH} < 2$ with ultrapure HNO_3 . Samples for the isotope studies were filtered with $0.45\text{-}\mu\text{m}$ filters (Mixed cellulose esters, 47 mm ; Millipore, USA), immediately after they were brought back to laboratory in the High Density Polyethylene (HDPE) bottles. The filters for the Fe isotope measurements were then stored at 4°C in a refrigerator. The filtered water samples for the sulfur isotope measurements were acidified to $\text{pH} < 2$.

Two yellow soil samples were collected, with one sampled in the HW area of Lake Hongfeng and the other in the Da Ba (DB) area of Lake Aha. Three kinds of macrophytes, including Hippochaete (*Equisetum ramosissimum* Desf.), Hornwort (*Ceratophyllum demersum* Linn.), and tape grass (*Vallisneria americana*) were collected in the Lake Aha watershed with gloved hands. The phytoplanktons were also sampled by handpicking in winter. These phytoplanktons were only rinsed with lake water and Milli-Q water ($18.2\text{ M}\Omega$), and then stored in a refrigerator until freeze-drying. Aerosol samples were collected with a homemade polyethylene rainwater sampler. The rainwater was filtered immediately after sampling, and the filters with aerosol were then stored in a refrigerator. Crucian carps were sampled for Fe isotope studies in the two lakes.

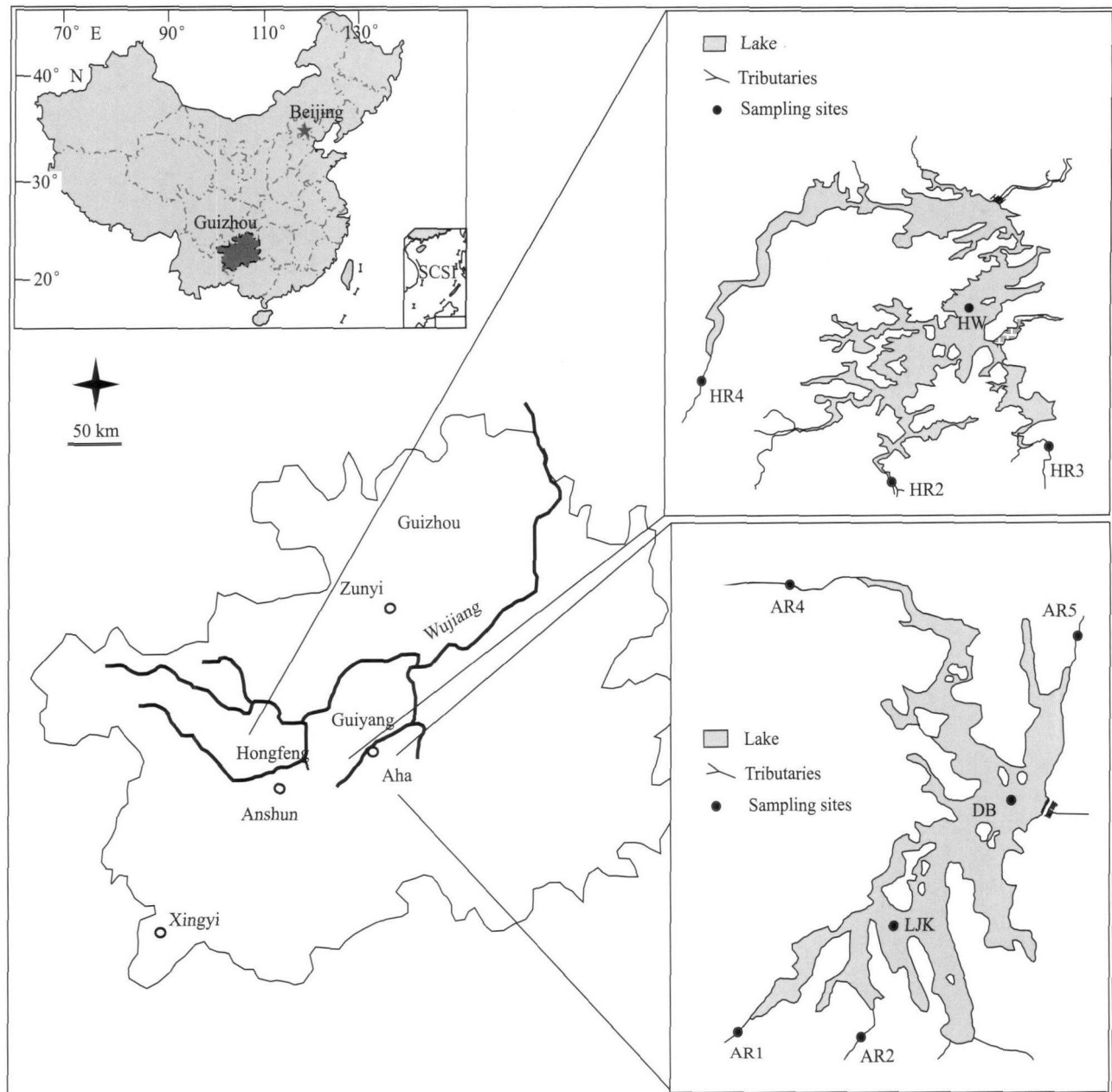


Fig. 1. Schematic map of Lake Hongfeng and Lake Aha and the sampling sites.

Sediments were collected with a homemade gravity corer (Wang et al., 1998) at HW of Lake Hongfeng and at LJK of Lake Aha in January 2007. Sediment cores were subsequently sliced into 1-cm segments in N_2 -filled plastic glove bags. The samples were then centrifuged immediately, and porewaters were filtered with plastic syringes in N_2 -filled bags. The porewaters of Lake Aha, analyzed in this study, were collected at the beginning of November 2006. The sediment samples were kept frozen in a refrigerator and the porewaters were stored at 4°C until the next treatment.

3 Analytical Methods

3.1 Environmental parameters

Environmental parameters, including pH value, water temperature, and Electrical Conductivity (EC), were measured with a multiparameter sensor in field. Cations and anions were analyzed on Ion Chromatography (IC, Dionex ICS-90, USA) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian Vista MPX; USA), respectively. Separated samples for Dissolved Organic Carbon (DOC) determination were filtered with glass microfiber filters (Whatman, GF/F, 25 mm; UK) and analyzed on a Total Organic Carbon (TOC) instrument (OI Analytical Aurora model; USA).

3.2 Sulfur isotopes

Dissolved sulfate were recovered as $BaSO_4$ after the addition of 10% $BaCl_2$. The precipitations of $BaSO_4$ were

rinsed with 18.2 M Ω Milli-Q water until there was no Cl⁻ detected. The precipitations were then combusted at 900°C in a muffle furnace. All sulfur isotope compositions were determined on Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS, IsoPrime JB144; GV Instruments, UK). Within the measurements, sigma, GBW04414 and GBW04415 were used as standards, and the results are reported in $\delta^{34}\text{S}$ as part per thousand deviations relative to Canyon Diablo Troilite standard with a reproducibility of $\pm 0.2\%$.

