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Weak chemical weathering during the Little Ice Age recorded by lake sediments

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Abstract Low magnetic susceptibility, low Sr content and hence high Rb/Sr ratio in the lake sediment sequence indicate a weak chemical weathering process under arid and cold climate of the Little Ice Age in a single closed lake watershed. According to different geochemical behavior between rubidium and strontium in earth surface processes, variation of Rb/Sr ratios in the lake sediment sequence can be used as an effective geochemical proxy with definite climatic significance of chemical weathering in watershed. Unlike chemical weathering process in tropic zone and modern temperate-humid climate, concordant changes in both Sr content and magnetic susceptibility with $\delta^{18}O$ values of Dunde ice core suggest that the weak chemical weathering was controlled by air temperature during the Little Ice Age maximum. After the Little Ice Age, chemical weathering intensity was controlled also gradually by precipitation with increasing in temperature.

Keywords: closed lake, Rb/Sr ratio, chemical weathering, the Little Ice Age.

Studies of climatic variability, especially of the Little Ice Age, are essential for modern climatic change and for evaluation of its trend in future. Chemical weathering is a universal link of climatic and environmental reconstruction between continent and ocean, catchment and lake. In recent years, the intensive interest in past global climatic change has renewed efforts to quantitatively understand process, products and contribution to sediments of chemical weathering under different tectonic and climatic conditions[1—3]. The chemical weathering process is restricted by regionally environmental conditions, thus chemical constituents of weathering products have recorded paleoclimatic and paleoenvironmental changes[1, 2]. Many studies have, however, been focused on millionnial- and/or millennial-scale chemical weathering responding to global paleoclimatic and atmospheric CO_2 concentration changes[2, 4, 5], or on chemical weathering process under present climatic conditions[1], little on short-time scale chemical weathering behavior in single watershed, including the Little Ice Age. Solute concentration, which has been commonly used for judging chemical weathering[4], on the other hand, is not an effective method for comparing the weathering rates and watersheds with diverse climatic conditions, because the concentration of major cations in watershed streams are evidently controlled by the evapotranspiration[5], especially in the watersheds with lower precipitation.

Due to different geochemical behavior between rubidium (Rb) and strontium (Sr) in chemical weathering process, variation of Rb/Sr ratios has been used as an effective geochemical proxy of chemical weathering intensity in nature[6—9]. In this paper, we provide a high-resolution vertical distribution of Rb/Sr ratio in sediments from the Daihai Lake (112°32′31″—112°48′40″E, 40°28′7″—40°39′6″N) by combining magnetic susceptibility with clay mineralogy, to discuss chemical weathering process recorded in lake sediment of the Little Ice Age and to reconstruct the history of the weathering intensity and paleoclimatic change in the last 500 years. The Daihai Lake, Inner Mongolia, is located in a transitional climate zone between semi-arid and semi-humid area which is a climatically sensitive area to the East Asian Monsoon. The lake gets along with chronically closed hydrological condition and hence the history of chemical weathering in watershed should be recorded in its sediments, so the closed lake is an ideal place for studying paleoclimatic change.

1 Sampling and analytical methods

A 78 cm-long sediment core for analysis was recovered from a water depth of 12.50 m in the central part of the Daihai Lake, and 78 samples were taken at 1-cm interval. The core sediments are composed of brown to grey-black silty clay and mud. According to radionuclide ^{210}Pb dating, modern sedimentary rate in the Daihai Lake is about 1.6—1.8 mm/a[10], so the core sediments recovered were deposited continuously during the last 500 years, namely a resolution of about 6 a for each sample. Samples were divided into two parts: one part was left uncrushed for clay minerals analysis and the other was grounded to a fine power in a mortar for analyzing Rb and Sr contents and magnetic susceptibility.

Magnetic susceptibility was measured with Bartington MS2 Meter at Lake Sediment and Environment Laboratory, Chinese Academy of Sciences. Rb and Sr contents in each sample were measured with a Japanese VP-320 XRF spectrometer. The relative standard deviation is less than 1×10^{-6}. Clastic mineral constituents were analyzed by D/Max-Rb type X-ray diffraction (XRD). Meanwhile, to obtain clay fraction of sample, the carbonate and organic matter in sediment were removed by HCl and H_2O_2. Afterwards, the <2 μm fraction and then the <0.5 μm fraction were separated from each sample by centrifugation respectively. The suspension was dropped on glass slide to gain an oriented clay specimens with a thickness of 3 mg/cm^2 and then they were dried in the air (air-dried, AD). After the AD oriented specimens were examined by XRD, all oriented specimens were saturated with glycolate liquid (GL) using an atomizer and then examined immediately by XRD again to determine the clay minerals and contents. Both AD and GL oriented specimens were studied twice by XRD at the Center of Materials Analysis, Nanjing University. Each specimen was scanned at 1° 2θ/min with Cu-K-Alpha radiation, 40 kV, 80 mA, 0.01° 2θ steps and scanning range of 2—36° 2θ. The error of ranges is less than 5%.

