Implication of boron isotope geochemistry for the pedogenic environments in loess and paleosol sequences of central China

Hai-Zhen Wei [a], Fang Lei [b], Shao-Yong Jiang [a,c,*], Hua-Yu Lu [b,**], Ying-Kai Xiao [d], Han-Zhi Zhang [b], Xue-Feng Sun [b]

[a] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, PR China
[b] School of Geographic and Oceanographic Sciences, Jiangsu Collaborative Innovation Center for Climate Change, Nanjing University, Nanjing 210093, PR China
[c] State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Resources, China University of Geosciences, Wuhan 430074, PR China
[d] Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810003, PR China

ABSTRACT

We investigated the boron isotopic composition in loess–paleosol sequences in five different profiles in the Chinese Loess Plateau. Three possible boron sources are identified: atmospheric input, carbonates, and weathered silicate rocks. Variations of [Sr], [B], $\delta^{11}B$ and the magnetic susceptibility correlate well with the pedogenic intensity in three out of the five studied profiles, where pedogenesis under a cold–dry climate indicates lower $\delta^{11}B$, lower [B], lower magnetic susceptibility and higher [Sr] values. Exceptions to the variations between the $\delta^{11}B$ and other known proxies were observed in arenaceous soils and the Red Clay sequence: the former suggested that vertical redistribution probably occurred with the boron migration, and the latter indicated an unknown mechanism of susceptibility enhancement. A better correlation between the $\delta^{11}B$ and magnetic susceptibility and the quantitative estimation of boron budget from each source confirms the influence of paleoenvironmental changes on boron geochemical cycle. Significant positive correlations in Sr/Ca vs. B/Ca and Mg/Ca vs. B/Ca reflect consistent enrichment behavior of those mobile elements into calcium carbonate. The preliminary results imply that boron isotopic compositions in soils can be a potential geochemical proxy to reconstruct the paleoenvironmental changes in loess–paleosol sequences.

© 2014 University of Washington. Published by Elsevier Inc. All rights reserved.

Introduction

The highly soluble character of boron favors its release into the environment, and a large relative mass difference between the two isotopes (^{11}B and ^{10}B) leads to significant isotopic fractionation of boron (Barth, 1993; Palmer and Swihart, 1996; Chetelat and Gaillardet, 2005; Xiao et al., 2013a). Boron isotopic compositions ($\delta^{11}B$) in nature vary in a wide range from $-70‰$ to $+75‰$ (e.g., Palmer and Swihart, 1996; Hogan and Blum, 2003; Williams and Hervig, 2004 Marschall and Jiang, 2011). There are unique physicochemical characteristics of boron: it has no redox reactions in nature and is always bonded to oxygen in the form of tetrahedral complexes (i.e., $B(OH)_4^-$) and trigonal complexes (i.e., $B(OH)_3$). The isotope fractionation between ^{10}B and ^{11}B is mainly controlled by their relative partition between tetrahedral

and trigonal species (Palmer and Swihart, 1996). Therefore, the applications of boron isotope variation has rapidly advanced to understand various geological and environmental processes, including high-temperature and low-temperature geochemical processes (Jiang et al., 2002; Kasemann et al., 2004; Tonarini et al., 2009; Jiang, 2010; Marschall and Jiang, 2011; Muttik et al., 2011; Harvey et al., 2014; Yuan et al., 2014), natural anthropogenic pollution sources (Petelet-Giraud et al., 2009), wastewater recharge monitoring (Widory et al., 2005), paleo-ocean pH reconstruction and global biogeochemical cycles (Hemming et al., 1998; Palmer et al., 1998; Palmer and Pearson, 2003; Liu et al., 2009; Wei et al., 2009; Yu et al., 2010).

