



Non-residual Sr of the sediments in Daihai Lake as a good indicator of chemical weathering

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ABSTRACT

The Rb/Sr ratio of lake sediments has been demonstrated to be a potential indicator of chemical weathering by increasing work. However, Rb and Sr in lake sediments are derived from both chemical weathering and physical erosion. Rb and Sr of different forms in lake sediments may record different environmental processes and information. In this study, the variation patterns of Rb and Sr of different forms in sediments of Daihai Lake were investigated. The results show that Rb and Sr of different forms display noticeably different variation patterns due to their different sources and associated environmental processes. Using the Rb/Sr ratios of bulk lake sediments to reflect chemical weathering is not accurate. The non-residual Sr of the sediments without detrital carbonates, representing the Sr leached from the catchment, can be used as an index of chemical weathering because the weathering of Sr minerals is very sensitive to climate change, and the non-residual Sr content of the sediment is determined more by Sr²⁺ influx than by the physicochemical conditions of lake water. The correspondence between the non-residual Sr and TIC/TOC in Daihai Lake also indicates that the non-residual Sr of the sediments is a good indicator of chemical weathering in the catchment.

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Introduction

Rubidium (Rb) and strontium (Sr) are easily fractionated on the Earth's surface, in response to their different geochemical behaviour during weathering processes (Goldstein, 1988; Chen et al., 1999). As typical dispersive trace elements, Rb and Sr are usually substituted in the structural sites of rock-forming minerals and are seldom composed of individual minerals. Rb tends to be dispersed in K-bearing minerals, such as muscovite and K-feldspar, while Sr prefers Ca-bearing minerals, such as plagioclase, amphibole, pyroxene and carbonate minerals. When these minerals outcrop on Earth's surface and are subjected to weathering, the former group (e.g., muscovite, biotite and K-feldspar) is typically more stable than the latter group (e.g., carbonate minerals, plagioclase, amphibole and pyroxene), resulting in the fractionation between Rb and Sr in weathering products.

As the main sink of transported surface materials in the continent, lakes receive large amounts of weathering products from rocks and soil in catchments. With the enhancement of chemical weathering, a greater amount of Sr is leached as dissolved Sr²⁺ from the rocks and soil and is transported into lakes, whereas Rb mainly remains in the rocks and soil, resulting in a decrease in the Rb/Sr ratio of lake sediments over the corresponding period. Thus, Jin et al. (Jin et al., 2001c, 2006)

used the Rb/Sr ratio of bulk sediments in Daihai Lake as a potential indicator of the chemical weathering intensity in the catchment.

In fact, physical and chemical weathering, reflected in water as suspended particles and dissolved matter, respectively, act together to denude the continents (Gaillardet et al., 1997). Dissolved materials are finally deposited in sediments in their non-residual form (exchangeable, carbonate and Fe–Mn oxides) through physical adsorption, chemical precipitation and biological uptake, whereas the suspended particles (insoluble materials) are mainly deposited in their residual form. Thus, various forms of Rb and Sr in lake sediments record different environmental processes and information. This fact may affect the reliability of using the Rb/Sr ratios of bulk sediments to reflect paleoclimate/paleoenvironment change, especially for the researches performed over short terms (e.g., decadal scale) and/or in the catchments where the changes in physical and chemical weathering have opposite effects on the Rb/Sr ratios of lake sediments (Xu et al., 2010).

Today, questions still remain regarding what information Rb and Sr of different forms represent and whether or how Rb and Sr from terrigenous detritus inputs affect the application of the Rb/Sr ratios of bulk lake sediments as an indicator of chemical weathering. In this study, the variations in contents of Rb and Sr of different forms in a sediment core were investigated to distinguish the environmental information encoded by these elements of different forms in lacustrine sediments.

Daihai Lake was selected as the study site because it is an ideal place for paleoclimate/paleoenvironment research. It is a closed lake

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in Inner Mongolia in north-central China that sits at a critical juncture at the confluence of warm, moist monsoonal circulations and cold, dry polar airflows (Fig. 1). It is influenced both by the Asian summer and winter monsoons and by the Westerlies (Fig. 1). Owing to the basin structure and geographical location, the sedimentary record of Daihai Lake serves as a target proxy for improving our understanding of monsoonal variability and environmental responses (Xiao et al., 2004; Peng et al., 2005; Xiao et al., 2006).

Study site

Daihai Lake (40°29' to 40°37'N, 112°33' to 112°46'E) lies ca. 10 km east of Liangcheng County in Inner Mongolia, north-central China (Fig. 2). It has an area of 133.5 km², a maximum water depth of 16.1 m and a mean water depth of 7.4 m, and an elevation of 1221 m (Wang et al., 1990). The lake basin is bordered by the Manhan Mountains to the north and the Matou Mountains to the south. Hills are distributed to the east of the lake, and plains are present along its western shore. The highest peaks of the Manhan and Matou Mountains reach elevations of 2305 and 2035 m, respectively. The lake catchment covers 2289 km², and five major rivers enter the lake, whereas no rivers drain the lake.

