Minor element variations during the past 1300 years in the varved sediments of Lake Xiaolongwan, north-eastern China

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Abstract: Synchrotron radiation X-ray fluorescence measurement provides a nondestructive in situ analysis of elements. We present a high-resolution minor element dataset covering the past 1300 years from the varved sediments in Lake Xiaolongwan. The variations of lithogenic elements (Rb, Sr, Ti, Zn, As and Fe) in the lake sediment show distinct decadal to centennial features during the past 1300 years. The Medieval Warm Period has a low value of lithogenic elements. In contrast, the Little Ice Age may be a period with stronger physical weathering and a higher value of lithogenic elements. Principal components analysis of our geochemical dataset suggests a link between high Rb/Sr ratio and Zr abundance in the sediment that could be related with both chemical weathering process and dust input. The variations of biogenic bromine (factor-3) show a pattern similar to the decadal drought index in Korea. Wet conditions favor bromine accumulation in lake sediment because high precipitation may transport more bromine from forest soil and increase plankton production in the lake. Spectral analysis of factor-3 yields notable periodicities of 2.6, 3.5, 53–55, 87–89 and 105–110 years, implying that precipitation variability for the past 1400 years could be associated with El Niño–Southern Oscillation and solar activity.

Keywords: varved sediment; Lake Xiaolongwan; synchrotron radiation X-ray fluorescence; bromine.

Introduction

Annually laminated sediment sequences provide valuable archives to understand high-resolution paleoclimatic change because of precise chronology and the large variety of proxies contained in the sediments (Björck et al. 1996; Zolitschka 1996; Lamoureux 1999; Brauer et al. 2000; Ojala et al. 2012). It is well known that climate varies at quasi-periodicities ranging from orbital, centennial to millennial, multi-decadal to interannual timescale, in response to different external and internal forcings. Therefore, as it is one important topic of paleoclimatic research, it is crucial to understand the processes of high-frequency paleoclimatic variations (e.g., El Niño–Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO), the Arctic Oscillation/North Atlantic Oscillation and the Atlantic Multi-decadal Oscillation) for a better assessment of the probability of such variations in the coming decades. However, few techniques can be used to obtain high-resolution data at annual to seasonal timescale.

Recently, micro X-ray fluorescence (μXRF) and synchrotron radiation X-ray fluorescence (SRXRF), the nondestructive methods analyzing chemical elements in the sediments, have been developed (Ojala & Alenius 2005; Weltje & Tjallingii 2008; Brauer et al. 2009; Francus et al. 2009; Boës et al. 2011). They provide a powerful analytical technique to detect most chemical elements of the periodic table down to limits of a few ppm (Francus et al. 2009). Based on the high-resolution X-ray fluorescence (XRF) scanning on impregnated sediments and micro-facies analyses on thin sections, Brauer et al. (2009) presented a new approach to studying annually laminated sediments and interpreting seasonal paleoclimatic signals. SRXRF measurement is a new method to analyze elements under a synchrotron beam combined with measurements of the XRF (Daryin et al. 2005; Kalugin et al. 2005, 2007; Goldberg et al. 2007). Kalugin et al. (2007) presented a 800-year record of annual temperature and precipitation from the in situ element...
analysis (Br content and Sr/Rb ratio) in the sediment of Lake Teletskoye.

Here, we present high-resolution minor element data from varved sediments in Lake Xiaolongwan by using SRXRF method.

Site description
Lake Xiaolongwan (42°18'N, 126°21'E, altitude: 655 m asl) is located in the Longgang Volcanic Field (Fig. 1). There are nine maar lakes and ca. 160 craters and calderas in the area. The lake was formed by alkali basalts phreatomagmatic eruptions in the late Pleistocene. Lake Xiaolongwan is a dimictic lake with a surface area of 0.079 km², a maximum depth of 15 m and a catchment area of 0.16 km². In the lake catchment, exposed rocks are mainly trachybasaltic tephra except the Archeozoic Migmatite Group present in the mountain ridge and hillside in the northern part of the lake catchment. The lake has humic fresh water with brown color (pH 6.7) (Chu et al. 2008). Water transparency was 1.5 m estimated with a Secchi disk in the field.

