**Relationship of pyroclastic volcanism and lake-water acidification to Jehol
Biota mass mortality events (Early Cretaceous, northeastern China)**

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ABSTRACT

Geochemical analysis of the 14.4-m-thick lacustrine succession of the Lower Cretaceous
Yixian Formation (Jehol Group) has yielded new insights concerning vertebrate mass
mortality events in the Lake Sihetun volcanic caldera in western Liaoning Province
(northeastern China) that produced the Jehol Biota fossil lagerstätten. The long-term
evolution of the caldera system resulted in a shift from felsic to mafic magma chemistry,
accompanied by a reduced frequency of pyroclastic eruptions, declining hydrothermal
activity, and lower lacustrine productivity. The basal Tetrapod Beds exhibit strong
hydrothermal influence, as indicated by enrichments of boron (B), certain alkalis (Rb, Cs),
rare-earth elements (REEs), yttrium (Y), and many metals (e.g., Co, Cr, Cu, Ge, Mo, Ni, Sb,

U, V, and W), and by strongly negative molybdenum isotope compositions ($\delta^{98}\text{Mo}$ to -2.50‰) that may record large fractionations between molybdate and thiomolybdate species in the Sihetun caldera hydrothermal system. In contrast, the overlying Fish Beds and Non-Fossiliferous Beds have an elemental and Mo-isotopic composition similar to calc-alkaline basalts ($\delta^{98}\text{Mo} = -0.29 \pm 0.04\text{‰}$) in the surrounding watershed, suggesting weathering of Yixian Formation volcanic rocks as the major source of sediment. During its <700-kyr-long history, Lake Sihetun was affected by four environmental cycles, each commencing with a series of pyroclastic eruptions that triggered systematic changes in lakewater chemistry. Following each eruption interval, enhanced weathering of volcanic ash in the surrounding watershed caused lakewater pH to decrease and lacustrine productivity to increase. Continued weathering of bases from basement volcanic rocks subsequently produced alkaline conditions in the lake, leading to precipitation of authigenic carbonate layers and lower lacustrine productivity. Analysis of geochemical redox proxies strongly suggests that the Lake Sihetun water column was completely oxic, in contrast to earlier inferences of a stratified anoxic water column, and that ubiquitous lamination in the lacustrine succession was due to other factors such as widespread microbial mats and/or rapid sediment deposition.

Keywords: molybdenum isotopes; boron; vertebrates; fossil lagerstätte; lacustrine facies; maar

1. Introduction

The Lower Cretaceous Yixian Formation (Jehol Group) of western Liaoning Province,

China, is famous for an abundance of exceptionally well-preserved vertebrate and invertebrate animal and plant fossils belonging to the Jehol Biota (Wang et al., 1989, 1998, 1999; Pan et al., 2001; Chang et al., 2003). These lagerstätten contain articulated skeletons, soft tissues with preserved color patterns and stomach contents, and twigs with leaves and flowers still attached (Zhang, 2001; Zhou et al., 2003), including key fossils of early angiosperms and feathered dinosaurs (Fürsich et al., 2007). These deposits have been extensively investigated for insights concerning vertebrate evolution and mass mortality events (Wang et al., 1998, 1999; Chang et al., 2003; Zhou et al., 2003). Key factors contributing to exceptional fossil preservation in these deposits include rapid burial and anoxic low-permeability sediment porewaters, both related to high concentrations of volcanic ash, which effectively sealed off the fossil remains and prevented destruction through bioturbation or scavenging (Zhou et al., 2003; Jiang et al., 2011, 2014). Volcanic activity was intense during deposition of the Yixian Formation, possibly due to increased subduction along the Pacific margin of North China during the Early Cretaceous (Wang et al., 1983). Regional volcanism was thus essential in generating the setting within which these fossil lagerstätten accumulated (Guo and Wang, 2002; Chang et al., 2003; Zhou et al., 2003).

An important unresolved issue is the mechanism of Jehol Biota mass mortality events. Early studies generally attributed these events to volcanic eruptions within the Sihetun caldera (Chen et al., 1998; Ji et al., 1998; Xu et al., 1999, 2001; Wang et al., 1998, 1999; Liu et al., 2002; Guo and Wang, 2002; Guo et al., 2003; Zhou et al., 2003). Owing to lack of association of some fossil-bearing layers with volcanic tuffs, a hydrologic mechanism was subsequently advanced, i.e., seasonal limnic overturn of a stratified watermass with anoxic deepwaters (Fürsich et al., 2007; Pan et al., 2012a). It was also proposed that the fossil

remains of terrestrial and lacustrine organisms accumulated through different processes, the former being associated with volcanoclastic debris flows that form discrete fossil lagerstätten, and the latter being distributed more widely through the succession and, thus, representing a regular mortality process within the lake (Pan et al., 2012b). A recent study has refocused on the role of pyroclastic eruptions in mass kills of both terrestrial and lacustrine biota, linking them to the effects of pyroclastic density flows (Jiang et al., 2014).

Almost all of the existing studies of depositional processes and mass mortality mechanisms have been based solely on field and petrographic data—indeed, there has been very little geochemical analysis of the lacustrine succession to date, with the most important publication on this topic being in Chinese (Ke et al., 2008). The aim of the present study is to provide elemental and Mo isotopic data for the lacustrine succession of the Lower Cretaceous Yixian Formation in order to investigate secular changes in lakewater chemistry (e.g., pH and redox conditions) and their relationship to volcanism and vertebrate mass mortality events. Here, we show that regular fluctuations in lakewater chemistry, especially pH, were induced by cycles of volcanic activity that also triggered mass kills of terrestrial and lacustrine life. This study is the first to infer such relationships on the basis of geochemical data for the Lower Cretaceous Jehol Group, providing novel insights into environmental controls on vertebrate mass mortality in paleolacustrine systems.

2. Molybdenum isotopes

Variation in the Mo isotopic composition of different Earth reservoirs is approximately known. The bulk silicate earth (BSE) and the mantle have $\delta^{98}\text{Mo}$ ($= \delta^{98/95}\text{Mo}$) values between +0.04‰ and +0.1‰ (Burkhardt et al., 2014; Greber et al., 2015), and there appears to be little

isotopic fractionation associated with endogenic magmatic processes. The continental crust has evolved $\delta^{98}\text{Mo}$ values between +0.1‰ and +0.4‰ (Voegelin et al., 2014; Greber et al., 2015; Yang et al., 2015). Molybdenites have an even larger range of $\delta^{98}\text{Mo}$ variation, ranging from ca. -0.9‰ to +0.8‰ (Wieser and de Laeter, 2003; Malinovsky et al., 2005; Pietruszka et al., 2006; Hannah et al., 2007; Mathur et al., 2010; Greber et al., 2011, 2014; Wang et al., 2016).

River water $\delta^{98}\text{Mo}$ ranges from ~0‰ for streams draining basaltic terrains in Iceland (Pearce et al., 2010) to +2.4‰ for crystalline terrains in Canada (Archer and Vance, 2008). Although Neubert et al. (2011) inferred that the Mo-isotopic composition of river waters is inherited largely unchanged from its lithogenic source, the fact that the global weighted mean $\delta^{98}\text{Mo}$ for river waters (+0.7±0.4‰; Archer and Vance, 2008) exceeds that of average continental crust (+0.1‰ and +0.4‰; Greber et al., 2015) requires fractionation during weathering or transport. Weathering is thought to lead to preferential uptake of lighter Mo isotopes by soil particles, causing an increase in the $\delta^{98}\text{Mo}$ of soil and ground water (Archer and Vance, 2008; Pearce et al., 2010). On the other hand, hydrothermal sources yield markedly lower $\delta^{98}\text{Mo}$ values (to -3.4‰) (Pearce et al., 2010), which may be the result of strong fractionation (to -5.3‰) between MoO_4^{2-} and MoS_4^{2-} in open hydrothermal systems without quantitative conversion of Mo species (Tossell, 2005).