Daihai Lake is a brackish lake with an average TDS (total dissolved solid) of 4658.6 mg/L (Table 1) (Zhou et al., 2008). The main cation and anion are Na⁺ and Cl⁻, respectively. Na⁺ takes up approximately 89.46% of TZ⁺, while Cl⁻ takes up approximately 71.16% of TZ⁻. The sediments mainly consist of quartz, feldspar, micas, carbonate, and clay minerals (Jin et al., 2001b).

Daihai Lake is located at the transition between semi-humid and semi-arid areas in the middle temperate zone of China. The mean annual temperature in the area is 5.1°C, with average temperatures of 20.5°C and

–13.0°C in July and January, respectively. The mean annual precipitation is 423 mm, and ca. 80% of the annual precipitation falls from June to September, with a peak value of 122 mm occurring in August. The mean annual evaporation reaches 1162 mm and is 2.8 times the annual precipitation. The lake is covered with ca. 60 cm of ice from November to March. In the lake area, the winter climate is controlled by the dry and cold northwesterly winter monsoon, which generates frequent dust storms from late autumn to spring, whereas the summer climate is dominated by the warm and moist southeasterly summer monsoon, which is responsible for most of the annual precipitation and rainstorm activities (Gao, 1962; Zhang and Lin, 1992).

Materials, chronology and methods

In the summer of 1999, two sediment cores, designated DH99a and DH99b, were extracted from the central part of Daihai Lake using a corer driven by a Japan-made TOHO drilling rig (Model D1-B). DH99a (40°35.165'N, 112°40.057'E) was recovered at a water depth of 13.1 m, with a sediment depth of 11.96 m. DH99b (40°35.134'N, 112°40.061'E), ca. 60 m southeast of DH99a, was recovered at a water depth of 13.1 m, with a sediment depth of 24.10 m (Peng et al., 2005; Xiao et al., 2006; Sun et al., 2009). The cores were cut continuously into 2-cm segments to obtain samples for laboratory analyses.

The upper 3 m of DH99b was analysed in this study. The chronology sequence of the core sediment consists of 12 AMS ¹⁴C dates (Sun et al., 2009), and the age control of this study is based on the upper two AMS ¹⁴C dates, corresponding to the depths of 2.00 m and 4.00 m (Table 2).

The non-residual Rb and Sr contents in the sediment samples were obtained upon extraction with 1 M HCl according to the procedure recommended by the ASTM D3974-81 Practice B (Snape et al., 2004;