3.3 Fe isotopes

Digestion and purification were carried out in clean room at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry Chinese Academy of Sciences (IG CAS), Guiyang, China. All the vessels were carefully acid cleaned. The concentrated HCl, HNO₃, and HF used were all distilled twice, and 18.2 M Ω Milli-Q water was used throughout the procedures.

3.3.1 Digestion

The samples were pretreated with different methods before acid digestion. All the riverine particulates, lake particulates, and aerosols were first dried in an oven covered with Teflon materials inside at 50°C. The sampled fish was steamed in a Teflon beaker, and the fish meat was separated from the bones. Lake sediments, fish, macrophytes, and phytoplanktons were then dried with a freeze dryer. The freeze-dried samples were immediately crushed into powder, and the sediments and soils were crushed to <200 mesh with acid-cleaned mortar. In order to remove the high content of organic matter in the sediments and biological samples, they were all combusted in a muffle furnace at a temperature of 550°C (Bergquist and Boyle, 2006). All the samples were put into quartz beakers, and the quartz beakers were then put into bigger beakers to avoid contamination during combustion. Porewaters were only evaporated to dryness on a hotplate.

All the pretreated samples were soaked with 3 mL aqua regia and 0.5 mL concentrated HF for 48 h in acid-cleaned Teflon beakers (7 mL, Savillex; USA). The beakers were then left on the hotplate before evaporation to dryness at 80°C. Another 3 mL aqua regia and 0.5 mL concentrated HF was added and the closed beaker was left on the hotplate for 72 h at 140°C. The procedures were repeated until the samples were thoroughly digested. The distilled HClO₄ was also used for some samples that were not easily dissolved. The digested samples were then evaporated to dryness and repeated three times with 0.5 mL concentrated HCl to remove excess HNO₃ and HF. Finally, the samples were dissolved into 1 mL 7N HCl+0.001% H₂O₂ for column purification.

3.3.2 Column purification

According to Maréchal et al. (1999) and Tang et al. (2006a), samples were all purified with anion exchange column chromatography using AGMP-1 resin (100–200 mesh, chloride form; Bio-Rad, USA) with minor modification of the procedures. Before the first use, the resin was soaked in 0.5N HNO₃ and Milli-Q water (18.2 M Ω) several times. The supernatants were all decanted. The polypropylene column had a height of 4.3 cm and a diameter of 6.8 mm. First, the column was precleaned with 2 mL 0.5N HNO₃ alternating with 10 mL Milli-Q water (18.2 M Ω) three times, and another 5 mL Milli-Q water was used to ensure that HNO₃ was thoroughly removed. The column was then preconditioned with 5 mL 7N HCl + 0.001% H₂O₂ and 4 mL 7N HCl + 0.001% H₂O₂. All the prepared samples were carefully loaded onto the column. A moment later, the matrixes were striped with 35 mL 7N HCl + 0.001% H₂O₂, and Fe was eluted with 20 mL 2N HCl + 0.001% H₂O₂. All the samples were purified twice. The purified Fe eluates were evaporated to dryness, and the evaporation was repeated with 0.2 mL concentrated HNO₃ three times to drive off HCl. Finally, the purified Fe was redissolved in 1% HNO₃ with a concentration of 5–10 ng/mL for the mass spectrometry. The recoveries of Fe were >95%. The procedural blanks, including digestion, column purification, and evaporation, were always less than 0.34% of the total Fe extracted from the samples.

3.3.3 Mass spectrometry

Fe isotope measurements were performed on Nu Plasma instruments HR MC-ICP-MS (Nu Instruments, UK), at the Laboratory of Isotope Geology, Ministry of Land and Resources, Institute of Geology, Chinese Academy of Geological Sciences (CAGS). The standards and samples were all dissolved in 1% HNO₃ and introduced into the plasma via a DSN-100 desolvation nebulizer (Nu Instruments, UK). With the sample introduction system, the molecular interferences were reduced and the sensitivity was improved. The instrumental mass biases were corrected by applying the sample-standard bracketing method throughout the analyses. Prior to each analysis, the system was washed with 10% HNO₃ and 1% HNO₃ for 3 min and 2 min, respectively. The performance of the instrument has been assessed by repeated analyses of an in-house standard (CAGS-Fe3) relative to the international isotopic standard IRMM-014. At high-resolution mode, the average Fe isotope values of a long-term analysis (16 months) of CAGS-Fe3 were $\delta^{57}\text{Fe}=1.23\text{‰} \pm 0.11\text{‰}$ (2SD) and $\delta^{56}\text{Fe}=0.83\text{‰} \pm 0.08\text{‰}$ (2SD). The detailed procedures are described in Zhu et al. (2008). All data were reported in $\delta^x\text{Fe}$ ($x=56, 57$) as parts per thousand deviations

Table 1 Hydrochemical parameters and sulfur isotope compositions of riverine and lake samples

Sample	Date	T (°C)	pH	EC ($\mu\text{s/cm}$)	DOC (ppm)	NO ₃ ⁻ (ppm)	SO ₄ ²⁻ (ppm)	$\delta^{34}\text{S}$ (‰)
AR1-S	08/2006	21.6	8.18	901.8	1.96	2.38	522.24	-14.0
AR1-W	01/2007	8.6	7.88	652.4	1.20	4.26	403.20	-13.8
AR4-S	08/2006	21.8	8.04	715.9	1.67	3.68	389.76	-10.2
AR4-W	01/2007	7.4	8.42	285.0	1.28	7.04	572.16	-9.6
HR4-S	08/2006	24.5	7.13	719.5	2.50	6.03	336.96	-14.4
HR4-W	01/2007	5.6	7.29	546.7	0.98	10.85	247.68	-14.7
AR2-S	08/2006	21.6	7.66	646.1	4.01	12.99	230.40	-8.7
AR2-W	01/2007	9.3	7.71	679.0	8.27	7.14	217.92	-8.4
AR5-S	08/2006	22.6	8.28	595.8	6.16	8.18	115.2	0.9
AR5-W	01/2007	7.4	8.28	480.1	3.74	10.82	125.76	-2.3
HR3-S	08/2006	24.9	8.07	393.9	5.08	0.77	47.04	-3.2
HR3-W	01/2007	3.9	9.72	402.5	3.04	4.44	88.32	-6.5
HR2-S	08/2006	26.3	8.04	300.6	7.16	0.76	53.76	-7.2
HR2-W	01/2007	4.2	7.67	360.5	2.45	2.41	81.60	-6.7
AHLJK-S	07/2006	30.9	8.35	628.4	10.26		203.52	-7.4
AHLJK-W	01/2007	7.3	7.95	520.9	2.10	6.73	231.36	-8.6
AHDB-S	08/2006	25.0	8.19	533.9	4.54	4.31	189.12	-7.6
AHDB-W	01/2007	7.9	7.49	500.3	2.41	7.23	200.64	-7.7
HFHW-S	08/2006	28.1	9.37	293.2	5.21	0.30	66.24	-5.3
HFHW-W	01/2007	8.0	8.31	359.0	3.28	6.67	96.00	-7.2
HFDB-W	01/2007	8.1	7.75	362.1	3.03	10.89	104.64	-7.9