In aqueous systems, sediment $\delta^{98}\text{Mo}$ depends mainly on benthic redox conditions. For euxinic watermasses in which aqueous sulfide ($\text{H}_2\text{S}_{\text{aq}}$) exceeds ~11 µM, sediments acquire $\delta^{98}\text{Mo}$ values close to that of the watermass (e.g., +2.3‰ for modern seawater; Siebert et al., 2003) owing to conversion of molybdate to particle-reactive thiomolybdate species and subsequent quantitative uptake of Mo by the sediment (Helz et al., 1996; Erickson and Helz,

2000; Poulson et al., 2006; Neubert et al. 2008a). In some volcanic lakes, large quantities of H₂S and/or SO₂ may be released into the water column, potentially exceeding the threshold for thiomolybdate formation and scavenging. For oxic and suboxic watermasses, sediment $\delta^{98}\text{Mo}$ reflects large negative fractionations associated with adsorption of molybdate onto Fe-Mn-oxyhydroxides or other mineral phases during incomplete removal of Mo from the water column (Nägler et al., 2005; Neubert et al., 2008a,b; Scheiderich et al., 2010). Owing to the tendency of molybdate to adsorb onto particle surfaces, redox cycling of Mn- or Fe-oxyhydroxides within the water column can accelerate the transfer of Mo to the sediment-water interface, leading to isotopically light signatures in the sediment (Barling and Anbar, 2004; Goldberg et al., 2009; Dahl et al., 2010; Wirth et al., 2013).

3. Study site

The study section at Sihetun (41°35'28"N, 120°41'56"E) is located ~25 km south of the city of Beipiao in western Liaoning Province, northeastern China (Fig. 1A). The sample collection site is at the Sihetun Fossil Museum, which is operated by the Institute of Vertebrate Palaeontology and Palaeoanthropology, Chinese Academy of Sciences (Wang et al., 1998).

The Yixian Formation is the basal formation of the Lower Cretaceous Jehol Group, which rests on Precambrian basement and consists of up to ~4000 m of volcanic and volcanoclastic rocks with intercalated sedimentary beds that have been radiometrically dated to ~130-120 Ma (Fig. 1B; Jiang and Sha, 2006; Jiang et al., 2014). Major eruptions produced felsic to intermediate magmas in Plinian-style eruptions having maximum volumes of 200-320 km³ and column heights of 18-38 km (Guo et al., 2003; Peng et al., 2004). The

Yixian Formation is subdivided into three members representing major cycles of volcanic activity, with each cycle characterized by a gradual evolution of magma chemistry from mafic through intermediate to felsic (Chang et al., 2003; Peng et al., 2004).

The “lacustrine succession” of the Yixian Formation (also called the “Jianshangou Unit”; Jiang and Sha, 2007) accumulated in a 20-40 km² maar (a volcanic crater lake) named ‘Lake Sihetun’ (Fig. 1C; Guo et al., 2003; Pan et al., 2012b) that was one of many maars within the Early Cretaceous Beipiao-Fuxin Basin (Sha, 2007; Sha et al., 2007). Most maars are broad, shallow water bodies with maximum depths of a few tens of meters (Bogaard and Schmincke, 1984; Begét et al., 1996; Funicello et al., 2003). Maars can be subject to frequent explosive hydromagmatic eruptions as well as episodic crater collapse (Lorenz, 1986; Begét et al., 1996; Funicello et al., 2003), although evidence for these processes in Lake Sihetun is limited (Guo et al., 2003).

The lacustrine succession contains beach-nearshore, fan delta, and lake floor facies (Jiang and Sha, 2007; Jiang et al., 2012), with the present study samples coming from the lake floor facies. The sediments are mainly thinly laminated, dark to light grayish shale, siltstone, mudstone, and fine-grained sandstone with only minor stratigraphic variation in lithology and bedding character (Fig. 2; Wang et al., 1998). The laminae are the product of turbidity currents (both meso- and hyperpycnal flows) generated either during volcanic eruptions (Jiang et al., 2014) or through mass debris flows of unconsolidated volcanoclastic debris into Lake Sihetun (Jiang and Sha, 2007; Hethke et al., 2013). Many beds contain a tuffaceous component, and thin (0.5 to 5 cm) tuffs are intercalated throughout the succession, documenting frequent volcanic eruptions (Jiang et al., 2012; Hethke et al., 2013). Also present are occasional authigenic limestone beds and calcite veins of hydrothermal origin.

The 14.4-m-thick lacustrine succession can be divided into three stratigraphic units based on fossil content. The lower unit, the ~7-m-thick “Tetrapod Beds”, contains an abundance of fossil vertebrates including excellently preserved specimens of *Caudipteryx*, *Confuciusornis* (Fig. 2A), *Liaoningornis*, *Protarchaeopteryx*, *Psittacosaurus*, and *Sinosauropteryx* (Hou et al., 1995; Chen et al., 1998; Ji et al., 1998; Xu et al., 1999; Zhang et al., 2008). Fish (e.g., the teleost *Lycoptera*), invertebrates (e.g., the conchostracan *Eosestheria*), and insect larvae (e.g., *Ephemeropsis* sp.; Fig. 2B) are abundant in these strata (Chang et al., 2003). The middle unit, the ~1.5-m-thick “Fish Beds”, has yielded fossil fish (e.g., the teleosts *Lycoptera* sp. and *Peipiaosteuspani*) but no other vertebrates, and the upper unit, the ~6-m-thick “Non-Fossiliferous Beds”, contains plant remains (e.g., *Eosestheria*) but has not produced any vertebrate fossils (Fig. 2C-D). The lacustrine succession contains frequent brownish tuffaceous interlayers, the highest concentrations of which are found in the middle (Beds 25-29) and at the top (Bed 18) of the Tetrapod Beds, reflecting two intervals of heightened pyroclastic eruptive activity (Guo et al., 2003).

There are at least 22 layers with large concentrations of vertebrate fossils distributed through the Tetrapod Beds, although these fossiliferous layers are concentrated in the tuff-rich intervals (Fig. 2E; Zhou et al., 2003). Each layer appears to represent a single mass mortality event, during which nektonic reptiles and fish were killed in large numbers and rapidly buried. The enclosing sediments contain abundant euhedral microcrystals and framboids of pyrite that formed both inside and on the surface of fossils, indicating anoxic porewater conditions during burial (Leng and Yang, 2003). Soft-tissue preservation may also have been promoted by low-pH porewaters (cf. Briggs and Kear, 1993), a consequence of the highly acidic composition of the volcanic ash (Guo et al., 2003).

Volcanic lava layers near the base and top of the lacustrine succession have yielded $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 125.7 ± 2.6 Ma and 124.2 ± 2.5 Ma, respectively (Zhu et al., 2007), which are consistent with an earlier $^{40}\text{Ar}/^{39}\text{Ar}$ date of 124.6 ± 0.1 Ma for a tuff in the middle of the lacustrine succession (Fig. 1B; Swisher et al., 1999; note: cited age errors are 2σ). Based on these data, Zhu et al. (2007) concluded that the lacustrine succession accumulated at a rate of at least ~ 2 cm kyr⁻¹, and that the host lake existed for an interval of no longer than ~ 700 kyr. However, because the durations of hiatuses between the lake sediments and the volcanic lavas are unknown, and maar lakes can be filled in at much higher rates, these estimates represent a minimum sedimentation rate and a maximum duration for Lake Sihetun. However, based on the inference that laminae in the lacustrine succession represent varves, Zhang and Sha (2012) concluded that these strata accumulated at a much higher rate, ~ 20 -70 cm kyr⁻¹, which implies a span of existence for Lake Sihetun of only ~ 20 -70 kyr. These estimates (i.e., 20-700 kyr) span the range of lifespans commonly exhibited by maars (Robinson, 1994; Mingram, 1998).