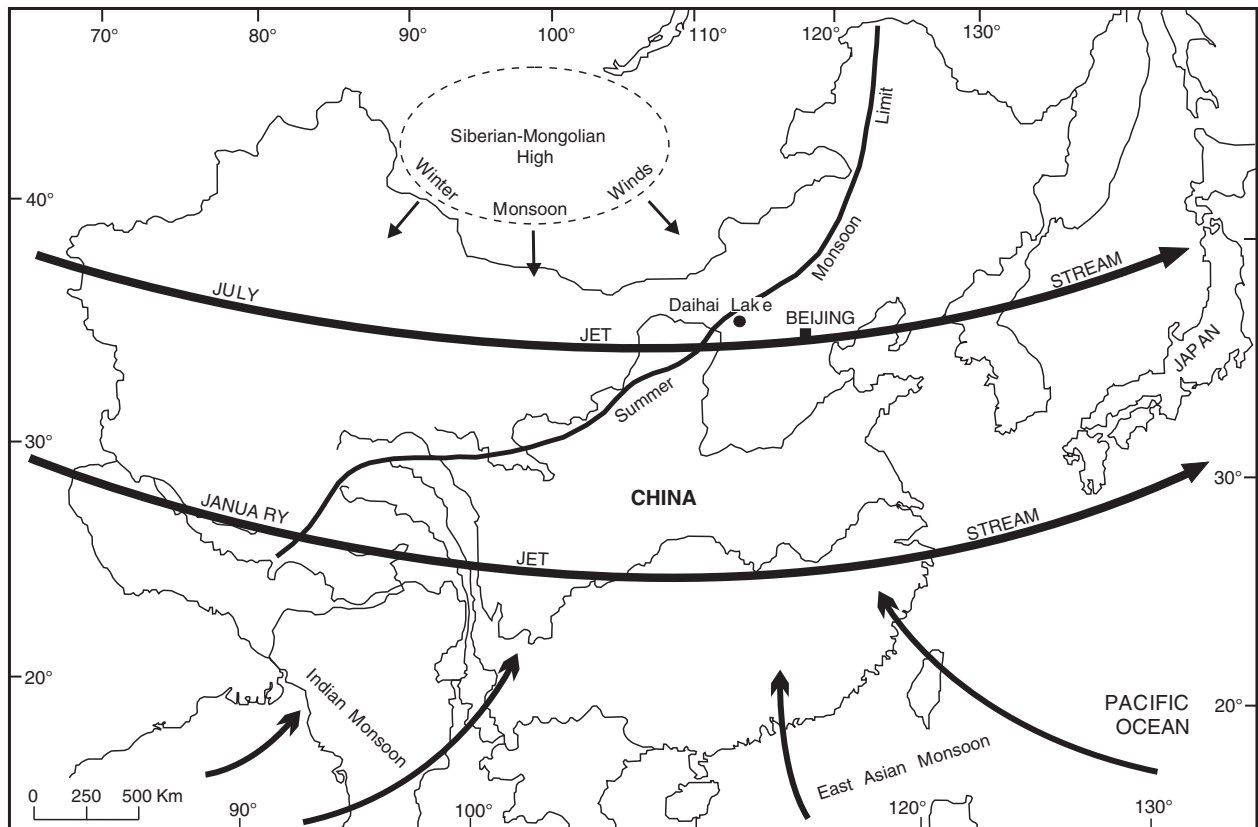


Figure 1. Map showing the climatic system of China, including the East Asian and Indian summer monsoons, the winter monsoon associated with the Siberian-Mongolian High, and the Westerlies generalised as the mean location of the jet stream. Compiled from Gao (1962), Zhang and Lin (1992), and Xiao et al. (2004).

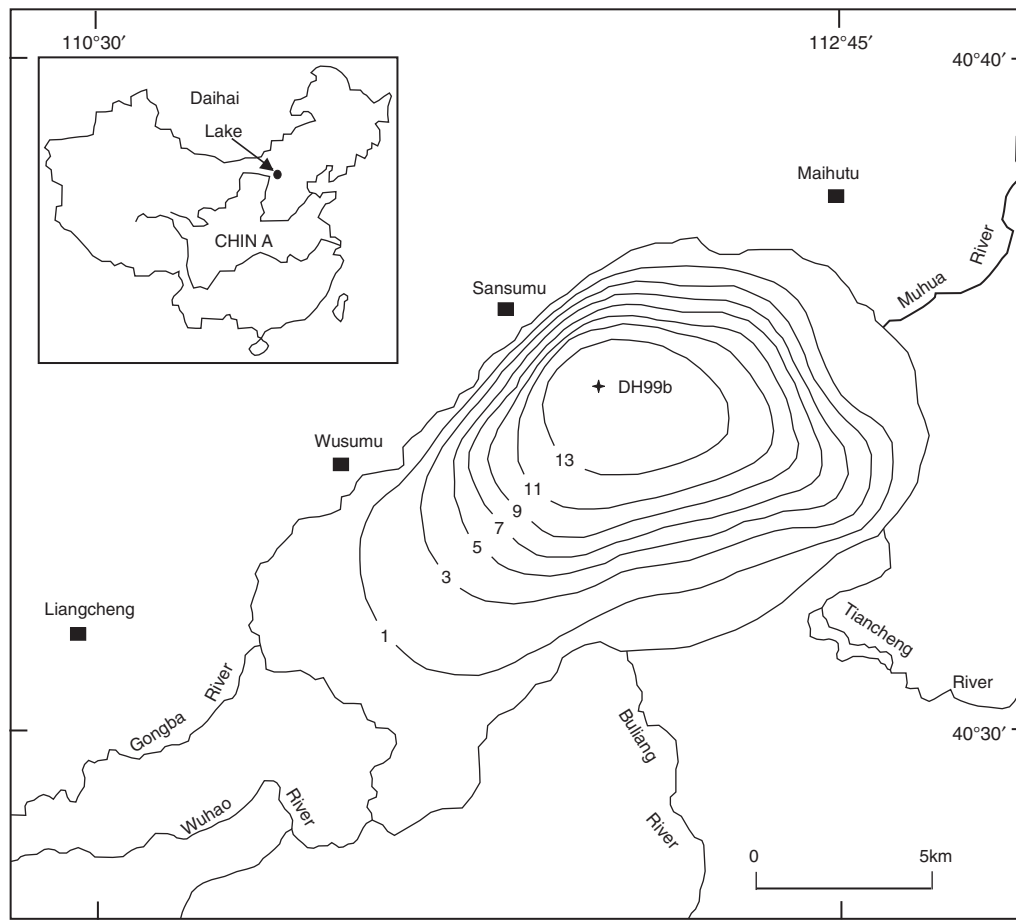


Figure 2. Map of Daihai Lake showing the location of the DH99b core.

Lavilla et al., 2006). This standard practice indicates that the metals released from the sediment upon acid extraction are bound as hydroxides, carbonates, sulphides, oxides and organic materials. The use of lower HCl concentrations, despite being a common practice, may be ineffective because the acidity can be neutralised by carbonates present in the sediment (Luoma and Bryan, 1981; Snape et al., 2004). In contrast, higher HCl concentrations can lead to the attack of residual sediment phases (Luoma and Bryan, 1981; Ying et al., 1992). The extractions were carried out in 50-ml-capacity polyethylene tubes using a 0.5-g sample mass and a 20-ml extract volume. After 2 h of agitation, the extract was separated by centrifugation (4000 rpm, 20 min). The extractions were performed in triplicate, and the three supernatants were combined and brought up to a final volume of 100 ml by adding de-ionised water. The residue was washed by adding 20 ml of de-ionised water and shaking for 15 min, followed by centrifugation. The supernatant was then decanted and discarded. The residues were washed twice and then dried in a freeze drier, followed by digestion with HF and HNO₃ in screw-top PTFE-lined stainless bombs (Qi et al., 2000). The reagent blanks were treated in the same manner as the samples. The Rb and Sr contents of different forms were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with an average precision of less than 5% at the Institute of Geochemistry, Chinese Academy of Sciences.