Present climatic conditions are determined by the East Asian monsoon and characterized by pronounced seasonality. In summer, rainfall is mainly associated with the Southeast Asian summer monsoon (Fig. 1). In winter and spring, the strength of the winter monsoon and westerlies creates favorable conditions for snow and dust storms. Winter is very cold with a minimum temperature below −40°C in the study area. The lake is ice-covered from the end of November until early April.

Annually laminated sediments have been reported in the maar lake sediment in the Longgang Volcanic Field. These remarkable lakes have been the subjects of numerous studies focused on reconstructing paleoclimatic changes at high resolution (Mingram et al. 2004; Schettler et al. 2006; Chu et al. 2008, 2009; Jiang et al. 2008; Parplies et al. 2008; You et al. 2008; Stebich et al. 2009; Wang et al. 2012).

Materials and methods

Sediment cores and varve chronology
A series of overlapping cores (freeze cores, gravity cores and piston cores) have been retrieved from Lake Xiaolongwan since 2001 (Chu et al. 2008, 2009). In this study, a sediment core was retrieved in 2010 using a gravity core developed at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The core was transported upright back to the laboratory. In the laboratory, the cores were dried further by inserting paper towels before the cores were split, opened and sampled.

Overlapping sediment slabs (65 mm × 20 mm × 10 mm) were taken from the core using aluminum trays. The slabs were shock-freezeed using liquid nitrogen, freeze-dried, vacuum-penetrated with synthetic resin and manufactured into thin sections. Scales in centimeters were marked on the thin sections with a pencil. Varves were identified, counted and recorded each centimeter from thin sections using a Leitz light microscope.

Minimum varve and maximum chronology were based on counting varves three times by one person. Varve chronological errors do exist due to discontinuous dinocyst layers (lenticular structure) or less distinct couplets in some varves (Fig. 2A).

SRXRF in situ analysis
Considering the biogeochemical elements analyzed in this study, we did not use the thin section for SRXRF analysis since the synthetic resin may contaminate the sample in the thin section. Additional sediment blocks (60 mm × 10 mm × 5 mm) were taken from the core using aluminum trays. The SRXRF measurements were carried out at the hard X-ray beamline (BL15U) of Shanghai Synchrotron Radiation Facility (SSRF). The sediment blocks were fixed on a seven-axis sample stage, which was driven by step motors. The incident beam energy of 19.98 keV was used for the determination of elements with atomic mass less than that of Mo. The beam size is 80 μm × 100 μm. A seven-element Si(Li) detector was used to collect the SRXRF signal from samples with a scan time of 20 s. The European Synchrotron Radiation Facility freely provided the Python Multichannel Analyzer that was used for fitting the measured SRXRF spectra of sediments. The fitted peak area was normalized by the region of interest (ROI) from 110 to 250 channels. The ROI is a method to define an elemental X-ray spectrum, generate a quantitative elemental map and obtain the sum of all the X-ray counts from selected region. The Chinese national standard material GSD1 was used to control the analysis quality. Normalized elemental intensities (Br, Rb, Sr,
Zr, Ti, Fe, Mn, Cu, Zn and K) were hence obtained. After standardization, the relative standard deviation of the intensity of elements (Br, Rb, Sr, Zr, Ti, Fe, Mn, Cu, Zn and K) is better than 15%.

It was difficult to transpose the SRXRF dataset into the varve chronology established on impregnated slabs. Indeed, we had to let the sediment blocks dry before analysis because they were prone to quick shrinkage during SRXRF analysis due to their high organic and water contents. Thus, the shrinkage rate for each sediment block was calculated by comparing with the corresponding thin section, and the SRXRF measurements were eventually transferred to the varve chronology established on thin sections.