4. Materials and methods

4.1. Sample collection and elemental-mineralogic analyses

A total of 40 samples were collected from the conformable 14.4-m-thick lacustrine succession in the lower Yixian Formation at intervals of 10 to 60 cm along the freshly cut walls of a fossil-excavation pit at the Sihetun Fossil Museum. The samples analyzed in the present study were collected in 1997 and previously used in studies by Pan et al. (2001) and Zhu et al. (2007). Note that this sample suite extends only through the upper 12 meters of the 14.4-m-thick lacustrine succession owing to incomplete exposure of its base at the time of

sample collection. For comparison, we also analyzed three basalt samples from the Yixian Formation that were collected ~10-15 km northwest of the Sihetun study site.

Samples were coarsely crushed with a steel jaw crusher and then powdered in an agate mill to a grain size of <200 mesh (75 μm). Trace-element compositions were analyzed using ICP-MS (Agilent 7500a) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Samples were digested in custom-made Teflon bombs. Sample aliquots of 75 mg were weighed and dissolved in 3 ml of acid (a 1:2 mixture of 6N HF and 6N HNO_3) at 180°C for 12-24 hours. The sample solutions were then taken up in dilute HNO_3 and further diluted with ultraclean H_2O to a final volume of 100 ml with addition of 20 ppb In, Re, Rh, and Bi as internal standards. Analytical precision and accuracy were evaluated by duplicate analyses of samples and three international standard reference rocks, BCR-2, BHVO-2, and GSR-6. Analytical precision reported as $1 \times \text{RSD} (\%)$ is better than 8% for elements other than Tm, Lu, Cd, Ta and Be, which have RSDs of ~10% due to low analyte concentrations.

Analysis of major elements was performed on a subset of samples at the State Key Laboratory of Continental Dynamics, Northwest University in Xi'an by X-ray fluorescence (XRF) using fused disks. H_2O and CO_2 were determined gravimetrically and volumetrically, respectively. Analysis of total organic carbon (TOC), total inorganic carbon (TIC), and total sulfur (TS) was performed using an Eltra CS-2000 elemental analyzer at the University of Cincinnati per methods described in [Algeo and Maynard \(2004\)](#). Elemental enrichment factors were calculated as $X_{\text{EF}} = (X/\text{Al})_{\text{sample}} / (X/\text{Al})_{\text{AUCC}}$ ([Tribovillard et al., 2006](#)), where X is the element of interest and AUCC is the composition of average upper continental crust (per [Rudnick and Gao, 2003](#)).

Sample mineralogy was determined by X-ray diffraction (XRD) using an X/Pert PRODY2198 at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences-Wuhan. Samples were analyzed at a scan rate of $0.418^{\circ} \text{ s}^{-1}$ with Cu K_{α} radiation (40 mA and 40 kV). XRD peaks were identified using a catalog for commonly occurring sedimentary minerals.

4.2. Molybdenum isotope analysis

Purification of Mo isotopes was carried out in a metal-free clean room fitted with a HEPA-filtered air supply and laminar flow benches. The dilution of solutions was performed using deionized “Milli-Q” water. All labware, including Teflon and disposable plastics, was cleaned in concentrated reagent-grade acids and 18 M Ω de-ionized H₂O prior to use. The ultra-pure acids (HCl and HNO₃) used during separation chemistry were further purified by sub-boiling quartz-distillation two times, and the HF acid was purified by sub-boiling distillation in a Teflon still. We have found that these acid purification methods are effective at decreasing Mo blank values, as well as its isobaric interferences with Zr and Ru.

Prior to Mo isotope ratio measurements, potential isobaric interferences due to Zr and Ru as well as polyatomic interferences caused by matrix elements (e.g., Na, Mg, Ca, K, Fe) in the samples were eliminated as follows. First, a ~0.05-gram aliquot of each sample was digested in acid (a 1:2 mixture of 6N HF and 6N HNO₃) at ~150°C in a Teflon bomb for 48 hours. In order to avoid any potential Mo isotope fractionation during column chemistry, a ⁹⁷Mo-¹⁰⁰Mo spike was added to the samples prior to purification. We used the method proposed by [Siebert et al. \(2006\)](#), modified with the addition of a 7N HCl digestion step in combination with H₂O₂. Column separation of Mo from the sedimentary matrix was achieved

by ion-exchange chromatography using the chelating resin Bio-Rad AG-MP1 (Archer and Vance, 2004, 2008). Samples were loaded and rinsed in 7M HCl with admixture of 1% H₂O₂ to remove Zr, Ru, and substantial amounts of other elements. The Mo fraction was then eluted in the final 0.5M HNO₃ stage and followed flushing through a cation resin column (BioRad AG50W-X8 resin, 200–400 mesh) to remove any residual iron. This method was found effective in the separation of Mo from most matrix elements, including Zr and Ru, and the Mo recovery from this column is normally >90%.

The samples were diluted in 5% HNO₃ for multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) (Thermo Scientific Neptune) measurements at the China University of Geosciences, Wuhan. Typical operating conditions and Mo-isotope-ratio measurement protocols for this instrument were described in Archer and Vance (2008). The MC-ICP-MS measurement utilizes the external normalization technique of a ⁹⁷Mo-¹⁰⁰Mo double spike to correct the instrumental mass bias, as proposed by Siebert et al. (2001) and Archer and Vance (2008). The Mo isotope compositions in sediments, expressed as δ^{98/95}Mo, and defined as $[(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}} - 1] \times 1000\text{‰}$ relative to the JMC Mo standard solution lot 602332B (Anbar, 2004; Siebert et al., 2003).

To assess data quality, we repeatedly analyzed the JMC standard solution containing the admixed double spike. Replicate analyses of SDO-1 yielded a mean δ⁹⁸Mo of 1.10‰±0.09‰ (2σ) relative to the JMC standard solution. This value is in good agreement with previously reported values (Poulson-Brucker et al., 2009; Duan et al., 2010; Scheiderich et al., 2010; Goldberg et al., 2013), indicating that the isotopic composition of our JMC standard solution is the same as that of other laboratories. The external δ⁹⁸Mo uncertainty of sample measurements, propagated through the double-spike reduction process, is better than 0.06‰.

4.3. Principal components analysis

Principal components analysis (PCA) was applied to a dataset matrix consisting 40 samples and 44 geochemical proxies, with the latter comprising 37 elemental concentrations, ΣREE , Ce/Ce*, Eu/Eu*, La/Sm, La/Yb, Sm/Yb, and $\delta^{98}\text{Mo}$ (note that the 14 REEs were not among the 37 elements in order to avoid weighting results heavily toward the REEs). One problem with PCA of compositional data is that negative correlations are commonly forced owing to the constraint imposed by summation of elemental concentrations to 1.0 (Aitchison, 1983; Jolliffe, 2002). This issue is less of a concern when the compositional data used represent only a fraction of the total sample, as in the present study in which the only major elements used were Al and Fe, whose summed concentrations averaged $16.4 \pm 4.8\%$. We also minimized forced negative correlations by normalizing each variable to its geometric mean, i.e., $x' = \log[x/g(x)]$, where x' is the transformed variable, and $g(x)$ is the geometric mean of x calculated as $(\prod_{i=1}^n x_i)^{1/n}$ (Aitchison, 1983; Jolliffe, 2002). This procedure converts each variable to a Z-score having a mean of zero and a standard deviation of one, which has the merit of imposing no fixed maximum value on each variable.