In combination with other geochemical proxies, boron isotope variation has also been applied widely in recent years to understand various earth surface processes. For instance, the $\delta^{11}B$ and [B] values of the rainwater and snow were studied to characterize the sources and fractionation processes during the boron atmospheric cycle (Rose-Koga et al., 2006). Chetelat and Gaillardet (2005) found that the dissolved boron and its isotopes are suitable tracers of contamination, and they estimated the contribution percentage of each distinct component to the total dissolved boron in the Seine River in Paris. The contribution of silicate weathering to the dissolved boron budget in river systems was identified based on the boron isotope geochemistry in

* Correspondence to: S.-Y. Jiang, State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, PR China.
** Corresponding author.
E-mail addresses: shyjiang@cug.edu.cn, shyjiang@nju.edu.cn (S.-Y. Jiang), huayulu@nju.edu.cn (H.-Y. Lu).

dissolved and solid loads in different rivers of the Changjiang basin (Chetelat et al., 2009). A study on secondary clay in suevite at the Ries crater indicated that the boron and hydrogen isotopic composition of clay phase could provide useful constrains for evaluating past surficial environments (Muttik et al., 2011). Because of the easy migration of boron through continental ecosystem and the large boron isotopic fractionation during water–rock interactions and vegetation cycling, many contributions have focused on the study of soil boron chemistry (Goldberg et al., 1993, 1996; Goldberg, 1997; Goldberg and Su, 2007) and the quantification of matter exchange and weathering rates (Rose-Koga et al., 2000; Cividini et al., 2010; Lemarchand et al., 2012;).

Chinese loess is regarded as one of the best continental archives of paleo-climatic and paleo-environmental changes of the Late Cenozoic era (Liu, 1985; Liu and Ding, 1998). It is well known that loess and intercalated paleosols are aeolian in origin: loess is a dust deposit that formed during the glacial period, and paleosols formed by accretion of dust during the interglacial period under a warm and humid climate that favored pedogenesis (Liu, 1985; Kukla et al., 1988; An et al., 1990; Guo et al., 1998; Lu and Sun, 2000). As the variation of pedogenic intensity in the Chinese loess–paleosol sequence serves as a record of quantitative information on paleoenvironmental evolution, a variety of physical and geochemical proxies of the pedogenic intensity have been explored, such as magnetic susceptibility (An et al., 1990; Zhou et al., 1990), Zr/Sr ratio, mean grain size of bulk soils, coarse fraction content (Vandenberghe et al., 1997; Lu and An, 1999; Lu et al., 2004; Chen et al., 2006), as well as Rb/Sr ratios (Chen et al., 1999; 2001) and Sr/CaO content (Tan et al., 2002).

Magnetic susceptibility was first introduced as a climate proxy in the Luochuan Profile in the Loess Plateau by Heller and Liu (1982), and has been evaluated as the most robust index with a good correlation with the marine oxygen isotopes (Kukla et al., 1988; Balsam et al., 2005). However, both the source and causes of magnetic susceptibility signal remain controversial, and the mechanism of susceptibility enhancement in Chinese loess is more complicated than expected because further investigation revealed that pedogenesis may not be the only factor responsible for determining magnetic susceptibility (Sun and Liu, 2000). Additional proxies related to elemental ratios have mostly depended on typical mineral types (or typical loess region) and are easily affected by further geological processes (e.g., weathering and eluviation), and so these proxies are not universally applicable.

The boron isotope characteristics of various natural reservoirs have been well studied, and the isotopic fractionations that occurred with different geological processes are gradually becoming understood (Palmer and Swihart, 1996; Marschall and Jiang, 2011; Xiao et al., 2013). So far, the relationships between climate and weathering intensity are poorly understood despite their critical importance on environmental and economic issues for the next century. Therefore, understanding how the physical and chemical weathering regime evolved during the last glacial–interglacial climate periods should provide important insights into the links and forcing parameters that drive continental rock weathering and matter transfer between earth surface reservoirs. It motivates this exploration of the applicability of boron isotopes as a potential proxy to indicate the paleoenvironment of the loess–paleosol sequences.