2 Analytical results

As shown in fig. 1, Rb/Sr ratio and magnetic susceptibility are in the ranges of 0.41—0.68 and 50—137 (10^{-8} m^3 • kg^{-1}) respectively, with a negative correlation. Due to little variation of Rb contents ((109—125)×10^{-6}) in lake sediments, variation of Rb/Sr ratios relies chiefly upon Sr activity during chemical weathering. The negative relationship between Sr content and Rb/Sr ratio, as shown in fig. 2, could confirm this. It is caused by the strong affinity of Rb for clay minerals and Sr loss to solution during weathering leaching process[8, 11].

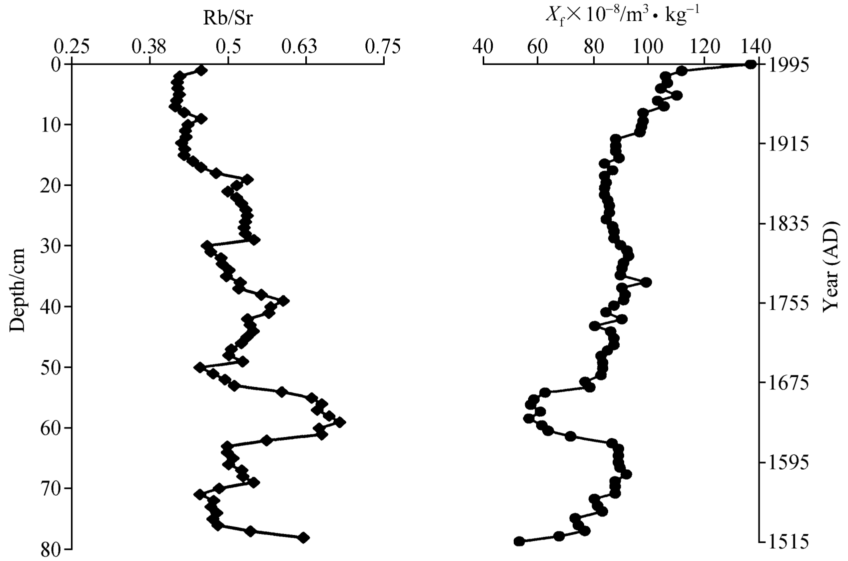

Fig. 1. Rb/Sr ratio and magnetic susceptibility of lake sediments from the Daihai Lake, northern China.

Though the clastic debris constituents in the whole core are the same on the whole including mainly quartz, feldspar, micas and carbonate, clay minerals are different. For example, at the intervals with higher Rb/Sr ratios, clay contents are 9%—12%, and illite, chlorite and muscovite are dominant in the sediments. At lower Rb/Sr periods, there are talc and kaolinite besides illite, chlorite and muscovite and relatively high clay contents (15%—18%). Moreover, some gypsum (<2μm) was found at 50 cm depth (AD1695 to AD1700).

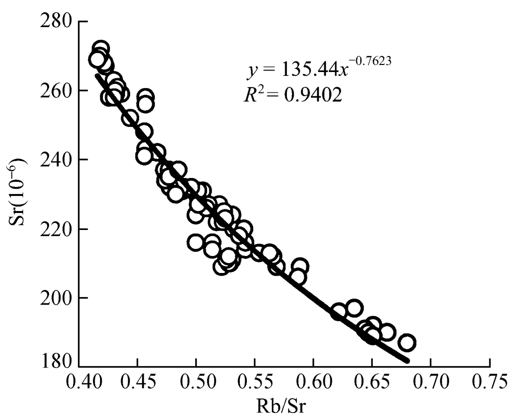

Fig. 2. Relationship between the Rb/Sr ratio and Sr content in the Daihai Lake sediments.