Results and discussion

Varve chronology

Previous works have demonstrated the annual nature of the laminations in the sediments in Lake Xiaolongwan (Chu et al. 2008, 2009). Fig. 2 shows dinocyst varves from the thin section X2010 B1 taken with a gypsum plate under partly polarized light (minerals show in color with this configuration). The dinocyst varves consist of a brown-colored dinocyst layer and light-colored mixed layer. The light-colored layer consists of organic matter (plant detritus, diatoms and chrysophyte cysts) and clastics (sometimes rich in a layer) (Fig. 2). Fig. 3 shows the three varve counts used to establish the varve chronology. The maximum difference between the counts is 76 years.

Element variations

Fig. 4 shows the time series of Br, Rb, Sr, Ti, Zn, As, Fe, Zr and Rb/Sr during the past 1300 years in the sediment sequence of Lake Xiaolongwan using the mean value of varve chronology from Fig. 3. No visible correlation has been found between varve thickness and elemental variations (Fig. 4). This can be explained by the fact that in Lake Xiaolongwan, the varve thickness is not a good proxy since both dinocyst and clastic layers often display a lenticular structure. Moreover, the variation of varve thickness integrates paleoclimatic signal both from local minerogenic input or biogenic sedimentation and from long-distance source (dust).

Rb, Sr, Ti, Zn, As and Fe covary with each other stratigraphically as confirmed by the Pearson coefficient among these elements ($r > 0.5$, $p < 0.001$). The variations of Rb and Sr concentrations are highly correlated with a very high coefficient of 0.96 (Pearson coefficient, $r = 0.96$, $p < 0.001$). All these elements are slightly increasing from AD 750 to AD 2000 (Fig. 4). The periods with high concentration of elements (Rb, Sr, Ti, Zn, As and Fe) are in the AD 1360–1470, AD 1570–1700 and AD 1900 to the present. Br and Zr show an independent variation pattern with the other elements. It may imply different geochemical process regulating these elemental variations. However, there is no significant relationship between Br and Zr ($r = 0.14$, $p < 0.01$). The periods with relative high Br concentration are in the AD 1040–1300, AD 1580–1610, AD 1630–1650, AD 1700–1800 and AD 1900 to the present (Fig. 4).

Rb, Sr, Ti, Zn, As, Zr and Fe are typical lithogenic elements. Relatively, lower values of lithogenic elements are found during the Medieval Warm Period (MWP) (extending from AD 900 to 1300 (Jones and Mann 2004)) and suggest weaker physical weathering conditions. In contrast, higher values of lithogenic elements are found during the most courses of the Little Ice Age (LIA) (AD 1300–1900) and recent century with stronger physical weathering. However, the global appearance of the MWP and the LIA is questioned (Jones & Mann 2004). The LIA was not a continuous cold climate and was interrupted by some warm spells (Chu 1973). As a good tracer of organic material in lakes (Phedorin et al. 2000; Kalugin et al. 2007), the higher Br concentration is observed both in the MWP and the LIA.

Extracting the paleoclimatic and paleoenvironmental signal from elements

Previous studies suggested that the variation of minor elements in lake sediment is controlled by various factors, such as physical and chemical weathering processes (Boyle 2000), relative contribution between biogenic and terrigenous, particle size, regional climate change and human activity (Daryin et al. 2005; Jin et al. 2006; Cuven et al. 2010; Chu et al. 2011; Zeng et al. 2012).

Regional climate change can affect the transport of element composition from the catchment to a lake. In a warm and wet period, the fluxes of mobile elements and biogenic elements to the lake floor might be accelerated, but denser vegetation cover in the warm period might restrain this process. Physical weathering could be mainly affected by precipitation and vegetation cover that is also regulating the transfer of clastics from the catchment to lake. In our study lake, dust activity is another important factor affecting elemental composition of the
Fig. 4. Time series of series of Br, Rb, Sr, Ti, Zn, As, Fe, Zr, Rb/Sr ratio and varve thickness. The varve thickness (mm/year) is the average value for each centimeter. The elemental concentration is normalized intensity (counts/counts).
lake sediments. The study area is located in the path of dust storms. In spring, cold winds shifting southward from Siberia create favorable conditions for the development or intensification of cyclones and anticyclones resulting in an increase of surface wind speed and the occurrence of dust storms (Liu 1985).