Table 2 Fe isotope compositions of the studied samples

Sample	Date	$\delta^{56}\text{Fe}$ (‰)	$\delta^{57}\text{Fe}$ (‰)	Sample	Date	$\delta^{56}\text{Fe}$ (‰)	$\delta^{57}\text{Fe}$ (‰)
AR1-S	08/2006	-0.31	-0.41	Aerosol-2	10/2006	0.12	0.17
AR1-W	01/2007	-0.03	-0.06	Soil-1	08/2006	0.08	0.13
AR4-S	08/2006	-0.88	-1.29	Soil-2	08/2006	0.11	0.15
AR4-W	01/2007	-0.13	-0.22	S-LJK1cm	01/2007	-0.59	-0.90
HR4-S	08/2006	-0.89	-1.36	S-LJK6cm	01/2007	-1.31	-1.92
HR4-W	01/2007	0.04	0.06	S-LJK10cm	01/2007	-1.75	-2.53
AR2-S	08/2006	-0.49	-0.73	PW-LJK5cm	10/2006	-2.03	-3.03
AR2-W	01/2007	-0.35	-0.52	PW-LJK7cm	10/2006	-0.24	-0.36
AR5-S	08/2006	0.07	0.05	PW-LJK11cm	10/2006	0.12	0.21
AR5-W	01/2007	-0.12	-0.16	S-HW2cm	01/2007	0.00	0.00
HR3-S	08/2006	0.06	0.12	S-HW4cm	01/2007	0.14	0.18
HR3-W	01/2007	0.04	0.06	S-HW6cm	01/2007	0.13	0.18
HR2-S	08/2006	0.03	0.03	PW-HW2cm	01/2007	-0.57	-0.80
HR2-W	01/2007	0.10	0.21	PW-HW4cm	01/2007	-0.37	-0.53
AHLJK-S	07/2006	-0.42	-0.65	PW-HW6cm	01/2007	-0.31	-0.42
AHLJK-W	01/2007	-0.21	-0.33	Phytoplankton-AH	01/2007	0.08	0.12
AHDB-S	08/2006	-0.16	-0.25	Phytoplankton-HF	01/2007	0.36	0.53
AHDB-W	01/2007	-0.09	-0.17	Hippochaete	10/2006	-0.43	-0.69
HFHW-S	08/2006	0.13	0.23	Hornwort	10/2006	-0.10	-0.16
HFHW-W	01/2007	-0.04	0.00	Tape grass	10/2006	-0.38	-0.54
HFDB-W	01/2007	0.08	0.12	Crucian carp-AH	01/2007	-0.82	-1.22
Aerosol-1	10/2006	0.08	0.14	Crucian carp-HF	01/2007	-0.92	-1.38

All the Fe isotope data are reported as an average of duplicate analyses.

relative to IRMM-014.

$$\delta^x\text{Fe} = \left(\frac{[^x\text{Fe}/^{54}\text{Fe}]_{\text{sample}}}{[^x\text{Fe}/^{54}\text{Fe}]_{\text{IRMM}}} - 1 \right) \times 1000 \quad (1)$$

All the data obtained from this study are plotted in Figure 2, and the data are reported as an average of duplicate analyses, except the aerosol-2 sample.

4 Results

The temperature, pH value, EC, DOC, NO₃⁻, SO₄²⁻, and sulfur isotope data of river water and lake water are listed in Table 1. All the Fe isotope data obtained in this study are summarized in Table 2, where a variable range of $\delta^{56}\text{Fe}$, from -2.03‰ to 0.36‰, was displayed.

4.1 Hydrochemistry

As is shown in Table 1, the water samples had a pH

value of 7.13–9.72. Although the rainwater samples have pH values that ranged from 3.55 to 6.83, with an average value of 4.53 (Han and Liu, 2005), all studied water samples had a pH value of >7. The high pH values might result from the high buffer capacity in the Karst area. Even for the rivers seriously contaminated with acid coal mine drainages, the pH values ranged from 7.13 to 8.42 due to the lime powder added at upstream sites. However, the EC became high, with a range of 285.0–938.3 $\mu\text{s/cm}$ for river water samples and 293.2–628.4 $\mu\text{s/cm}$ for lake water samples. And the sulfate concentrations were also high in the contaminated rivers as a result of oxidation of pyrite, with an average value of 412 ppm. With the exception of the river water of AR2, which was seriously contaminated by sewage, all river water and lake water samples in summer have higher DOC concentrations than those in winter. It is suggested that DOC concentrations of epilimnetic waters is influenced by natural and anthropogenic allochthonous inputs and by autochthonous primary production (Sachse et al., 2005).

During peak flow periods in summer, significant amounts of dissolved organic carbon flow into the river or even the lake with high water discharge (Ingri et al., 2000), which could result in the increase of DOC in the studied water samples in summer. High primary production could also play an important role in the increase of DOC concentrations and pH values of lake water in summer. In contrast, there was a significant decrease of NO₃⁻ concentration, especially for river waters that are less contaminated, which might be as a result of the dilution of rainwater during summer.

4.2 Stable isotopic composition

Sulfur isotope compositions of studied water samples and Fe isotope data of natural samples have been measured in this study. The $\delta^{34}\text{S}$ values of the studied samples range

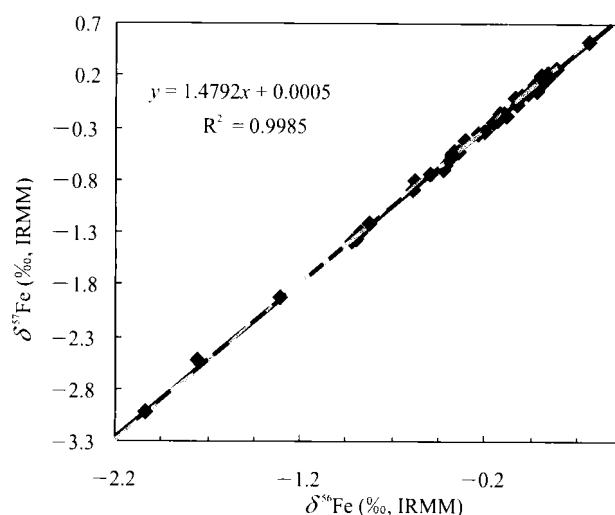


Fig. 2. Three isotope plots of data obtained in this study. All the data lie perfectly on the line with a slope of 1.4792 (—), being consistent with the theoretical mass fractionation line (----).

from -14.7‰ to 0.9‰ . River waters (AR1, AR2, AR4, and HR3) seriously contaminated with coal mine drainages tend to have more negative $\delta^{34}\text{S}$ values, with a range of -14.7‰ to -8.4‰ , while river waters (AR5) that are mainly deteriorated with sewage effluent have high $\delta^{34}\text{S}$ values, ranging from -2.3‰ to 0.9‰ . There is little seasonal variations for water samples that are seriously contaminated with coal mine drainages. Compared with most lakes in the world ($+5\text{‰}$ to $+15\text{‰}$; Krouse and Grinenko, 1991), water samples from Lake Hongfeng and Lake Aha tend to have light sulfur isotopic compositions (-8.6‰ to -5.3‰) that can be explained by the dominated influences of coal mine drainages. Seasonal variations were also clearly observed for epilimnetic waters, in particular, of Lake Hongfeng, and it is suggested that rainwater is the main contributor for the increase of $\delta^{34}\text{S}$ in summer (Song et al., 2008b).