Results and discussion

Variation patterns of Rb and Sr of different forms

The variations in the contents of the residual and non-residual Rb and Sr in Daihai Lake are shown in Figure 3. The non-residual Rb contents varied from 1.3 to 2.9 µg/g, with an average value of 2.1 µg/g, while the residual Rb contents varied from 118 to 159 µg/g, with an average value of 143 µg/g. The CVs (Coefficients of Variance) of non-residual and residual Rb were 0.222 and 0.053, respectively. The non-residual Sr contents varied between 102 and 759 µg/g, with an average value of 257 µg/g, whereas the residual Sr contents varied between 88 and 126 µg/g, with an average value of 107 µg/g. The CVs of non-residual and residual Sr were 0.57 and 0.071, respectively. The non-residual Sr contents exhibited remarkably high values over the interval between 1620 and 1200 cal yr BP, as shown in Figure 4. The results indicate that almost all of the Rb is sequestered in the residual (silicate) phase, while more than half of the Sr is bound to the non-residual form in the sediment samples.

Rb mainly exists in the residual phase, whereas Sr is mainly present in the residual and carbonate phases in soil and rocks (Dasch, 1969; Liu et al., 2002). The carbonates in the sediments in the central part of

Table 1
Concentration of the major ions and TDS^a of water in Daihai Lake in 2004 (Zhou et al., 2008).

Ions	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻	TDS
Concentration (mg/L)	5.93	1483.0	30.93	137.90	448.40	99.87	317.18	2135.3	4658.6

^a TDS: total dissolved solids.

Table 2
Radiocarbon dating results for Daihai Lake (Sun et al., 2009).

Laboratory number	Depth (m)	Dating material	$\Delta^{13}\text{C}$ (‰)	AMS ^{14}C age (^{14}C yr BP)	Calibrated age (cal yr BP)
Tka-12097	2.00	Organic matter	-24.8	1550 ± 70	1592–1302
Tka-11998	4.00	Organic matter	-25.5	2310 ± 70	2487–2150

Daihai Lake are predominantly authigenous in origin (Wang et al., 1990). Therefore, according to the applied extraction method, the elements of the non-residual form extracted by 1 M HCl represent the leached part from the weathering crust, and the residual form represents terrigenous debris. The residual Rb and Sr are carried into the basin together with the silicate input resulting from physical erosion, whereas the non-residual Sr is mainly from the leaching of rocks and soil during chemical weathering and transported as dissolved Sr^{2+} .

The highly inert nature of Rb is confirmed by the low content and small fluctuation range of non-residual Rb in the sediments of Daihai Lake. The amount of Rb leached from catchments is small and does not change perceptibly as the climate changes. This phenomenon is also verified by the low and almost invariant content of non-residual Rb throughout the entire sediment core profile of Huguangyan Lake (Zeng et al., 2011). Therefore, non-residual Rb cannot be used to reconstruct the paleoclimate/paleoenvironment.

The residual Rb and Sr contents show a negative correlation throughout the entire core profile ($r^2 = -0.685$, $p < 0.001$), possibly because of their different parent minerals with different grain size. Rb is quite rich in clay and mainly exists in the residual phase, while Sr is distributed in coarse-grained sand and silt fractions, occurs in both the residual and carbonate phases, and is leached as the carbonate decomposes (Chen et al., 1998; Koinig et al., 2003; Kalugin et al., 2007). It has been demonstrated that Rb and clay positively correlate with each other in Daihai Lake (Jin et al., 2001a). The contents of fine-grained sediments and coarse-grained sediments are normally negatively correlated. Accordingly, residual Rb and residual Sr display the reversed changes in the sediment core.

Meanwhile, the residual Rb and Sr contents of the sediment are also influenced by the Rb and Sr content of the weathering crust. Strong

chemical weathering makes the weathering residue rich in Rb and depleted in Sr. In most cases, particle grain size (physical weathering) and chemical weathering have opposite effects on the residual Rb and Sr contents of lake sediments. Under wet climate conditions, chemical weathering is stronger, which leads to a higher Rb/Sr ratio in the weathering residue. At the same time, high precipitation enhances the soil erosion over the lake region and increases the transport capacity of streams and rivers, leading to coarser clastic materials available for river transport and subsequent deposition in the central part of the lake (Smith, 1996). The coarse clastic materials are rich in Sr and depleted in Rb compared with the fine materials. As a result, the residual Rb and Sr content/ratio of lake sediments cannot be used to reflect paleoclimate in the catchment when the leaching of Sr from rocks/soil in catchments is substantial, such as in Daihai Lake.