5. Results and discussion

5.1. Magmatic association and chemical evolution of Lake Sihetun caldera

The general magmatic association of volcanic and volcanoclastic rocks of the Yixian Formation is calc-alkaline, as shown by an AFM diagram (Fig. 3A; Winchester and Floyd, 1977; Pearce, 1996). Calc-alkaline series compositions are typical of continental volcanic systems in general (Ross and Bédard, 2009) and of the Yixian Formation in particular (Ke et

al., 2008). This magmatic association is confirmed for the majority of the study samples by a Zr/Y vs. Th/Yb crossplot (Fig. 3B), although some lacustrine succession samples as well as three basalt samples fall within the transitional field. The subset of study samples exhibiting the highest ratios (i.e., Zr/Y >10 and Th/Yb >10) were subject to significant hydrothermal inputs (see Section 5.2). In proximity to volcanic systems, the chemistry of ground and surface waters is commonly hydrothermally influenced (e.g., Pennisi et al., 2000).

The Sihetun lacustrine succession exhibits systematic upsection decreases in SiO₂, Al₂O₃, and K₂O+Na₂O and increases in CaO and Mg# (Fig. 4; Table 1). The upsection change in SiO₂ content is particularly large, from 67-70% at the base of the profile to 43-48% at its top, indicating a shift from felsic through intermediate to mafic volcanic inputs to Lake Sihetun during its depositional history, which extended over an interval of at least tens of thousands of years (see Section 3). The strongly felsic chemistry of the lowermost part of the lacustrine succession is consistent with formation of Lake Sihetun through a large-scale explosive eruption associated with highly silicic magmas (Guo et al., 2003). Smaller pyroclastic eruptions of felsic composition continued during deposition of the Tetrapod Beds, some of which were the main cause of mass mortality events of lake fauna (Zhou et al., 2003; Jiang et al., 2011). An ensuing interval of more limited and quiescent volcanic activity is reflected in the shift toward more mafic compositions in the Fish and Non-Fossiliferous beds (Fig. 4). Similar patterns of secular evolution of magma chemistry can be found in maars of various ages (e.g., Altaner and Grim, 1990; Riede et al., 2011).

5.2. Lake sediment mineralogy and elemental composition

The mineralogy of the Sihetun lacustrine succession was determined via XRD analysis (Fig. 5A). The major mineral components are smectite, illite, feldspar, alunite, quartz, and

calcite. Smectite, which represents a weathering product of more mafic volcanoclastic material, generally increases upsection, reflecting the progression toward more mafic magma compositions in younger strata (Fig. 4). Feldspar is somewhat more abundant in the lower part of the section, possibly because potassium feldspars in the more felsic units weather less readily than plagioclase feldspars in the more mafic units (White et al., 2001; cf. Goldich's weathering series). Alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) is a low-temperature weathering product of feldspars that is common in hydrothermal systems (Ece et al., 2008); it is found mainly in the Tetrapod Beds (Fig. 5A), in which other lines of evidence indicate that hydrothermal influences were strongest (see Section 5.5). Quartz shows no obvious vertical trend, and calcite increases upsection in an irregular manner. All mineral components show a measure of cyclic variation upsection that is superimposed on these overall secular trends and that is related to intervals of pyroclastic eruptive activity in the Sihetun caldera (see Section 5.4).

Elemental associations can provide insights into the processes of accumulation and/or formation of the lacustrine succession. We determined elemental associations using principal components analysis (PCA) of the elemental and isotopic dataset (Table 2). Most loading is associated with the first two principal components (PC-1 and PC-2), which account for 31% and 29% of total sample variance, respectively (no other component accounts for more than 16% of variance). PC-1 and PC-2 each show a strong affinity with a specific suite of elements.

PC-1 is associated with boron (B), certain alkalis (Rb, Cs), all rare-earth elements (REEs), yttrium (Y), and many metals (e.g., Co, Cr, Cu, Ge, Mo (modestly), Ni, Sb, U, V, and W), as well as total organic carbon (TOC) (Fig. 6A). This suite of elements is similar to that associated with hydrothermal fluids in the Yellowstone caldera system (i.e., As, B, Cl, Cs,

Cu, Ge, Li, Mo, Sb, and W) (Balistrieri et al., 2007), with which the Lake Sihetun caldera has the shared characteristic of hydrothermal circulation through upper continental crust. Boron enrichment, in particular, is regarded as a reliable hydrothermal proxy in such systems (Balistrieri et al., 2007). The elemental associations in PC-1 thus appear to have been influenced primarily by hydrothermal fluids that, moreover, were probably acidic in nature, as suggested by B and REE concentration patterns (see Section 5.3).

The association of TOC with PC-1 (Fig. 6A) suggests a link between hydrothermal influences and lacustrine productivity. Sediment organic carbon concentrations in many maars, especially those subject to infrequent magmatic activity, are controlled by climate fluctuations (e.g., Robinson, 1994; Mingram, 1998; Fuhrmann et al., 2003). In more magmatically active maars, algal productivity can be strongly influenced by volcanic eruptions. In some maars, direct tephra deposition leads to productivity declines owing to reduced sediment permeability at the sediment-water interface and a consequent reduction in the diffusive flux of remineralized organic phosphorus back to the water column (Barker et al., 2003). In contrast, tephra deposition within the watershed of a maar commonly leads to enhanced productivity owing to increased weathering and riverine nutrient supply, an effect that can persist for decades to centuries following an eruption (Barsdate and Dugdale, 1972; Hickman and Reasoner, 1994; Lotter et al., 1995; Telford et al., 2004). This latter relationship is indicated for the Sihetun lacustrine succession by the repeated development of organic carbon-rich layers above intervals of intense pyroclastic activity (Fig. 6A). The close association of trace metals with TOC may indicate uptake of the former by the latter in the burial environment, e.g., as a result of limited post-depositional redistribution of trace metals (Thomson et al., 1998; Morford and Emerson, 1999).

PC-2 exhibits a strong positive association with aluminum (Al), iron (Fe), and high-field strength elements including thorium (Th), hafnium (Hf), zirconium (Zr), and gallium (Ga) (Fig. 6A). This association suggests derivation via leaching of the underlying basement rocks. Because maars are closed water bodies that are not fed by large hydrographic basins, the chemistry of the lake waters commonly reflects that of the volcanic basement underlying the maar. For example, waters of Lake Nyos in Cameroon are enriched in dissolved Mg and Fe owing to hydrothermal weathering of basaltic basement rock (Kling et al., 1989; Giggenbach, 1990). In the Taupo Volcanic Zone of New Zealand, lake waters are enriched in SiO₂, Na, Cl, and SO₄²⁻ derived from hydrothermal weathering of felsic volcanic basement rocks, as well as in high-field-strength (e.g., Hg, As, Sb, and Tl), large ion lithophile (e.g., K, Rb, Cs, Ba, Sr, and Eu²⁺), and transition elements (e.g., Mn, Zn, Cu, and Mo) from magmatic fluids (Timperley and Vigor-Brown, 1986; de Ronde et al., 2002). Hydrothermal weathering of basement rock can be intense owing to leaching related to high concentrations of magmatic CO₂ (Degens and Kulbicki, 1973; Pflumio et al., 1994) or sulfur compounds (de Ronde et al., 2002; Balistrieri et al., 2007). PC-2 thus represents a suite of elements of primarily lithogenic origin.

PC-2 exhibits a negative association with calcium carbonate (CaCO₃), manganese (Mn), and δ⁹⁸Mo (Fig. 6A). Since CaCO₃ is present as a micritic chemical precipitate forming laminae enclosed by siliciclastic strata (Hethke et al., 2013), the negative association of CaCO₃ with PC-2 is due mainly to dilution effects, i.e., greater calcite content resulted in lower concentrations of all lithogenic elements. The similar behavior of Mn in the study samples is likely due to substitution of Mn(II) for Ca(II), which is common in carbonates deposited under modestly reducing (i.e., suboxic) conditions (Dromgoole and Walter, 1990).