The studied samples displayed a significantly variable range of $\delta^{56}\text{Fe}$, from -2.03‰ to 0.36‰ , which is shown in Table 2 and Figure 3. Riverine SPM samples have more variable $\delta^{56}\text{Fe}$ values (-0.89‰ to -0.10‰) than those of lake samples (-0.42‰ to 0.13‰). The sediments of Lake Aha have lighter Fe isotopic compositions relative to IRMM-014, ranging from -1.75‰ to -0.59‰ , while those of Lake Hongfeng have similar isotopic compositions to igneous rocks, ranging from -0.13‰ to 0.00‰ . The porewaters of Lake Hongfeng are all lighter than the corresponding sediments, and porewaters of Lake Aha have more variable $\delta^{56}\text{Fe}$ values, ranging between -2.03‰ and 0.12‰ . Aerosols and soils did not show significant variations in $\delta^{56}\text{Fe}$, with an average value of 0.10‰ and 0.10‰ , respectively. A few biological samples have also been analyzed. They all have slightly light Fe isotopic compositions: -0.43‰ for Hippochaete (*Equisetum*

ramosissimum Desf.), -0.10‰ for Hornwort (*Ceratophyllum demersum* Linn.), and -0.38‰ for tape grass (*Vallisneria americana*). Crucian carp muscles sampled in Lake Aha and Lake Hongfeng have similar $\delta^{56}\text{Fe}$ values, -0.82‰ and -0.92‰ , respectively, which is similar to the tuna muscle studied in Walczyk and von Blanckenburg (2002). In contrast to the light Fe isotope compositions, the phytoplankton samples have $\delta^{56}\text{Fe}$ values of 0.08‰ and 0.36‰ .

5 Discussion

5.1 Fe isotope variations of lake suspended particulates

As can be seen from Table 2, the suspended particulates of Lake Aha tend to have lighter Fe isotope compositions (-0.42‰ to -0.09‰) than those of Lake Hongfeng (-0.13‰ to -0.04‰). During low water-flow periods in winter, epilimnetic particulates at LJK have a $\delta^{56}\text{Fe}$ value of -0.21‰ . With the increase of water flow in summer, an increase of the $\delta^{34}\text{S}$ value of dissolved sulfate (-8.6‰ to -7.4‰) has been observed because of the retention of rainwater in epilimnion (Table 1; Fig. 4). Meanwhile, there is a significant decrease of $\delta^{56}\text{Fe}$ value for the corresponding SPM sample appeared at LJK. It is reported that the light Fe isotope compositions were resulted from the increase of organically bonded Fe particulates in high flow period (Song et al., 2008a). The aerosol particles have limited contributions.

In the case of Lake Hongfeng, the seasonal variation of the $\delta^{56}\text{Fe}$ value at HW was different from that of LJK, although increases of the $\delta^{34}\text{S}$ value of dissolved sulfate had also been observed at both stations (Fig. 4). Lake Hongfeng is a mesotrophic water system. During summer stratification, a significant amount of phytoplankton can be observed in epilimnion. So phytoplankton is an important component of the SPM sample. It is proposed that the $\delta^{56}\text{Fe}$ value of phytoplankton is more reflective of extracellular-adsorbed Fe, rather than intracellular Fe (Bergquist and Boyle, 2006). In the present study, the phytoplankton sample had also been analyzed where extracellular Fe and intracellular Fe were both included, and tended to have a higher $\delta^{56}\text{Fe}$ value of 0.36‰ (Table 2). Therefore, the heavy Fe isotope compositions might also be a result of adsorbed Fe. It could be an explanation for the higher $\delta^{56}\text{Fe}$ value of HW particulates in summer than that in winter (Fig. 4). In contrast, Lake Aha has lower primary production and a narrow surface area. The tributary input could play an important role in the lower $\delta^{56}\text{Fe}$ values of epilimnetic particulates of Lake Aha.

5.2 Possible influences on Fe isotope compositions of riverine SPM

As can be seen in Figure 5, suspended particulates in AR1, AR4, HR4, and AR2 tend to have lighter Fe isotope compositions (-0.89‰ to -0.38‰) in summer, and there are significant increases of $\delta^{56}\text{Fe}$ values during winter, except AR2 (Fig. 5). AR1, AR4, HR4, and AR2 are all rivers contaminated by coal mine drainage, which are characterized by high concentration of SO_4^{2-} and by lower and steady $\delta^{34}\text{S}$ values (Table 1; Fig. 6). During summer, high water flow makes the rivers cloudy, with the formation of reddish-brown Fe particles after the oxidation of pyrites. Therefore, the $\delta^{56}\text{Fe}$ of riverine SPM is more reflective of Fe particles of pyrite origin.

Previously, numerous studies were carried out on Fe isotopic compositions of pyrite, and a variable range of -3.5‰ to $+1.2\text{‰}$ was displayed, as summarized in Fehr et al. (2008) and Roger et al. (2008). It seems that pyrite formation, especially under anoxic conditions, tends to have lighter Fe isotopic compositions, although it is suggested by theoretical calculations that pyrite is expected to have heavier isotopes relative to most other Fe-bearing minerals (Polyakov and Mineev, 2000; Beard and Johnson, 2004). According to Roger et al. (2008), the microbial-induced pyrite oxidation produced little Fe isotope fractionation. During peak flow periods, it was not easy for the Fe particles to settle down to the riverbed. The suspended particles sampled at the upstream site of AR1 had a $\delta^{56}\text{Fe}$ value of -0.31‰ , indistinguishable from that sampled (-0.38‰) at the downstream site, which implied that limited Fe isotope fractionation can be expected along the river in summer. However, we only got $\delta^{56}\text{Fe}$ values of riverine SPM, but no data of the starting pyrite. So, detailed studies need to be done for further discussions.

Several studies have been carried out to determine the fractionation factors between $\text{Fe(III)}_{\text{aq}}$ and Fe(III) precipitations. Generally, it is suggested that ^{54}Fe will preferentially precipitate (Bullen et al., 2001; Johnson et al., 2002; Welch et al., 2003; Balci et al., 2006; Egal et al., 2008). As indicated by Balci et al. (2006), the precipitates tend to have low $\delta^{56}\text{Fe}$ values (-1.46‰ to -0.04‰) than the coexisting $\text{Fe(III)}_{\text{aq}}$ in synthetic, acidic, ferric sulfate solutions, which mimics the conditions of acid mine drainages. When water flow decreases during winter, $\text{Fe(III)}_{\text{aq}}$ will gradually precipitate along the river. Therefore, the increases of $\delta^{56}\text{Fe}$ of riverine particulates might be induced by the precipitation processes. However, high concentrations of DOC have been detected in AR2 (Table 1), which could be contaminated by sewage effluent, as high concentrations of NO_3^- have also been observed.