Principal components analysis (PCA) was used to better understand the relationship among different elements. This statistical technique has been successfully used elsewhere to study geochemical dataset in order to understand the structure of the variance of the parameters (e.g., Muller et al. 2008). Table 1 shows the PCA scores. Based on the PCA results, we try to extract paleoclimatic and paleoenvironmental information from elements, although it is difficult to attribute proxy data to single climate variables (e.g., temperature, precipitation and dust) for complex physical, chemical and biogeochemical processes.

The first component includes almost all analyzed elements (Ti, Fe, Zn, As, Rb and Sr) except zirconium and bromine. Titanium, iron, rubidium and zinc are the typical elements mainly coming from lithogenic materials. In this volcanic area, arsenic is also enriched by high-temperature processes, such as burning forest and volcanic eruption (Farmer et al. 1986). Strontium is chemical mobile element in the environment. Considering that the factor-1 includes both chemical immobile elements and easily leached elements, we suggest that the variations may mainly indicate the clastic input from soil erosion.

The second component includes Rb, Sr and Zr. During chemical weathering, strontium is more reactive, whereas rubidium is more inert (Zeng et al. 2012). In this component, however, zirconium is an immobile element resistant to chemical weathering. The studied area is located in the Longgang volcanic field, exposed rocks being mainly trachybasaltic tephra and lava enriched in minerals such as plagioclase and amphibole. Thus, the high Sr value is expected. The values of Rb and Sr from six tephra samples support this hypothesis ($\text{Rb} = 46.8 \text{ ppm}, \text{Sr} = 617.9 \text{ ppm}, \text{Rb/Sr} = 0.08$, mean value by using ICP-MS method). However, the Rb/Sr ratio ($\text{Rb/Sr} = 0.56$, mean value of all samples, uncalibrated) in the lake sediments is higher than the tephra. It suggests that the elements in lake sediment may not only come from tephra. A dust sample (collected in the 2002 dust event in the area) has higher Rb/Sr ratio and higher zirconium concentration ($\text{Rb} = 109.5 \text{ ppm}, \text{Sr} = 155.7 \text{ ppm}, \text{Rb/Sr} = 0.7, \text{Zr} = 153.7 \text{ ppm}$, measured by using ICP-MS). It is similar to the dust collected in the Dunde ice core, northern China ($\text{Rb/Sr} = 0.8, \text{Zr} = 148.8 \text{ ppm}$) (Wu et al. 2009). Thus, the second component might be partly related to dust input.

Fig. 5B compares factor-2 with an ice core dust record from Tibet, and historical documents from Korea (Fig. 5C) and China (Fig. 5D). The historical dust documents in China are not consistent with the historical dust records from Korea. The discrepancy could be explained by the fact that the historical dust documents in China include regional dust activities from the nearby Gobi desert. In contrast, the dust documents in Korea may be associated with long-distance dust transport. Moreover, the historical dust documents might only record very strong dust events.

Ice core records offer the possibility to study the dust activity. Although the dust input in the Lake Xiaolongwan sediment should have both the long-distance dust transport and short-distance local dust sources, the variations of the factor-2 are generally correlated with the dust record from Tibetan ice core (Thompson et al. 2000). Early studies only regarded the Hexi Corridor, deserts and sandy desert areas in northwestern China as the major dust source regions for long-distance transportation. Recent studies, however, demonstrated that the Tibetan Plateau is one of the key dust source areas for the long-distance transport because frequent strong winds in combination with the high elevation of the Plateau cause fine particles to be easily lifted into the zone, where the westerlies can transport them to Korea, Japan, the northern Pacific Ocean and North America (Fang et al. 2004; Chen 2010).