The boron isotopic compositions in the acid-soluble fraction of soils in five individual profiles along a north-south direction of the Chinese Loess Plateau were studied in this work. We discuss the correspondence of boron isotope variations with the paleoclimate changes since the late interglacial period and the correlations among $\delta^{11}B$ values and other proxies, in an attempt to understand the influence of paleoenvironmental evolution on the boron geochemical cycle. It opens the possibility of evaluating the potential of boron isotope proxies for the reconstruction of paleoenvironment in loess–paleosol sequences not only in the Loess Plateau of China but also elsewhere worldwide.

Materials and methods

Geological settings

The Loess Plateau is located in the arid and semiarid area of Central China. Loess–paleosol sequences in the Loess Plateau representing the last glacial and interglacial periods are well preserved; these sections are composed of an upper loess unit and an underlying paleosol (Lu and Sun, 2000; Lu et al., 2004). According to the route of summer monsoon from the Pacific Ocean and the Indian Ocean that delivered the major source of atmosphere input to the arid area, five individual loess–paleosol profiles along the south-north direction were selected: Yangguo Profile (YG), Yangguo Reservoir Profile (YGSK), Luochuan Profile (LC), Dali Profile (DL), and Zhenbeitai Profile (ZBT) (Fig. 1, Table 1). The previous understanding of paleoclimatic variations recorded by the loess–paleosol sequence in this area was given by Lu and Sun (2000) and Lu et al (2004), and the detailed stratum information of each profile is described in Table 1.

To avoid any anthropogenic contamination and (or) mixture of boron geochemical information from vegetation cycling, agriculture irrigation and human activities, all samples starting from the S0 stratum (or deeper) were collected in newly drilled wells; soil samples from the surface layer (i.e., L0 stratum) were sought out carefully in each profile. The average grain sizes of the soil sediments varied from 19 to 35 μm. In this preliminary study, the sampling intervals varied according to the stratum information in each profile, with the more intensive sampling performed in the contact zones of loess, paleosol, and Red Clay.

Materials used during experiment

Milli-Q water (Resistivity, 18.2 MΩ cm) was used throughout the experiments. Concentrated HCl, acetic acid (HAc) and HNO₃ were purified twice by sub-boiling distillation. Solution of NIST 951 boric acid, saturated NaHCO₃ (Sigma-Aldrich, SP) was prepared using the Milli-Q water. As the Loess Plateau is an arid area, all samples were dry without visible soil solutions at the sampling locations.

Boron extraction from the acid-soluble fraction of soil samples

All samples were ground to powder of approximately 150 mesh using an agate mortar, dried in a super-clean oven at 60°C for 6 h, and cooled down in a desiccator prior to weighing. A duplicate chemical leaching procedure was employed as shown in Supplementary Figure S1: (i) ~2 g of solid soil sample was weighted; (ii) exactly 3.0 mL of 1 mol L⁻¹ HAc was added to dissolve the solid sample and then ultrasonically shaken for 2 h at room temperature; (iii) the sample was centrifuged at 4000 rpm for 20 min to separate the insoluble residue from the transparent solution, and the insoluble solid was treated continuously with Step (ii) until reaching six cycles of leaching. The extraction assay of boron from the leaching procedure is discussed in detail in the Results section. The transparent solution collected from all cycles of extraction was ready for ion-exchange column in the next step.

Boron purification procedure

Setup of peristaltic pump coupled with mini exchange-column

A setup consisting of a peristaltic pump coupled with exchange-columns for ion-exchange extraction of boron by Amberlite IRA 743 boron-specific resin was modified in our laboratory (Wei et al., 2014a) based on the procedure reported by Hemming and Hanson (1992). It consisted of a multi-channel peristaltic pump (205U Watson Marlow, 16 channels), peristaltic pump tubings (0.12 mm in diameter) and Teflon resin columns (250 μL in volume). The pump speed is tunable at the range from 0.5 to 50 rpm, allowing the optimization of the flow through the column for each step of the procedure.