Non-residual Sr as a good indicator of chemical weathering

Under natural conditions, lake sediments have two material sources. One source is the terrigenous debris directly brought in by physical erosion, which exists in the sediments mainly in the residual form. The other source is dissolved substances produced by chemical weathering, which are deposited in lake sediments in the non-residual form through physical adsorption, chemical precipitation and biological uptake. Thus, the elements of the different forms of lake sediments represent different sources and environmental processes.

Previous studies have shown that the Rb/Sr ratio in weathering residues increases as the weathering intensity increases due to the higher Sr activity and the more inert nature of Rb (Parrington et al., 1983; Chen et al., 1998, 1999). Based on a series of acid-leaching experiments, Chen et al. (1996) showed that Rb is stable while Sr readily passes into solution. They suggest that part of the Sr is leached into solution during weathering and transported as dissolved Sr^{2+} . When Sr^{2+} is carried into a lake, it is deposited into the sediments through in-lake processes, including absorption and/or co-precipitation. A positive relationship between Rb/Sr versus $1/\text{Sr}$ in Daihai Lake further indicated that the variations in the Rb/Sr ratios chiefly depended on the Sr activity during weathering (Jin et al., 2006). Furthermore, Jin et al. (2006) indicated that the Rb/Sr ratios of bulk sediments in Daihai Lake could be interpreted

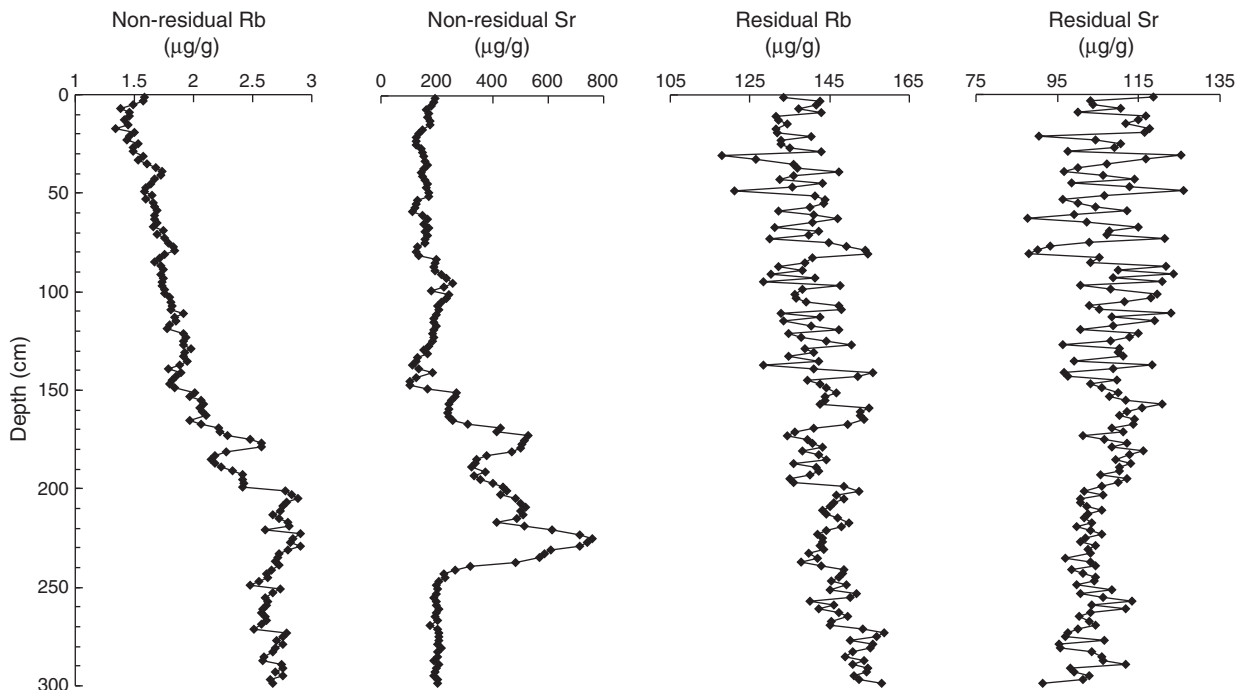


Figure 3. Variations in Rb and Sr of different forms of the sediments in Daihai Lake.

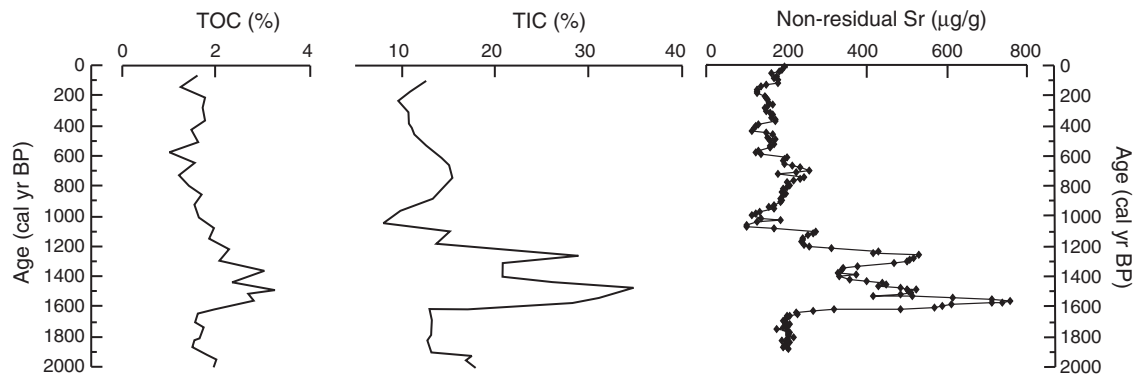


Figure 4. Comparison of non-residual Sr with TOC and TIC. The TOC and TIC data are from Sun and Xiao (2006).