3 Discussion

3.1 Rb/Sr and chemical weathering intensity

Rubidium and strontium are easily fractionated in earth surface geochemical process due to different geochemical behavior[6, 7]. Sr, however, would not be changed during erosion and sedimentation process, and even long-term contact with lake water or interlayer medium water, and not reached equilibrium with Sr of various water bodies[12]. Moreover, the radiogenic Sr increases from ^{87}Rb decay should not be considered for centennial-scale Sr contents change here due to a long half-time of ^{87}Rb decay (4.88×10^{10} a). It is seen from the studies on active and relict weathering profiles and loess-paleosol sequence that Rb/Sr ratio in weathering products would increase significantly with the enhancement of weathering intensity[7, 8, 11]. Consequently, Rb/Sr ratio in lake and ocean sediments would decrease with the enhanced weathering in watershed, resulting in more Sr into basin. In addition, the bedrocks exposed in the Daihai Lake watershed are chiefly the Tertiary basalt and the Archean metamorphic igneous rock. Here we can assume reasonably that the rock types did not change over at least one thousand years. By variation of Rb/Sr ratios in lake sediments, we can reconstruct the chemical weathering history affected by paleoclimatic change.

Three sections of higher Rb/Sr ratio in the core depths of 62—54 cm (AD 1615—1665), 41—38 cm (AD 1745—1765) and 29—19 cm (AD 1820—1880)[10] are shown in fig. 1. It can be seen that there are three stages with lower intensity of chemical weathering in the last 500 years in the Daihai watershed. Correspondingly, there are three relatively strong chemical weathering periods with lower Rb/Sr ratios between them. The acid-leaching experiments[11] have proved that Rb is stable while Sr is easy to remove into solution, resulting in an increasing of Rb/Sr ratio in weathering relic products. The Rb/Sr ratio variability for lake sediments deposited continuously, therefore, substantially reflects the leaching degree of source area.

3.2 Weak chemical weathering during the Little Ice Age

The climatic study of the Little Ice Age plays a significant role in understanding present climate and in predicting future trend, and has become a frontier in current PAGES[13—15]. In the Daihai watershed, cold and arid climate caused an acute reduction of precipitation (about 50 mm/a) during the Little Ice Age according to historical document[16]. The chemical weathering certainly would be weakened under this condition. Thus, three weak weathering periods with higher Rb/Sr ratios in lake sediments probably represent relatively arid and/or cold stages during the last 500 years in the Daihai area. Through comparison with historical documents, these higher Rb/Sr sections are equivalent in age to three periods of arid and cool climate[14, 16]. The first is the coldest "Little Ice Age" maximum, and the other two are two cold and dry periods. Especially, during AD 1615—1665, an increase in Rb/Sr ratio significantly suggests that this period should be the Little Ice Age maximum[14, 15, 17], in agreement with historical records. The coldest period around AD 1625—1630[13, 17] has the highest Rb/Sr ratio (at depth about 59 cm) from the Daihai lake sediments (fig. 1). The weak chemical weathering is also reflected by magnetic susceptibility variation from lake sediments. In arid and cold periods, fine-grained magnetic mineral into basin would decrease significantly with the reduction of weathering and pedogenesis[18], illustrating that peak of Rb/Sr ratio is correlative to low value of magnetic susceptibility (fig. 1). A very significant feature is that the negative correlation between Rb/Sr ratio and magnetic susceptibility of lake sediment shown in fig. 1 responds to the striking similarity between them in the loess-paleosol sequence[7]. This suggests that Rb/Sr ratio respond sensitively to paleoclimatic change that affects chemical weathering and pedogenetic intensity.

3.3 Chemical weathering and paleoclimate

In the short-term period, silicate weathering is a function of changes in air temperature and precipitation. For example, there is less chemical weathering in arid glacial periods than in more humid interglacial[1, 5, 19]. Thus Rb/Sr ratio preserved well in sediments can further be regarded as a proxy for temperature and precipitation, especially in the watershed with lower precipitation as the Daihai area[2, 5].

Fig. 3 shows approximately 50 a running average of Sr contents in the Daihai Lake sediments, precipitation in the Daihai area[20] and $\delta^{18}O$ values from the Dunde ice core[21] during the last 500 years. Because oxygen isotopic ratios from ice core, $\delta^{18}O_{ice}$, primarily reflect air temperature[21, 22], and because both Dunde and Daihai are located in a transitional zone of the East Asian monsoon[21], variation of $\delta^{18}O_{ice}$ values from the Dunde ice core can reflect air temperature change trend in the Daihai area. Much of Sr in either basalt or high-calcium igneous rock is held within plagioclase feldspar. Plagioclase decomposes more easily than other principal minerals in these rocks, resulting commonly in the marked loss of Sr during more intense weathering process. During the Little Ice Age, cold and arid condition resulted from acute reduction of precipitation largely weaken the intensity of chemical weathering[16, 20] (fig. 3), bringing about more coarser plagioclase fragments and lower Sr content (i.e. higher Rb/Sr ratio) into basin and more brackish ostracoda and *Betula* pollen during the periods with low lake water level[10, 16]. The coincident peaks between Sr contents in lake sediments and $\delta^{18}O$ values from the Dunde ice core[21] during