The negative association of $\delta^{98}\text{Mo}$ with PC-2 will be addressed in detail in [Section 5.5](#).

5.3. Lake water chemistry and evolution

Maars are commonly broad, shallow (tens of meters deep) water bodies lacking stratification and, thus, ventilated throughout (e.g., [Bogaard and Schmincke, 1984](#); [Begét et al., 1996](#); [Funciello et al., 2003](#)). In contrast, Lake Sihetun is thought to have been a stratified watermass with an anoxic hypolimnion, an inference based mainly on the ubiquity of lamination and absence of bioturbation in the lacustrine succession ([Jiang et al., 2012](#); [Zhang and Sha, 2012](#); [Hethke et al., 2013](#)). However, some of these laminae have been interpreted as the remains of benthic microbial mats that, if widespread, would have effectively isolated the sediment from an overlying oxic water column ([Pan et al., 2012b](#); [Zhang and Sha, 2012](#)). Sedimentary deposits rich in pyroclastic material would also allow only limited oxygen penetration of the sediment column owing to the low-permeability character of such deposits, an effect reported from the South China Sea following the 1991 eruption of Mount Pinatubo in the Philippines ([Wiesner et al., 1995](#); [Haeckel et al., 2001](#); [Kuhnt et al., 2005](#)). In view of these conflicting considerations, it must be concluded that past studies have shed little light on the actual redox characteristics of the Lake Sihetun watermass.

The geochemical proxies of the present study provide insights regarding redox conditions in Lake Sihetun. Other than Mo (see [Section 5.5](#)), no redox-sensitive trace metal shows measurable enrichment in the study samples ([Table 3](#)). However, sedimentary trace-metal concentrations may be unreliable redox proxies in lacustrine systems owing to low aqueous concentrations and, hence, insufficient supply for removal to the sediment via

authigenic processes (cf. [Algeo and Maynard, 2008](#)). Another redox proxy is molar $C_{org}:P$, in which both carbon and phosphorus are derived from photosynthates, and which has the advantage of being independent of watermass salinity ([Algeo and Ingall, 2007](#)). Although marine phytoplankton have relatively uniform $C_{org}:P$ of ~106:1 (the Redfield ratio), lacustrine seston have generally higher and more variable ratios (~100-500:1) owing to moderate to strong nutrient phosphorus deficiency in lakes ([Hecky et al., 1993](#)). In the study units, systematically low $C_{org}:P$ ratios (mean 20 ± 15 ; [Fig. 4](#)) are therefore indicative of fully oxic conditions in the Lake Sihetun watermass, regardless of the initial $C_{org}:P$ of the lacustrine phytoplankton. The juxtaposition of laminated sediments with oxic bottomwaters may have been due to the presence of benthic microbial mats ([Pan et al., 2012b](#); [Zhang and Sha, 2012](#)) and/or rapid sediment deposition via turbidity currents ([Jiang et al., 2014](#); see [Section 3](#)), both of which would have suppressed bioturbation and sediment ventilation. Although the deep watermass of Lake Sihetun was probably oxic, it is thought that anoxic porewater conditions developed quickly in microenvironments around organic remains following depositional events owing to low sediment permeability ([Leng and Yang, 2003](#); [Zhou et al., 2003](#)).

Maars commonly exhibit acidic conditions, especially when fumaroles vent CO_2 - or sulfur-rich magmatic volatiles into lake waters. In small maars with high volatile loading, lakewater pH can be <1, as at El Chichon, Mexico ([Casadevall et al., 1984](#)), whereas larger maars with greater freshwater inflow tend to show more limited development of acidic conditions, as in Yellowstone Lake (pH >4.9) ([Gemery-Hill et al., 2007](#)). The pH of Lake Sihetun waters was at least moderately acidic as suggested by two lines of evidence. First, at alkaline to neutral pH, REEs are mainly complexed with carbonate anions, in which form they are readily absorbed by various particulates, including Mn- and Fe-oxyhydroxides, Al

oxides, solid carbonate phases, and clay minerals (Byrne and Sholkovitz, 1996). In contrast, under acidic conditions REE enrichment is controlled by complexation with organic matter (Bau, 1999; Luo and Byrne, 2004; Quinn et al., 2006) or sulfate anions, although the latter tend to show middle REE enrichment (Schijf and Byrne, 2004), which is not observed in the study samples.

The REE distributions of lacustrine succession samples show strong enrichment of light REEs relative to middle and heavy REEs (Fig. 7). Even though Σ REE is significantly associated with PC-1 (Fig. 6A), there is no obvious difference in REE distributions between samples in which PC-1 versus PC-2 is dominant (Fig. 7). The observed REE distributions, showing light REE enrichment with little variation for elements lighter than Gd (Fig. 7), is a pattern similar to that reported for REE adsorption onto organic substrates (Stanley and Byrne, 1990; Byrne and Kim, 1990). Thus, REE distributions in the study samples are consistent with adsorption onto organic matter during intervals of more acidic conditions in Lake Sihetun, although post-depositional sorption/desorption processes (e.g., Chen et al., 2015) may have subsequently modified REE-TOC associations in the burial environment.

A second feature that supports acidic conditions in Lake Sihetun is its boron chemistry. Boron is commonly present in substantial amounts in acidic volcanic and hydrothermal fluids as boric acid (H_3BO_3) or halogenides (e.g., BF_3) (Hem, 1985; Anovitz and Grew, 1996; Leeman and Sisson, 1996), or it can be derived via leaching of country rocks (Pflumio et al., 1994; Vengosh et al., 1994; Schmitt et al., 2002). It is removed to the sediment mainly through low-temperature hydrothermal reactions, adsorption onto clay minerals or organic matter, and co-precipitation with carbonate minerals (Spivack et al., 1987; Williams et al., 2001; Lemarchand et al., 2002). However, boron is readily remobilized from the sediment,

especially in response to changes in aqueous pH or ionic concentrations (Leeman and Sisson, 1996; Mather and Porteous, 2001; Ravenscroft and McArthur, 2004), with lower pH promoting the release of borate from particulate (mainly clay-mineral) surfaces (Zeebe and Wolf-Gladrow, 2001; Wallmann et al., 2008). In the Sihetun lacustrine succession, strong covariation of B with TOC (Fig. 8) and lack of covariation with Al (Fig. 5) suggest adsorption onto (or co-precipitation with) organic matter rather than clay minerals. Given the general association of B enrichment with lower pH, it appears probable that organic matter accumulation was also associated with more acidic conditions.

5.4. Eruption episodes and compositional cyclicity

Superimposed on the secular trend in magma chemistry of the study section (Fig. 4) are four intervals of closely spaced pyroclastic tuffs that are recognizable based on a combination of field observations, geochemical composition, high volatile content, and associated vertebrate fossil layers (Fig. 9; Guo et al., 2003). These intervals are located near the base (11.5-12.0 m), middle (9.4-10.0 m), and top (7.0-7.4 m) of the Tetrapod Beds, and in the lower Non-Fossiliferous Beds (4.6-5.0 m). The geochemical proxy in our dataset that best defines the four tuffaceous intervals is the Hf/Y ratio (Hf and Y are strongly associated with PC-2 and PC-1, respectively). Hf/Y ratios are low and relatively invariant (~0.2) through much of the lacustrine succession but rise to higher values (0.5-2.0) within the tuffaceous intervals (Fig. 9B). The second and third intervals exhibit the highest Hf/Y ratios as well as enrichments of the volatile elements S, F, and Cl to concentrations ~2× to 10× greater than background levels (Guo et al., 2003). Thus, the pyroclastic eruptions generating the tuffaceous intervals were associated with high volatile emissions, as well as with numerous

fossil tetrapod beds, documenting a relationship between eruption frequency and/or intensity and vertebrate faunal mortality events (Guo et al., 2003; Zhou et al., 2003).