The third component only includes bromine, a typical biogenic element. Bromine is essential for growth of plants, bacteria and plankton. In lake sediments, bromine comes mainly from biogenic matter in soil and plankton in the lake (Leonova et al. 2011). Warmer temperature and higher precipitation would increase mobility of bromine from soil in the catchment. In Lake Teleskoye, a positive correlation has been observed between the Br values and annual temperature (Kalugin et al. 2007). In this study, higher Br values occur during most of the MWP (AD 1030–AD 1300). However, there are also several peaks during the LIA (around AD 1580, AD 1650, AD 1700, AD 1740 and AD 1810). Precipitation may also be a main factor for transporting Br from forest soil and increasing plankton production in the lake. Fig. 6 shows the variations of factor-3 with a decadal drought index in Korea (Kim & Choi 1987) (Fig. 6).

A negative correlation (Pearson coefficient: $r = -0.25, n = 97, p < 0.05$) can be observed between factor-3 (averaging the factor-3 to the decadal time scale as the decadal drought index) and the decadal drought index. Wet period seems to be favorable to bromine accumulation in lake sediment. In order to examine periodicity statistically, spectral analysis (Schulz & Mudelsee 2002) was carried out on the factor-3. The spectral analysis shows periodicities ($1.9–2.3, 2.6, 3.5, 8.7–8.9$ and $105–110$ years) at a confidence level $>95\%$, and periodicities ($53–55$ and $160–177$ years) at a confidence level $>99\%$. Previous studies shown classical ENSO periodicities at $2–8$ years (Allan 2003), ENSO-related multidecadal periodicities at $50–70$ years (MacDonald & Case 2005; Fagel et al. 2008) and solar oscillations at $440, 360, 260, 230, 180, 168, 155, 147, 123, 106$ and $88$ years (Stuiver & Brazunas 1993). The periodicities of factor-3 may imply that variability of precipitation for the past $1300$ years could be associated with ENSO and solar activity.

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<th>Table 1. Rotated matrix component of elements.</th>
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Notes: Extraction method: PCA; rotation method: varimax with Kaiser normalization.
Fig. 5. Comparative diagrams of factor-2, the historical dust document and dust content in a Tibetan ice core. A. Factor-2 data derived from the PCA. B. Dust content (per milliliter of sample for particles ≥ 0.63 μm) in a Tibetan ice core (Thompson et al. 2000). C. The decadal dust documents in Korea from official historical documents in the Samguksgagi (three Kingdoms period) (57 BC–AD 935), the Goryeosa of the Goryeo dynasty (AD 918–1392) and the Annals of the Joseon dynasty (AD 1392–1910). D. The historical dust documents in China (Zhang 1984).

Fig. 6. Factor-3 and the decadal drought index in the Korea. The decadal drought index in the Korea is from Kim and Choi (1987). The factor-3 data with 11-point running average are derived from the PCA. A negative correlation (Pearson coefficient: $r = -0.25$, $n = 97$, $p < 0.05$) can be observed between factor-3 (averaging the factor-3 to the decadal timescale as the decadal drought index) and the decadal drought index.
Conclusions

SRXRF in situ analysis of varved sediments in Lake Xiaolongwan proved to be a powerful tool for the analysis of minor elements with high resolution. It is great potential for detecting seasonal paleoclimatic signals and understanding high-frequency paleoclimatic variations (ENSO and PDO). The complexity of physical, chemical and biogeochemical processes at Lake Xiaolongwan did not allow for a simple interpretation of elemental data in terms of climate variables such as temperature, dust and precipitation. However, PCA analysis helped to disentangle the interpretation of geochemical proxies. PCA-1 includes both chemical immobile elements and easily leached elements, suggesting that the variations may mainly indicate the clastic input from soil erosion. Considering the higher Rb/Sr ratio and Zr in modern dust, we interpreted factor-2 (Rb/Sr ratio and Zr) to be related with both chemical weathering process and dust input. Bromine (factor-3) comes mainly from biogenic matter in soil in the catchment and plankton in the lake. Wet periods are favorable to bromine accumulation in lake sediment. The MWP was associated with low value of lithogenic elements. In contrast, the LIA may be a period with stronger physical weathering with higher value of lithogenic elements. Finally, the high density of measurement on varved sediments allowed the disentangle the interpretation of geochemical proxies. PCA-1

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