to be the direct result of changes in the fluxes of dissolved materials controlled by climate change within the individual catchment. Stronger chemical weathering leads to more dissolved Sr^{2+} being transported into the depositional basin, resulting in a decrease in the Rb/Sr ratio. Essentially, the use of the Rb/Sr ratios of lake sediments as an indicator of chemical weathering within a watershed is only related to the non-residual Sr content, which is positively correlated with the intensity of chemical weathering.

It is well known that Sr acts as an analogue to Ca during chemical weathering because both are alkaline earth elements with similar ionic radii and the same valence (Bailey et al., 1996). However, there may be some differences between the deposition mechanisms of Ca^{2+} and Sr^{2+} in lake water. Jin et al. (2005) carried out a sequential extraction experiment on 14 sediment samples from Daihai Lake. The results indicated that most of the elements determined were combined with detrital minerals due to the relatively low activity during weathering, except Ca and Sr. Figure 5 shows the distributions of the different fractions of non-residual Ca and Sr of the sediments in Daihai Lake. Ca was predominantly deposited as carbonate (79%), while Sr was mainly deposited in the carbonate (48%) and Fe–Mn oxide (42%) fractions (data from Jin et al. (2005)).

The deposition of Ca^{2+} as CaCO_3 is closely related to the effects of the physicochemical conditions of lake water, in addition to the Ca concentration in the lake water. However, except for carbonate, a large amount of Sr^{2+} precipitates as Fe–Mn oxide and exchangeable fractions through absorption and co-precipitation, which is mainly influenced by material influx (Jin et al., 2006). The authigenic calcium carbonates in lake sediments mainly reflect hydrological changes in lake water. The high calcium carbonate content is often considered to be indicative of a warm and dry

climate, which is sometimes contradictory to the finding that a high Sr content in sediments reflects a high chemical weathering intensity and a warm and wet climate. For example, the non-residual Sr and total inorganic carbon (TIC) of the sediments in Huguangyan Maar Lake showed roughly opposite variation patterns (Zeng et al., 2012).

As discussed above, non-residual Sr of the lake sediments without detrital carbonates can be used as an index of chemical weathering, and a high non-residual Sr content implies strong chemical weathering because (1) non-residual Sr is indicative of the Sr leached from the weathering crust; (2) Sr-bearing minerals are sensitive to chemical weathering; and (3) the non-residual Sr content of sediments is influenced more by Sr^{2+} influx than lake water physicochemical conditions.

The superiority of non-residual Sr over Rb/Sr ratio

The Rb and Sr of bulk sediments contain composite information about different environmental processes, which may greatly complicate the environmental significance of the Rb/Sr ratios of bulk lake sediments. For example, environmental changes can influence the Rb–Sr fraction much easier for fresh rocks or slightly weathered rocks than highly weathered rocks (Dasch, 1969). As a result, chemical weathering may have stronger influence on the Rb/Sr ratios of bulk lake sediments in a slightly weathered catchment, while physical weathering may play a dominating role in a highly weathered catchment. In another scenario, if the physical loads in the catchment are very strong, even though the associated chemical weathering is expected to be enhanced, the chemical composition of the lake sediments may be dominated by terrigenous detritus but not chemical/biogenic depositions. Under this circumstance, the Rb/Sr ratios of the bulk lake sediments may serve as an indicator of

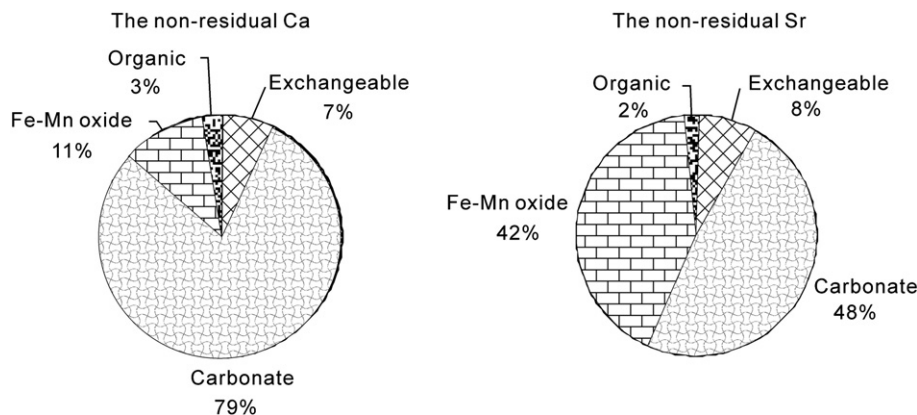


Figure 5. Distributions of the different fractions of non-residual Ca and Sr. The data are from Jin et al. (2005).

physical weathering intensity, but not or only partly of chemical weathering intensity.