The lacustrine succession exhibits regular compositional cyclicity related to the tuffaceous intervals described above. Each tuffaceous interval (“T”; proxied by Hf/Y) represents the base of a cycle that consists successively of organic-rich beds (“O”; proxied by TOC), carbonate-rich beds (“C”; proxied by CaCO_3), and background sediments (“B”; no proxy shown) (Fig. 9). Cycle 1 consists only of the basal tuffs and multiple organic-rich beds; it contains no carbonate-rich beds, although the strata between the organic-rich layers could be characterized as background sediments. Cycles 2 and 3 are similar, showing development of just one or two thin organic-rich beds directly above the basal tuffs that are overlain in turn by well-developed carbonate-rich intervals. Cycle 4 differs in showing only weak development of the basal tuffs but thicker intervals of organic- and carbonate-rich beds. This cyclicity reflects secular variation in some of the major sedimentary components of the study section (i.e., volcanic ash, organic matter, and calcium carbonate).

The source of the compositional cyclicity within the study section was probably regular changes in lake water chemistry that were triggered by the four eruption episodes represented by the tuffaceous intervals (Fig. 10). Each of the tuffaceous intervals represents a series of pyroclastic eruptions that were closely spaced in time (Guo et al., 2003). These eruption intervals were responsible for vertebrate faunal mass mortality events, yielding the well-known Jehol Biota fossil layers (Zhou et al., 2003; Jiang et al., 2011) and for general collapses of the lacustrine ecosystem (Pan et al., 2012b). Each eruption interval resulted in acidification of the surrounding watershed, triggering intensified weathering and nutrient fluxes into Lake Sihetun (Fig. 10; cf. Johnson and Parnell, 1986; Allen et al., 2000; Mingram

et al., 2004). This process caused a short-term increase in lacustrine primary productivity following the eruption intervals that is recorded by the organic-rich layers (cf. Mingram et al., 2004; Telford et al., 2004). Subsequently, the low pH of lake waters was neutralized through an influx of weathered bases from the lake catchment. Continued weathering of bases by acidified groundwaters then triggered carbonate precipitation in Lake Sihetun (Fig. 10; cf. Last and De Deckker, 1990; Lamb et al., 2000), a process possibly also promoted by the removal of CO₂ through high rates of lacustrine primary productivity. As acidic weathering in the watershed gradually tapered off, carbonate precipitation terminated, and as nutrient influxes decreased, primary productivity levels fell, finally yielding low-organic, low-carbonate background sediments. Similar patterns of secular variation in lakewater chemistry in response to variable rates of volatile venting (Giggenbach and Glover, 1975; Rowe et al., 1992) or episodic volcanic eruptions (Degens and Kulbicki, 1973) are known from modern maars.

Deviations within individual cycles from the general pattern of lakewater chemical changes described above reflect the long-term evolution of the Lake Sihetun magmatic system. Over its <700-kyr existence, the composition of magmas erupting from the Lake Sihetun caldera shifted from felsic to mafic (Fig. 4). This change was accompanied by a declining frequency of pyroclastic eruptions and reduced intensity of hydrothermal activity. Cycle 1 shows numerous organic-rich beds and a lack of carbonate-rich sediments because pyroclastic eruptions during this interval were more frequent and more acidic in composition (Fig. 9). Hydrothermal activity was also strongest immediately following formation of the Lake Sihetun caldera, as indicated by highly negative Mo isotopes (to -2.5‰) and significant Mo enrichments in the lower Tetrapod Beds (see Section 5.5). During cycles 2-4, pyroclastic

eruptions became relatively less frequent and their composition more basic (Fig. 4). Hydrothermal activity also declined in the upper Tetrapod Beds and overlying Fish Beds, as reflected in decreases in Mo_{EF} and increases in $\delta^{98}Mo$.

5.5. Molybdenum accumulation and isotopic fractionation

Molybdenum (Mo) concentrations and isotopic compositions show pronounced secular trends within the study section. The Mo enrichment factor (Mo_{EF}) is modestly elevated in the Tetrapod Beds (mean 4.6, peak ~10) but declines to upper-crustal background values in the Fish and Non-Fossiliferous beds (mean 1.3) (Fig. 9E). $\delta^{98}Mo$ increases upsection from $-1.36 \pm 0.49\text{‰}$ in the Tetrapod Beds to $-0.47 \pm 0.42\text{‰}$ in the Fish Beds and Non-Fossiliferous Beds, although with considerable sample-to-sample variation (Fig. 9F; Table 2). Covariation of Mo concentrations with $\delta^{98}Mo$ suggests mixing of two Mo-bearing fractions (Fig. 11). In the Tetrapod Beds, Mo concentrations are uniformly high (i.e., low $1/[Mo]$), thus yielding no covariation with $\delta^{98}Mo$, which ranges from about -0.1‰ to -2.5‰ . In the overlying Fish and Non-Fossiliferous beds, Mo concentrations exhibit pronounced positive covariation with $\delta^{98}Mo$, with the highest concentrations associated with $\delta^{98}Mo$ of about $+0.2\text{‰}$ and the lowest concentrations with $\delta^{98}Mo$ of about -1.5‰ .

The $\delta^{98}Mo$ of the Fish Beds and Non-Fossiliferous Beds is similar to that of calc-alkaline volcanic rocks in the surrounding area ($-0.29 \pm 0.17\text{‰}$; Table 1), which are the main source of lithogenic material to the Sihetun lacustrine succession (Ke et al., 2008). Thus, the relatively small amounts of Mo in the Fish and Non-Fossiliferous beds ($<5 \text{ mg kg}^{-1}$) most likely came from weathering of local volcanic rocks. The larger amounts of Mo in the Tetrapod Beds represent admixture of a second Mo-bearing fraction with a distinctly lower $\delta^{98}Mo$

composition. An important point is that there is no relationship at all between Mo_{EF} or $\delta^{98}\text{Mo}$ and the compositional cycles (Fig. 9) that were identified on the basis of other geochemical parameters (Fig. 5), indicating that Mo accumulation was not visibly influenced by the four pyroclastic eruption episodes or ensuing cyclic lakewater chemical changes described in Section 5.4.

The source of isotopically light Mo in the Tetrapod Beds ($\delta^{98}\text{Mo}$ of -2.5‰ to -1.0‰) is unlikely to be igneous rocks (mostly -0.3 to 0‰ ; Siebert et al., 2001, 2003; Pearce et al., 2010), average continental crust ($\sim 0\text{‰}$), or river waters ($+0.15\text{‰}$ to $+2.4\text{‰}$; Archer and Vance, 2008; Neubert et al., 2011), all of which have heavier compositions. Strong negative fractionation of Mo isotopes (up to -3‰) is common in oxic depositional facies (Barling et al., 2001; Siebert et al., 2003; Barling and Anbar, 2004; Goldberg et al., 2009), and such isotopically light Mo can be transferred in quantity to the sediment via a Mn-particulate shuttle (Morford and Emerson, 1999; Morford et al., 2005; Algeo and Tribovillard, 2009; Herrmann et al., 2012). In such systems, Mo scavenging efficiency is greatly enhanced under acidic conditions ($\text{pH} < \sim 6$) (Goldberg et al., 1996, 2009; Manning and Goldberg, 1996; Goldberg and Forster, 1998; Gustafsson, 2003; Barling and Anbar, 2004; Malinovsky et al., 2007). There are several arguments against operation of this process in the Lake Sihetun basin, however. First, Mo enrichment factors show no relationship to Mn concentrations (Figs. 5, 9; $r^2 = 0.01$), providing no evidence of a Mn-particulate shuttle (although Mn and Mo do not necessarily covary in lakes with active Mn-particulate shuttles; e.g., Wirth et al., 2013). Second, a Mn-particulate shuttle could not have existed in the oxic Lake Sihetun water column, although a limited one might have operated at the sediment-water interface if the chemocline hovered at that level. However, Mo uptake by secondary Mn-oxide minerals in

the diagenetic environment is accompanied by only a small negative fractionation relative to porewater Mo (ca. -0.5‰ ; [Reitz et al., 2007](#)), which cannot account for fractionations of $>-2\text{‰}$ in the lower Tetrapod Beds ([Fig. 9](#)). Third, given the strong pH-dependency of Mo scavenging efficiency, Mo concentrations should have varied cyclicly in concert with changes in lakewater pH ([Section 5.4](#)), which is not observed in the study section ([Fig. 9](#)).