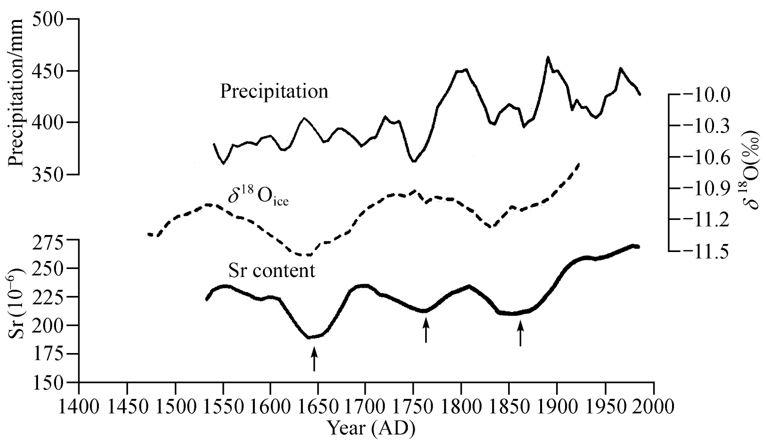

Fig. 3. Approximately 50 a running average of Sr contents in the Daihai Lake sediments, precipitation in the Daihai area and $\delta^{18}O$ values from the Dunde ice core during the last 500 years. The precipitation shown is from tree-ring reconstructed climate data[20]. The $\delta^{18}O$ values are from the Dunde ice core data[21]. Three arrows in the figure show three stages of weak chemical weathering during the Little Ice Age.

the last 500 years indicate that Sr leaching capacity chiefly depended upon air temperature variations under arid and cold condition[23]. The weaker the chemical weathering, the lower the air temperature, in the two cool periods after the Little Ice Age maximum (fig. 3). As both air temperature and precipitation increased after the Little Ice Age, the chemical weathering relied upon precipitation variations under modern humid and warm climatic conditions[19, 23], showing high Sr contents in lake sediments with increase in precipitation (fig. 3). Consequently, the chemical weathering rate could indicate air temperature and precipitation in single watershed under semi-arid and semi-humid climatic conditions. Weak chemical weathering, therefore, reflects regionally arid and cold paleoclimatic environment during the Little Ice Age.

4 Conclusion

The sediments deposited continuously in a closed lake under different paleoclimatic conditions display an evident variation of Sr distribution, reflecting chemical weathering history in single watershed by variation of Rb/Sr ratio. Low magnetic susceptibility, low Sr content and hence high Rb/Sr ratio in lake sediments deposited during the global Little Ice Age indicates a weak chemical weathering process in a single watershed which was controlled by arid and cold climate. Our work reported here on a geochemical investigation of a single watershed, with the aim at evaluating chemical weathering variation in the Little Ice Age, indirectly supports large-scale regional studies which suggested that both silicate and carbonate chemical erosion rates increased by about 20% during the Holocene compared with the Last Glacial Maximum (LGM, ^{14}C 18 ka BP)[23]. Furthermore, we find that air temperature plays a more important role in chemical weathering than precipitation during the dry and cold “Little Ice Age” maximum in single watershed located in a transitional zone of semi-arid and semi-humid, on the basis of variation trends of Sr content of lake sediments, precipitation from tree-ring data and $\delta^{18}O$ value from ice core during the last 500 years.

A good negative correlation between Rb/Sr ratio and magnetic susceptibility during the Little Ice Age as shown in fig. 1 further suggests that the Rb/Sr ratio in lake sediments can also be regarded as a good indicator for magnetic susceptibility of East Asian summer monsoon intensity and front position which are closely related to weathering behavior[7, 11, 18]. The Rb/Sr ratio, however, could provide more detailed information than magnetic susceptibility. For instance, there are two obvious peaks after the Little Ice Age maximum shown by Rb/Sr ratio (fig. 1), but the magnetic susceptibility curve does not show the changes, which correspond to sub-peaks of two post-glacial climate fluctuation that were documented by historical records [10, 16]. Instead, magnetic susceptibility is abnormally high near the surface layer that might be affected by human activities[18]. Those suggest that the Rb/Sr proxy should be much better than magnetic susceptibility in tracing paleoclimatic change recorded in lake sediments and loess-paleosol sequence[7, 11].

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