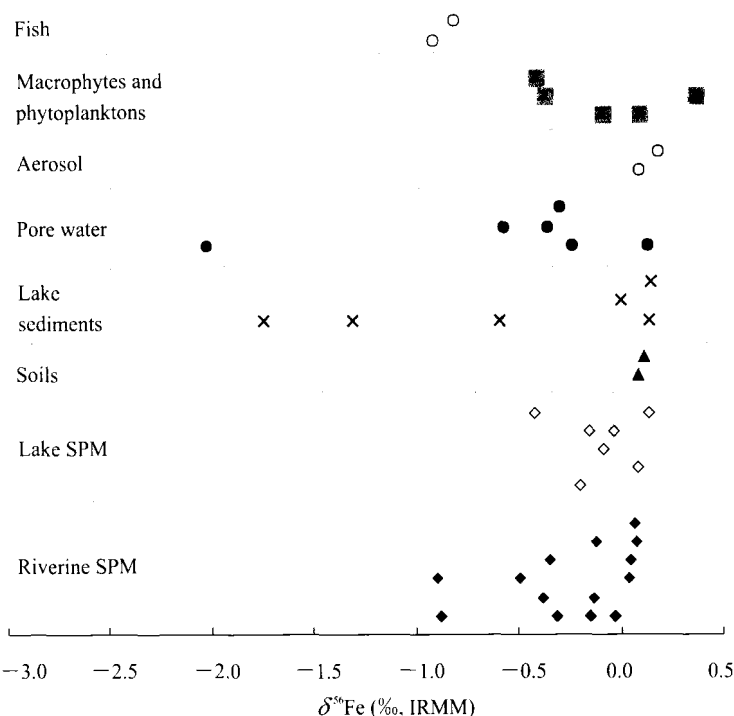


Fig. 3. Summary of $\delta^{56}\text{Fe}$ values of the studied natural samples. Shaded region represents the range of $\delta^{56}\text{Fe}$ of igneous rocks.

These organic matters make it difficult for the suspended particles to settle down along the riverbed. As a result, limited seasonal variations (Fig. 5) have been observed for AR2.

For AR5, HR3, and HR2, the suspended particulates had higher $\delta^{56}\text{Fe}$ values, ranging from -0.12‰ to 0.10‰ , which are similar to the average of igneous rocks (0.09‰ ; Beard et al., 2003). No significant seasonal variations were observed for AR5, HR2, and HR3. In contrast to the low and steady $\delta^{34}\text{S}$ values in mine drainage-contaminated rivers, AR5, HR2, and HR3 had higher and variable sulfur isotope compositions (Table 1; Fig. 6). Within these three rivers, AR5 was polluted by both factory drainage and sewage effluent, where there are high concentrations of DOC and NO_3^- . There are not much industrial pollutions for HR2 and HR3, except limited influences by agricultural wastewater. Detrital particles could provide important contributions to the Fe isotope compositions of HR2 and HR3, which is consistent with the propositions by Fantle and DePaolo (2004) and Ingri et al. (2006) that detrital particles have $\delta^{56}\text{Fe}$ values close to 0 or slightly positive. Two soil samples collected from the watersheds had $\delta^{56}\text{Fe}$ values of 0.08‰ and 0.11‰ (Table 2), respectively, and two aerosol samples showed $\delta^{56}\text{Fe}$ values of 0.08‰ and 0.12‰ (Table 2), respectively. It is implied that very limited Fe isotope fractionation occurred during weathering.

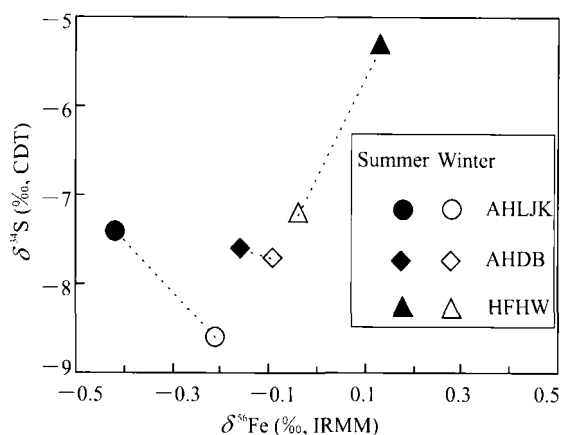


Fig. 4. Relationship between $\delta^{56}\text{Fe}$ and $\delta^{34}\text{S}$ in summer and winter at the sampling stations.

5.3 Fe isotope fractionation during early diagenesis of lake sediment

Sediments and porewaters were primarily studied to investigate Fe isotope fractionation during early diagenesis in lake sediments. As seen in Figure 7, depth profiles of LJK and HW were totally different. Sediment samples collected from LJK displayed significant, negative $\delta^{56}\text{Fe}$ values relative to IRMM-014. From 1 cm deep to 10 cm deep, the Fe isotope compositions of sediments became gradually lighter, ranging from -0.59‰ to -1.75‰ . However, porewaters from LJK displayed variations in the opposite trend, increasing from -2.03‰ to 0.12‰ (Table 2; Fig. 7), where the most variable $\delta^{56}\text{Fe}$ values were observed. In the case of HW, the Fe isotope composition of sediments was relatively constant with regards to depth, being similar to the average of igneous rocks. The corresponding porewaters had lower $\delta^{56}\text{Fe}$ values, ranging from -0.57‰ to -0.31‰ .

Several studies have been carried out on Fe isotope variations of marine sediments and Fe-Mn nodules. A relative wide range (-1.5‰ to 0.2‰) in $\delta^{56}\text{Fe}$ values has been observed (Beard and Johnson, 1999; Zhu et al., 2000; Levasseur et al., 2004; Chu et al., 2006; Severmann et al., 2006; Fehr et al., 2008). Dissimilatory Fe reduction (DIR) and pyrite formation are reported to be important for Fe isotope fractionations during early diagenesis in sediments (Severmann et al., 2006; Fehr et al., 2008). The adsorption of Fe(II) onto ferric oxide/hydroxide can also produce low $\delta^{56}\text{Fe}$ Fe(II)_{aq} (Icopini et al., 2004; Teutsch et al., 2005; Rouxel et al., 2008). For LJK, previous studies have indicated that dissimilatory Fe-reduction bacteria were detected through the sediment core, and the concentrations of pyrite and Acid Volatile Sulfide (AVS) were also high (Wang, 2003; Zhao, 2006). In this study, the lowest $\delta^{56}\text{Fe}$ value of -2.03‰ was observed near the sediment surface, and a similar variation trend was found to that of Severmann et al. (2006). Therefore, the Fe isotope