In fact, physical weathering and chemical weathering may exhibit opposite behavior and compete in controlling the Rb/Sr signals of bulk lake sediments in some cases (Xu et al., 2010). Stronger chemical weathering leads to more Sr leached from rocks/soil and lower Rb/Sr ratios in lake sediments. On the contrary, stronger physical weathering correlates to a higher fraction of terrigenous detritus and therefore higher Rb/Sr ratios of lake sediments. The trends regarding the Rb/Sr ratios of only two cores, among the eight studied surface cores from Qinghai Lake, are generally similar to those of the precipitation indicators, but the other cores do not exhibit such a relationship due to the opposite effects of chemical weathering and physical weathering (Xu et al., 2010).

In addition, terrigenous Rb and Sr have different grain sizes. Rb is quite common in clay, while Sr is distributed in sand and silt fractions (Chen et al., 1998; Koinig et al., 2003; Kalugin et al., 2007). Accordingly, the grain size of terrigenous inputs also affects the Rb/Sr ratios of bulk lake sediments.

As shown in Figure 3, the different forms of Rb and Sr in the sediments in Daihai Lake display noticeably different variation patterns due to different sources and different grain-size effects. Thus, the Rb/Sr ratios of the bulk lake sediments of Daihai Lake cannot accurately reflect chemical weathering. However, the non-residual Sr is closely correlated with chemical weathering. The effect of the residual Rb and Sr can be eliminated by using non-residual Sr instead of the Rb/Sr ratios of bulk lake sediments to reflect the change in chemical weathering.

Comparison of non-residual Sr with TIC and TOC

Chemical weathering is very sensitive to temperature and humidity (Velbel, 1993; White and Blum, 1995; Brady et al., 1999). Under cold and dry climate conditions, the dissolved Sr content is mainly controlled by temperature and decreases with decreasing temperature. Under warm and wet conditions, precipitation is more important, and increasing precipitation introduces more dissolved Sr into lake sediments (Chen et al., 1999; Jin et al., 2001c).

A mineralogical analysis of the samples collected from the surface sediments of Daihai Lake indicated that the deep water midlake zone was dominated by microcrystalline calcite yielded by inorganic precipitation in the lake water and calcareous shells produced by living organisms (Wang et al., 1990). These results suggest that the carbonates in the Daihai Lake sediment cores recovered from the central part of the lake are predominately authigenous in origin and were formed by chemical or biochemical processes. Authigenic carbonates formed in Daihai Lake by chemical and biochemical processes are closely associated with the evaporation of the lake water, which primarily controls the chemical composition and salinity of the lake water (Lerman, 1979; Wang et al., 1990). Given that the evaporation of lake water is mainly controlled by temperature and atmospheric humidity, and humidity is determined by temperature and atmospheric precipitation, we infer that the formation of authigenic carbonates in Daihai Lake can be linked predominantly with temperature. When temperature rises, evaporation is enhanced, leading to the supersaturation of Ca^{2+} and Mg^{2+} in lake waters and thus promoting the formation of carbonates in the lake. Therefore, the total inorganic carbon (TIC) of the sediments in Daihai Lake was inferred to reflect the temperatures over the lake region, and an increase in the TIC content implied an increase in temperature (Xiao et al., 2006).

The organic matter in lake sediments originates from two principal types of sources: autochthonous sources, including planktonic algae and aquatic plants living in the water, and allochthonous sources from terrestrial plants growing in the lake catchment (Lerman, 1979; Talbot and Johannessen, 1992; Meyers, 1994). The total organic carbon (TOC) of the sediments in Daihai Lake has been demonstrated to indicate the precipitation changes in the lake basin, with higher contents reflecting more precipitation (Cao et al., 2000; Sun and Xiao, 2006; Xiao et al., 2006). When the precipitation over the lake region intensifies, soil erosion in

the lake catchment is enhanced, and the transport capacity of streams and rivers entering the lake is increased, leading to relatively more land-derived organic matter being carried into the lake (Lerman, 1979; Håkanson and Jansson, 1983; Sun and Xiao, 2006; Xiao et al., 2006). Furthermore, the increased water input causes the salinity of the lake water to decrease, which is favourable for the planktonic algae and aquatic plants growing in Daihai Lake (Sun and Xiao, 2006).

As shown in Figure 4, the non-residual Sr content showed the highest values over the past 2000 yr during the period 1620–1200 cal yr BP, implying strong chemical weathering. Both the TOC and TIC of the DH99b core (the data from Sun and Xiao (2006)) exhibited the highest values during the same period over the past 2000 yr, which implied a warm and wet climate during this period. The warm and humid environment resulted in a significant enhancement in chemical weathering (Velbel, 1993; White and Blum, 1995; Brady et al., 1999), which caused much more Sr to be leached from the weathering profile (Dasch, 1969; Chen et al., 1999). Both the pollen (Xiao et al., 2004) and grain size (Peng et al., 2005) in Daihai Lake implied favourable hydro-thermo conditions during the corresponding period. Pollen data from the DH99a sediment core suggested that the forests in the area disappeared since 2900 cal yr BP ago, reflecting a cool and dry climate, but the recovery of woody plants that occurred from 1700 to 1350 cal yr BP implied an amelioration of the climate in the lake area during this episode (Xiao et al., 2004). The grain-size distribution observed in core DH99a indicated that the climate became dry during the late Holocene since 3100 cal yr BP ago (Peng et al., 2005). However, the Md values and the silt fraction contents increased considerably in the lake sediments from 1700 to 1000 cal yr BP, implying a significant intensification of the hydrological cycles in the lake area during this short interval.