A more likely source of the isotopically light Mo in the Tetrapod Beds is hydrothermal fluids. Thermodynamic calculations suggest that a strong negative Mo isotope fractionation (to -5.3‰) can result between oxidized molybdate (MoO_4^{2-}) and reduced thiomolybdate (MoS_4^{2-}), yielding isotopically light MoS_4^{2-} species within the fluid phase ([Tossell, 2005](#); [Pearce et al., 2010](#)). This difference is not expressed in reducing environments at the Earth's surface (e.g., the Black Sea; [Neubert et al., 2008a](#)) owing to quantitative conversion of molybdate to thiomolybdate. In open hydrothermal systems, however, it is possible that interactions between H_2S -rich fluids and oxic Mo species present in the country rock will result in formation of isotopically light MoS_4^{2-} species in the fluid phase. This mechanism is thought to be responsible for the exceptionally low $\delta^{98}\text{Mo}$ (to -3.44‰) and high dissolved Mo concentrations (to $>200\text{ nM}$) of hydrothermal springs in Iceland ([Pearce et al., 2010](#)) and for similar patterns seen in hydrothermal deposits of the Grimsel breccia in Switzerland ([Greber et al., 2011](#)). We therefore interpret the second Mo fraction in the study units to be hydrothermally sourced with a $\delta^{98}\text{Mo}$ composition of about -2.5‰ ([Fig. 11](#)).

Secular Mo trends in the lacustrine succession may be understood in the context of the long-term magmatic evolution of the Lake Sihetun caldera system ([Section 5.3](#)). Hydrothermal activity was probably greatest immediately following the formation of the Lake Sihetun caldera ([Fig. 10](#)). At that time, heated fluids within or overlying the remnant

magma chamber would have circulated upward and influenced the chemistry of the caldera lake water (e.g., [Brantley et al., 1987](#)). As the Sihetun caldera system aged, the level of hydrothermal activity is likely to have gradually decreased. This decrease can account for the shift of the hydrothermally sourced fraction from high concentrations with a $\delta^{98}\text{Mo}$ of about -2.5‰ to lower concentrations with a $\delta^{98}\text{Mo}$ of about -1.5‰ ([Fig. 11](#)). The upsection shift toward higher $\delta^{98}\text{Mo}$ compositions for the hydrothermal component reflects an increased fractionation relative to a hydrothermal MoS_4^{2-} source at cooler fluid temperatures ([Tossell, 2005](#)).

6. Conclusions

Geochemical analysis of the 14.4-m-thick Sihetun lacustrine succession has yielded new insights regarding the environmental conditions that produced the Jehol Biota fossil lagerstätte. The study units record major changes in lakewater chemistry and environmental conditions in Lake Sihetun, an Early Cretaceous volcanic maar in western Liaoning Province (northeastern China). The basal Tetrapod Beds were deposited under strong hydrothermal influence, as indicated by enrichments of boron (B), certain alkalis (Rb, Cs), rare-earth elements (REEs), yttrium (Y), and many metals (e.g., Co, Cr, Cu, Ge, Mo, Ni, Sb, U, V, and W), and by strongly negative molybdenum isotope compositions ($\delta^{98}\text{Mo}$ to -2.50‰) that may record large fractionations between molybdate and thiomolybdate species in the Sihetun caldera hydrothermal system. In contrast, the overlying Fish Beds and Non-Fossiliferous Beds have an elemental and Mo-isotopic composition similar to calc-alkaline basalts ($\delta^{98}\text{Mo} = -0.29 \pm 0.04\text{‰}$) in the surrounding watershed, suggesting weathering of Yixian Formation volcanic rocks as the major source of sediment. The long-term evolution of the Lake Sihetun

caldera system resulted in a shift from felsic to mafic chemistry, accompanied by a reduced frequency of pyroclastic eruptions, declining hydrothermal activity, and lower lacustrine productivity. During its <700-kyr-long history, Lake Sihetun was affected by four cycles of volcanic activity, each commencing with a series of pyroclastic eruptions that triggered changes in lakewater chemistry. Enhanced weathering following each eruption episode caused lakewater pH to decrease and lacustrine productivity to increase. Continued weathering of bases from basement volcanic rocks eventually produced alkaline conditions in the lake, leading to precipitation of authigenic carbonate layers. Analysis of geochemical redox proxies strongly suggests that the Lake Sihetun was completely oxic, in contrast to earlier inferences of a stratified anoxic water column, and that ubiquitous lamination in the lacustrine succession was due to other factors such as widespread microbial mats and/or rapid sediment deposition.

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1060 **Table captions**

1061

1062 Table 1. Major-element oxide concentration data for a subset of Sihetun lacustrine succession
1063 samples

1064

1065 Table 2. Mo-isotopic and elemental data for Sihetun lacustrine succession samples

1066

1067 Table 3. Trace metal enrichment factors for Sihetun lacustrine succession samples

Figure captions

Fig. 1. (A) Location map for Sihetun section. (B) Stratigraphic column of Yixian Formation (left) with expanded column of the lacustrine succession (right); note that only the upper 12 m was sampled (beginning at zero) owing to poor exposure of the basal 2.4 m of the succession. Green diamond marks the tuff dated by [Swisher et al. \(1999\)](#); black triangles mark the main tetrapod fossil layers, and pink bars correspond to intervals of concentrated felsic tuffs ([Guo et al., 2003](#)). (C) Interpretative cross-section of Early Cretaceous Lake Sihetun (a maar, or volcanic crater lake). No vent has been identified in the underlying volcanic units but extensive hydrothermal veining has been documented ([Wang et al., 1989](#)).

Fig. 2. Photographs of the Sihetun lacustrine succession. (A) *Confuciusornis* sp., one of the oldest known beaked birds, from the Tetrapod Beds ([Zhang et al., 2008](#); photograph courtesy of Institute of Vertebrate Paleontology and Paleoanthropology (IVPP)); (B) *Ephemeropsis* sp., an insect larva, one of the classic triumvirate of fossils defining the Jehol Biota (along with the teleost fish *Lycoptera* and the conchostracan *Eosestheria*; [Chang et al., 2003](#)); (C) The full ~12-m-thick study interval at the Sihetun Museum quarry; (D) Volcaniclastic sediments intruded by a conformable basalt layer, same location; (E) Whitish pyroclastic tuffs interbedded with gray laminated mudstone from the Tetrapod Beds, same location.

Fig. 3. Magmatic associations: (A) AFM ternary plot ([Winter, 2001](#)), and (B) Zr/Y vs. Th/Yb ([Ross and Bédard, 2009](#)). A = alkalis; F = iron, M = magnesium. In B, the dashed field encloses samples deposited under significant hydrothermal influence.