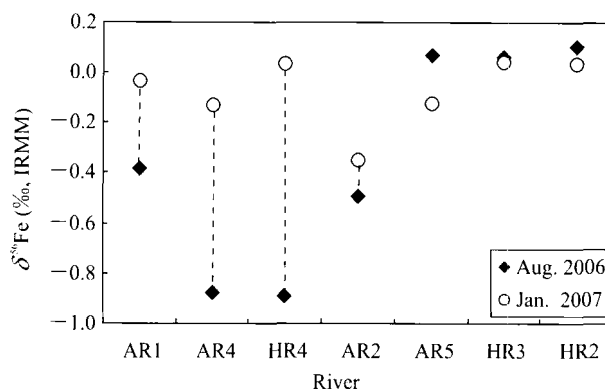


Fig. 5. Seasonal variations of $\delta^{56}\text{Fe}$ values of riverine-suspended particulates in summer (August 2006) and winter

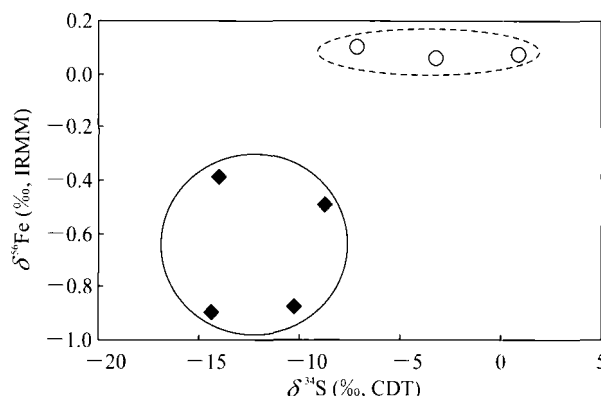


Fig. 6. $\delta^{56}\text{Fe}$ values of the studied riverine SPM samples in summer, and the corresponding $\delta^{34}\text{S}$ values of river water. Closed diamonds (♦) refer to samples collected from AR1, AR2, AR4, and HR4; open circles (○) refer to samples from AR5, HR2, and HR3.

fractionations are considered to be dominated by similar Fe recycling processes. The lowest $\delta^{56}\text{Fe}$ value of porewaters near the surface sediment might result from the active DIR and adsorption processes. There is a significant amount of Fe(III) oxides/hydroxides formed during pyrite oxidation in AR1, which provides the necessary reactive Fe for DIR and adsorption. During early diagenesis, a complex diagenesis of sulfur species as well as iron sulfides are occurring (Berner, 1984; Dević et al., 2006). With increases in burial depth, concentrations of Fe sulfides increase until they reach a depth of 17 cm, which is shown in Figure 8 (Zhao, 2006). The pronounced increase of $\delta^{56}\text{Fe}$ values (-2.03‰ to 0.12‰ ; Table 2; Fig. 7) of porewaters can be explained by the formation of a significant amount of Fe sulfides (Severmann et al., 2006). Meanwhile, the formation of sulfides will decrease the $\delta^{56}\text{Fe}$ value of sediments. It is coincidental that there is a pronounced increase of the $\delta^{56}\text{Fe}$ value of porewaters with the increase of depths at LJK (Fig. 7).

In contrast, there are limited inputs of reactive Fe particles for HW, and the concentration of sulfate is much lower than that of Lake Aha. The formation of sulfides, especially pyrite, is not expected to be important at HW.

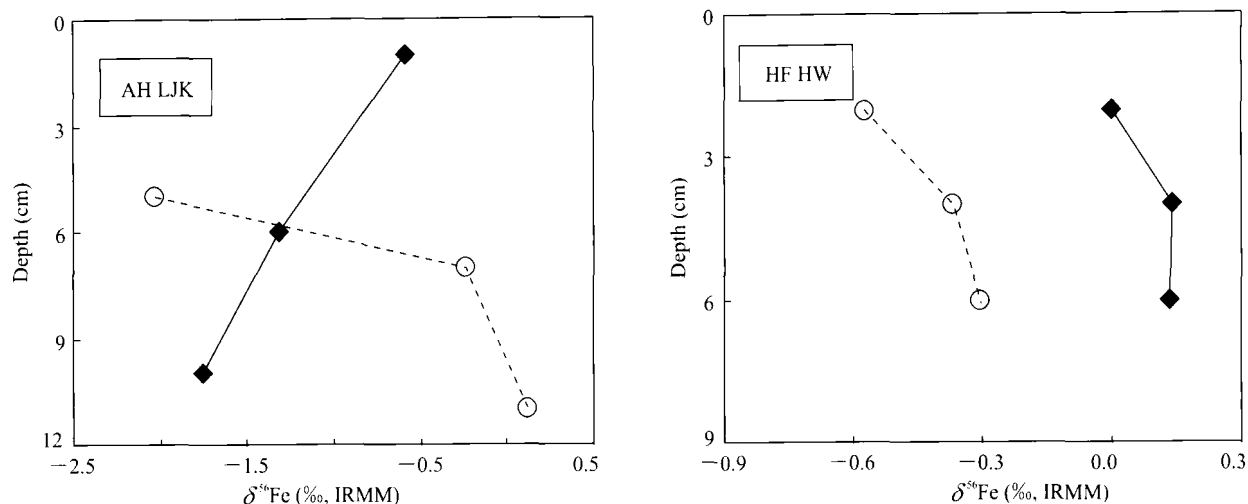


Fig. 7. Depth profiles of $\delta^{56}\text{Fe}$ values of sediments and porewaters at LJK station of Lake Aha (AH LJK) and at HW station of Lake Hongfeng (HF HW). Closed diamonds (\blacklozenge) refer to sediments; open circles (\circ) refer to porewaters.

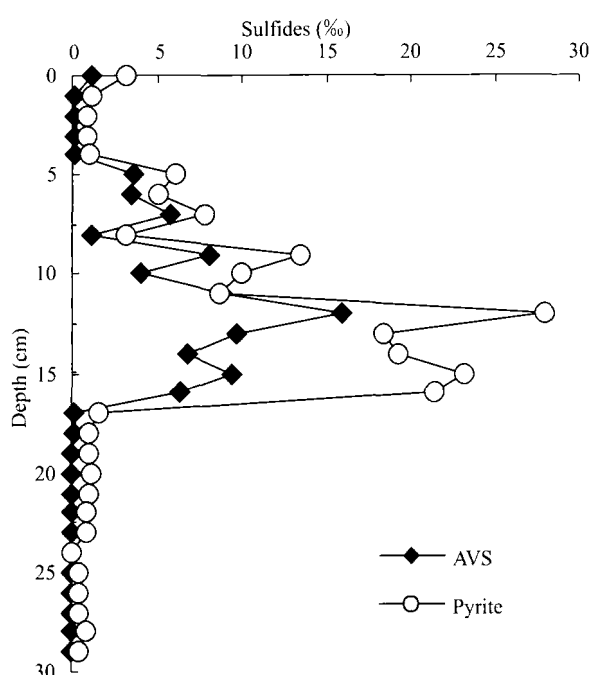


Fig. 8. Sediment profiles of pyrite and AVS for Lake Aha (modified from Zhao, 2006).