During the period 1200–600 cal yr BP, the TOC decreased gradually; meanwhile, the TIC and non-residual Sr experienced a process of “decrease–increase–decrease”, and they varied in a similar manner. The contents of both TIC and non-residual Sr during this period were persistently much lower than those during the previous period. These results suggest that reduced precipitation and temperature led to weakened chemical weathering and that chemical weathering was mainly controlled by temperature under low effective precipitation (precipitation/evaporation).

Since 600 cal yr BP, TOC, TIC and non-residual Sr all showed much lower values. Between 600 and 180 cal yr BP, which approximately corresponds to the period of the Little Ice Age (LIA) (Mann et al., 1998; Grove, 2004), both the TOC and TIC showed the lowest values over the past 2000 yr and implied a dry and cold climate. The non-residual Sr also presented the lowest values, which indicates a period of weak chemical weathering. After 180 cal yr BP, the TOC, TIC, and non-residual Sr all gradually increased, which indicates an increase in precipitation and temperature and the promotion of chemical weathering.

Humidity and temperature are the keys to chemical weathering (Velbel, 1993; White and Blum, 1995; Brady et al., 1999). The correspondence between non-residual Sr and TIC/TOC indicates that the non-residual Sr of the sediments in Daihai Lake is a good indicator of chemical weathering in the catchment.

Why have the Rb/Sr ratios of the bulk sediments in Daihai Lake been found to reflect chemical weathering in previous studies?

Although residual Rb and Sr are negatively correlated throughout the entire profile, the fluctuation ranges for both elements of the residual form are narrow compared with the fluctuation range for the non-residual Sr. The Coefficients of Variance (CVs) for residual Rb and Sr are 0.053 and 0.071, respectively, while the CV for non-residual Sr is 0.57. Thus, the effect of fluctuations in the residual Rb and Sr on the Rb/Sr ratios of the bulk sediments is weak, and the changes in the Rb/Sr ratios of the bulk sediments are determined by the non-residual Sr contents. Therefore, the Rb/Sr ratios of the bulk sediments in Daihai Lake can be assumed to reflect chemical weathering, and the conclusions of previous studies

are still reliable to some extent. However, it would undoubtedly be more accurate to use non-residual Sr than the Rb/Sr ratios of the bulk sediments to reflect paleoclimate/paleoenvironment change.

Conclusions

Rb and Sr in lake sediments are derived from both chemical weathering and physical erosion. Rb and Sr of different forms in sediments reflect different sources and environmental processes. In the sediments of Daihai Lake, Rb and Sr of different forms display quite different variation patterns. We have drawn the following conclusions.

1. Almost all Rb is sequestered in the residual form, while more than half of Sr exists in the non-residual form in the sediments of Daihai Lake.
2. The residual Rb and Sr contents display a negative correlation throughout the sediment core, possibly because of their different parent minerals with different grain sizes.
3. It is not accurate to use the Rb/Sr ratios of bulk sediments to reflect paleoclimate/paleoenvironment change, especially in the catchment where the physical weathering and chemical weathering have inverse effects on controlling the Rb/Sr ratios of lake sediments.
4. The non-residual Sr of the sediments in Daihai Lake, which represents the Sr leached from the catchment, can be used as an index of chemical weathering because the weathering of Sr minerals is very sensitive to climate change, and the non-residual Sr content of the sediment is determined more by Sr^{2+} influx than by the physico-chemical conditions of the lake water.
5. The non-residual Sr contents showed significantly higher values during 1620–1200 cal yr BP, implying strong chemical weathering. This correlates well with the high TIC and TOC in the sediments during the corresponding period. The non-residual Sr contents exhibited sustained low values after 1200 cal yr BP, indicating weak chemical weathering due to a cooler and drier climate.

Notably, when the non-residual Sr content of the lake sediment is used as an index of chemical weathering, the following factors should be considered. Firstly, it is a requirement that the Sr influx of detrital carbonates in lake sediments is negligible because this part Sr is not related to chemical weathering. Secondly, the dissolved Sr^{2+} would not quickly incorporate into the sediment when the lake water is unsaturated for the formation of carbonates, which may lower the time resolution of the non-residual Sr to reflect chemical weathering. Thirdly, the dilution of other materials in sediments may affect the sensitivity of the non-residual Sr to reflect chemical weathering. Therefore, detailed investigations on the variations of Rb and Sr of different forms in more lakes with different geographic/geological background would be desirable in further research.

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