But Lake Hongfeng is a mesotrophic water system. The primary production of phytoplankton is high. Phytoplanktons sampled at HW have a $\delta^{56}\text{Fe}$ value of 0.36‰ due to extracellular adsorption. Therefore, it is considered that the phytoplankton die-offs are important contributions for sediments. The lower $\delta^{56}\text{Fe}$ values of porewaters could result from DIR and adsorption processes. Generally, Fe isotope fractionations during Fe recycling at HW seem to be much lower than those of LJK. The differences between Lake Aha and Lake Hongfeng could result from the different characteristics between these two lakes. Fe isotope studies of different Fe pools in sediments will be necessary for further detailed discussions.

6 Conclusion

The studied natural samples from the Karst area displayed a wide range of $\delta^{56}\text{Fe}$ (-2.03‰ to 0.36‰). Most samples tended to have lighter Fe isotope compositions relative to IRMM-014. Suspended particulates collected from rivers seriously contaminated by coal mine drainages tended to have very light Fe isotope compositions during peak flow periods, and they all had significant seasonal variations, except AR2, which was also polluted by sewage effluent. The pronounced increase of $\delta^{56}\text{Fe}$ during winter could be explained by the preferential precipitation of the light Fe isotope. The $\delta^{56}\text{Fe}$ values of epilimnetic SPM in Lake Aha are generally affected by tributary inputs, while the autochthonous products have important influences for Hongfeng particulates. With a significant amount of reactive Fe(III) oxides and high concentrations of sulfate, the variable $\delta^{56}\text{Fe}$ values were considered to be produced by the reactive Fe recycling in LJK sediments. The low $\delta^{56}\text{Fe}$ of porewater near the sediment surface could result from DIR and adsorption processes. The pronounced increase of $\delta^{56}\text{Fe}$ of porewaters was possibly produced by the formation of sulfides. The formation of sulfides also induced a decrease of the $\delta^{56}\text{Fe}$ value of sediments with burial depth at LJK. However, HW sediments had similar Fe isotope compositions to the average of igneous rocks, and the corresponding porewaters had slightly negative $\delta^{56}\text{Fe}$ values, suggesting that there was a limited amount of sulfide formed in the HW sediments. The die-offs of phytoplankton could have important influences on the Fe isotope compositions of HW sediments. The differences between LJK and HW sediments suggest that reactive Fe and sulfate reduction are of great importance in Fe isotope fractionations during Fe recycling.

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References

- Balci, N., Bullen, T.D., Witte-Lien, K., Shanks, W.C., Motelica, M., and Mandernack, K.W., 2006. Iron isotope fractionation during microbially stimulated Fe(II) oxidation and Fe(III) precipitation. *Geochim. Cosmochim. Acta*, 70: 622–639.
- Balistreri, L.S., Murray, J.W., and Paul, B., 1994. The geochemical cycling of trace elements in a biogenic meromictic lake. *Geochim. Cosmochim. Acta*, 58(19): 3993–4008.
- Beard, B.L., and Johnson, C.M., 1999. High precision iron isotope measurements of terrestrial and lunar materials. *Geochim. Cosmochim. Acta*, 63: 1653–1660.
- Beard, B.L., and Johnson, C.M., 2004. Fe isotope variations in the modern and ancient Earth and other planetary bodies, in: *Geochemistry of non-traditional stable isotopes. Rev. Mineral. Geochem.*, 55: 319–357.
- Beard, B.L., Johnson, C.M., Cox, L., Sun, H., Neelson, K.H., and Aguilar, C., 1999. Iron isotope biosignatures. *Science*, 285: 1889–1892.
- Beard, B.L., Johnson, C.M., Skulan, J.L., Neelson, K.H., Cox, L., and Sun, H., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chem. Geol.*, 195: 87–117.
- Bergquist, B.A., and Boyle, E.A., 2006. Iron isotopes in the Amazon River system: Weathering and transport signatures. *Earth Planet. Sci. Lett.*, 248: 54–68.
- Berner, R.A., 1984. Sedimentary pyrite formation: an update. *Geochim. Cosmochim. Acta*, 48: 605–615.
- Brantley, S.L., Liermann, L.J., Gynn, R.L., Anbar, A., Icopini, G.A., and Barling, J., 2004. Fe isotopic fractionation during mineral dissolution with and without bacteria. *Geochim. Cosmochim. Acta*, 68(15): 3189–3204.
- Brantley, S.L., Liermann, L., and Bullen, T.D., 2001. Fractionation of Fe isotopes by soil microbes and organic acids. *Geology*, 29: 535–538.
- Bullen, T.D., White, A.F., Childs, C.W., Vivit, D.V., and Schultz, M.S., 2001. Demonstration of significant abiotic iron isotope fractionation in nature. *Geology*, 29: 699–702.
- Chu, N.C., Johnson, C.M., Beard, B.L., German, C.R., Nesbitt, R. W., Frank, M., Bohn, M., Kubik, P.W., Usui, A., and Graham, I., 2006. Evidence for hydrothermal venting in the Fe isotope compositions of deep Pacific Ocean through time. *Earth Planet. Sci. Lett.*, 245: 202–217.
- Clasen, J., and Bernhardt, H., 1974. The use of algal assays for determining the effect of Fe and phosphorus compounds on the growth of various algal species. *Water Res.*, 8: 31–44.
- Davison, W., 1993. Iron and manganese in lakes. *Earth-Sci. Rev.*, 34: 119–163.
- Dević, G., Pfenndt, P., Jovančičević, and Popovic, Z., 2006. Pyrite formation in organic-rich clay, calcitic and coal-forming environments. *Acta Geologica Sinica* (English edition), 80(4): 574–588.
- Egal, M., Elbaz-Poulichet, F., Casiot, C., Motelica-Heino, M., Négrel, P., Bruneel, O., Sarmiento, A.M., and Nieto, J.M., 2008. Iron isotopes in acid mine waters and iron-rich solids from the Tinto–Odiel Basin (Iberian Pyrite Belt, Southwest Spain). *Chem. Geol.*, 253: 162–171.
- Evans, J.C., and Prepas, E.E., 1997. Relative importance of Fe and molybdenum in restricting phytoplankton biomass in high phosphorus saline lakes. *Limnol. Oceanogr.*, 42: 461–472.
- Fantle, M.S., and DePaolo, D.J., 2004. Fe isotopic fractionation during continental weathering. *Earth Planet. Sci. Lett.*, 228: 547–562.
- Fehr, M.A., Andersson, P.S., Håleius, U., and Mörth, C.M., 2008. Iron isotope variations in Holocene sediments of the Gotland Deep, Baltic Sea. *Geochim. Cosmochim. Acta*, 72: 807–826.
- Han Guilin and Liu Congqiang, 2005. Strontium isotope and major ion chemistry of the rainwaters from Guiyang, Guizhou province, China. *Environmental Chemistry*, 24(2): 213–218 (in Chinese with English abstract).
- Icopini, G.A., Anbar, A.D., Ruebush, S.S., Tien, M., and Brantley, S.L., 2004. Iron isotope fractionation during microbial reduction of iron: The importance of adsorption. *Geology*, 32: 205–208.
- Ingri, J., Malinovsky, D., Rodushkin, I., Baxter, D.C., Widerlund, A., Andersson, P., Gustafsson, Ö., Forsling, W., and Öhlander, B., 2006. Iron isotope fractionation in river colloidal matter. *Earth Planet. Sci. Lett.*, 245: 792–798.
- Ingri, J., Widerlund, A., Land, M., Gustafsson, Ö., Andersson, P. S., and Öhlander, B., 2000. Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chem. Geol.*, 166: 23–45.
- Johnson, C.M., Beard, B.L., and Roden, E.E., 2008. The iron isotope fingerprints of redox and biogeochemical cycling in modern and ancient Earth. *Annu. Rev. Earth Pl. Sc.*, 36: 457–493.
- Johnson, C.M., Beard, B.L., Roden, E.E., Newman, D.K., and Neelson, K.H., 2004. Isotopic constraints on biogeochemical cycling of Fe. *Rev. Mineral. Geochem.*, 55: 359–408.
- Johnson, C.M., Skulan, J.L., Beard, B.L., Sun, H., Neelson, K.H., and Braterman, P.S., 2002. Isotopic fractionation between Fe (II) and Fe(III) in aqueous solutions. *Earth Planet. Sci. Lett.*, 195: 141–153.
- Krouse, H.R., and Grinenko, V.A., 1991. *Stable isotopes: natural and anthropogenic sulphur in the environment*. Chichester: John Wiley and Sons, 1–440.
- Levasseur, S., Frank, M., Hein, J.R., and Halliday, A.N., 2004. The global variation in the iron isotope composition of marine hydrogenetic ferromanganese deposits: implications for seawater chemistry? *Earth Planet. Sci. Lett.*, 224: 91–105.
- Li Zhihong, Zhu Xiangkun and Tang Suohan, 2008. Characters of Fe isotopes and rare earth elements of band formations from Anshan–Benxi area: implications for Fe source. *Acta Petrologica et Mineralogica*, 4(7): 285–290 (in Chinese with English abstract).

- English abstract).
- Maréchal, C.N., Télouk, P., and Albarède, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.*, 156: 251–273.
- Martin, J.H., 1990. Glacial-interglacial CO₂ change: the Fe hypothesis. *Paleoceanography*, 5: 1–13.
- Poitrasson, F., Halliday, A.N., Lee, D.C., Levasseur, S., and Teutsch, N., 2004. Fe isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth Planet. Sci. Lett.*, 222: 253–266.
- Polyakov, V.B., and Mineev, S.D., 2000. The use of Mössbauer spectroscopy in stable isotope geochemistry. *Geochim. Cosmochim. Acta*, 64, 849–865.
- Roger, B., Herbert, J.R., and Axel, Schippers., 2008. Iron isotope fractionation by biogeochemical processes in mine tailings. *Environ. Sci. Technol.*, 42: 1117–1122.
- Rouxel, O., Fouquet, Y., and Ludden, J.N., 2004. Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: Evidence from sulfur, selenium, and iron isotopes. *Geochim. Cosmochim. Acta*, 68: 2295–2311.
- Rouxel, O., Sholkovitz, E., Charette, M., and Edwards, K., 2008. Iron isotope fractionation in subtterranean estuaries. *Geochim. Cosmochim. Acta*, 72, 3413–3430.
- Sachse, A., Henrion, R., Gelbrecht, J., and Steinberg, C.E.W., 2005. Classification of dissolved organic carbon (DOC) in river systems: Influence of catchment characteristics and autochthonous processes. *Org. Geochem.*, 36: 923–935.
- Severmann, S., Johnson, C.M., Beard, B.L., and McManus, J., 2006. The effect of early diagenesis on the Fe isotope compositions of porewaters and authigenic minerals in continental margin sediments. *Geochim. Cosmochim. Acta*, 70: 2006–2022.
- Song Liuting, Liu Congqiang, Wang Zhongliang and Liang Lili, 2008b. Stable sulfur isotopic geochemistry to investigate potential sources and cycling behavior of sulfate in Lake Hongfeng, Guizhou province. *Geochimica*, 37(6): 556–564 (in Chinese with English abstract).
- Song Liuting, Liu Congqiang, Wang Zhongliang, Zhu Xiangkun, Tang Suohan, Li jin and Liang Lili, 2008a. Iron isotope behaviors during geochemical cycling and the implications in Lake Aha, Guizhou, China. *Acta Petrologica et Mineralogica*, 4(7): 317–325 (in Chinese with English abstract).
- Staubwasser, M., von Blanckenburg, F., and Schoenberg, R., 2006. Iron isotopes in the early marine diagenetic cycle. *Geology*, 34: 629–632.
- Tang Suohan and Zhu Xiangkun, 2006b. Separation of some elements using AG MP-1 anion exchange resin. *Geological Journal of China Universities*, 12(3): 398–403 (in Chinese with English abstract).
- Tang Suohan, Zhu Xiangkun, Cai Junjun, Li Shizhen, He Xuexian and Wang Jinhui, 2006a. Chromatographic separation of Cu, Fe and Zn using AG MP-1 anion exchange resin for isotope determination by MC-ICP-MS. *Rock and Mineral Analysis*, 25 (1): 5–8 (in Chinese with English abstract).
- Teutsch, N., von Gunten, U., Porcelli, D., Cirpka, O.A., and Halliday, A.N., 2005. Adsorption as a cause for iron isotope fractionation in reduced groundwater. *Geochim. Cosmochim. Acta*, 17: 4175–4185.
- Walczyk, T., and von Blanckenburg, F., 2002. Natural Fe isotope variations in human blood. *Science*, 295: 2065–2066.
- Wang Fushun, 2003. The geochemical behavior of trace metals near water-sediments interface in seasonally anoxic lakes. Guiyang, Institute of Geochemistry, Chinese Academy of Sciences, PhD thesis.
- Wang Yuchun, Huang Ronggui and Wan Guojiang, 1998. A newly developed sampler for collecting samples near the lacustrine sediment-water interface. *Geol.-Geochemistry*, 1: 94–96 (in Chinese with English abstract).
- Welch, S.A., Beard, B.L., Johnson, C.M., and Braterman, P.S., 2003. Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(II) and Fe(III). *Geochim. Cosmochim. Acta*, 67: 4231–4250.
- Weyer, S., Anbar, A.D., Brey, G.P., Münker, C., Mezger, K., and Woodland, A.B., 2005. Fe isotope fractionation during planetary differentiation. *Earth Planet. Sci. Lett.*, 240: 251–264.
- Zhao Youzhi, 2006. The distribution and micro-biogeochemistry behavior of sulfur speciation in sediment from the plateau lake: As exemplified by Lake Erhai and Lake Aha, China. Guiyang, Institute of Geochemistry, Chinese Academy of Sciences, PhD thesis.
- Zhu, X.K., Guo, Y., O’Nions, R.K., Young, E.D., and Ash, R.D., 2001. Isotopic homogeneity of iron in the early solar nebula. *Nature*, 412: 311–313.
- Zhu, X.K., O’Nions, R.K., Guo, Y., and Reynolds, B., 2000. Secular variation of Fe isotopes in north Atlantic deep water. *Science*, 287: 2000–2002.