Fig. 4. Major element chemistry of Sihetun lacustrine succession. Mg# is the molar ratio of Mg/(Mg+Fe); the low Mg# at 3.6 m is due to exceptional iron enrichment ($\text{Fe}_2\text{O}_3 = 16.9\%$) and may represent a hydrothermal deposit, and outliers at 8.6 m are from a limestone bed. Also shown are intervals of concentrated felsic tuffs (gray fields; see next figure) and tetrapod fossil lagerstätten (pink). Molar $\text{C}_{\text{org}}:\text{P}$ ratio is used as a paleoredox proxy; lacustrine seston typically yields values up to ~500, i.e., greater than the Redfield ratio of 106:1 (Hecky et al., 1993) (see Section 5.3).

Fig. 5. Mineralogy and chemostratigraphy of Sihetun lacustrine succession: (A) PC-1 and associated geochemical proxies (TOC, V, Cu, ΣREE , and B), and (B) PC-2 and associated geochemical proxies (CaCO_3 , Mn, Al, Fe, Hf, and Zr). Note that CaCO_3 and Mn are negatively correlated with PC-2. Dashed lines in elemental profiles represent average upper continental crustal concentrations (from Rudnick and Gao, 2003). Cumulative mineralogy profiles are based on XRD results.

Fig. 6. Principal components analysis. (A) Element-based. (B) Sample-based, by stratigraphic unit of the Sihetun lacustrine succession. Broad linear arrays of data in both panels suggest mixing of two main components in each unit; see text for discussion.

Fig. 7. REE distributions for samples dominated by either PC-1 or PC-2 (i.e., PC axis weight >0.6). The two sample groups show nearly identical distributions. The heavy dashed line represents the average REE distribution for all samples.

Fig. 8. Boron (B) versus total organic carbon (TOC). All three units of the lacustrine succession show significant positive covariation between these proxies.

Fig. 9. Profiles of (A) cumulative mineralogy, (B) Hf/Y and volatiles, (C) TOC, (D) CaCO₃, (E) Mo_{EF}, and (F) $\delta^{98}\text{Mo}$ for the lacustrine succession. High Hf/Y ratios and volatiles correlate with the main intervals of felsic tuffs (gray fields) and tetrapod fossil lagerstätten (pink); volatile content is the sum of sulfur, fluorine, and chlorine from Guo et al. (2003). Dashed lines represent average crustal Mo_{EF} (1.0) and $\delta^{98}\text{Mo}$ (ca. -0.2‰) (Archer and Vance, 2008). See text for discussion of cycles 1-4; T = tuffs, O = organic-rich, C = carbonate-rich, Bg = background sedimentation.

Fig. 10. Interpretative cartoon showing evolution of the Lake Sihetun system. Long-term secular evolution of magma chemistry and hydrothermal activity is shown at left, and cyclic changes in lakewater chemistry as a result of episodic pyroclastic eruptions is shown at right. The four panels represent conditions during deposition of the pyroclastic tuffs (T), organic-rich layers (O), carbonate-rich layers (C), and background sediments (Bg). ‘+’ and ‘-’ reflect generally acidic and alkaline conditions, respectively.

Fig. 11. $\delta^{98}\text{Mo}$ versus 1/[Mo] for the lacustrine succession. This crossplot defines two covariant relationships (blue and gray trends) in which one endmember has uniform [Mo] and high $\delta^{98}\text{Mo}$ (~0‰) and the second endmember has variable [Mo] and low $\delta^{98}\text{Mo}$ (-1.5‰ to -2.5‰). We infer that the two components are weathered volcanic basement and hydrothermal fluids, respectively.

1138 Table 1. Major element concentration data for the Sihetun section

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Mg#
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	
G31	48.3	0.41	9.3	2.6	0.18	2.5	16.4	0.73	3.23	0.39	16.4	100.5	0.62
F29	42.7	0.95	12.8	16.9	0.12	1.4	8.9	2.14	2.43	0.80	10.5	99.7	0.12
S2	53.1	0.18	14.0	3.3	0.10	4.3	8.6	0.93	1.48	0.04	13.6	99.6	0.69
P13	61.6	0.28	13.7	4.3	0.02	2.9	2.7	1.49	3.47	0.16	8.9	99.5	0.54
P43	6.7	0.04	1.3	1.0	0.74	1.7	48.3	0.04	0.32	0.64	39.4	100.3	0.74
P63	58.0	0.30	14.2	8.7	0.03	4.2	2.1	2.33	3.73	0.19	6.5	100.2	0.45
P66	62.7	0.38	10.8	6.7	0.05	2.8	2.9	1.42	3.02	0.75	8.1	99.7	0.42
P90	56.4	1.17	18.1	4.5	0.13	1.4	5.3	2.26	3.12	0.54	6.7	99.5	0.35
P114	70.2	0.50	10.2	3.5	0.02	1.8	1.5	0.97	3.69	0.38	6.8	99.6	0.47
P119	67.0	0.55	11.2	4.3	0.03	1.9	1.9	1.07	4.34	0.57	6.6	99.5	0.43

1139 Note: Mg# is the molar ratio of Mg/(Mg+Fe).

1140

1141 Table 2. Isotopic and elemental data for the Sihetun section

Sample	Layer	$\delta^{98}\text{Mo}$	δ	Li	Be	B	Al	Sc	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr
		(‰)		(mg/kg)	(mg/kg)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	(mg/kg)	(%)	(%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
K09	NFB	+0.06	0.02	54.6	2.3	27.3	12.6	6.5	59.8	45.8	2.6	0.087	6.3	25.4	17.0	64.9	14.8	1.1	1.8	160.2	264	17.8	140.5
K33	NFB	−0.57	0.03	76.4	2.4	24.5	13.6	8.4	63.5	51.8	3.9	0.048	7.2	24.9	20.2	60.4	16.1	1.2	10.0	161.6	220	14.6	150.7
G22	NFB	−0.08	0.02	25.8	1.3	22.2	7.5	4.5	42.0	28.5	2.3	0.256	3.9	20.0	55.7	31.6	8.3	0.6	7.1	86.4	243	11.6	80.4
F6	NFB	+0.33	0.02	35.2	1.3	2.4	11.5	2.9	35.8	6.1	2.6	0.239	5.9	37.2	8.7	55.3	12.2	0.8	13.8	41.0	423	7.2	113.1
F7	NFB	−0.20	0.02	30.7	1.9	18.9	7.1	5.7	179.4	49.4	2.2	0.010	2.7	15.6	13.4	37.9	10.2	1.0	7.6	104.6	125	19.1	81.7
F23	NFB	−0.29	0.01	60.7	2.8	26.2	13.8	6.8	134.2	38.9	3.4	0.015	7.9	37.6	21.2	78.2	16.8	1.2	9.9	166.2	156	13.8	125.6
F30	NFB	−0.49	0.02	49.0	2.4	31.8	12.0	6.8	139.8	47.5	2.4	0.015	6.3	31.6	19.4	55.4	14.9	1.3	6.5	161.2	328	12.2	110.1
F41	NFB	−0.81	0.02	56.0	2.4	26.1	12.7	8.0	111.8	43.1	2.8	0.048	10.3	31.6	20.7	52.1	15.0	1.4	1.6	165.9	206	16.4	128.5
T14	NFB	−0.87	0.04	69.6	2.6	21.0	12.3	7.1	66.0	32.6	2.2	0.028	9.6	24.9	17.1	56.0	15.8	1.4	0.9	151.3	336	27.4	131.3
T30	NFB	−0.28	0.02	79.4	3.0	15.9	12.8	5.5	39.1	20.5	2.1	0.011	5.0	12.2	11.2	46.8	16.1	2.8	2.3	123.6	146	7.5	107.5
T54	NFB	−0.97	0.05	84.2	3.3	26.5	13.4	6.4	67.2	35.1	2.2	0.017	7.0	17.9	16.6	64.1	16.6	1.5	0.8	141.2	183	14.0	121.0
S4	FB	−0.21	0.03	72.7	3.3	23.9	11.9	7.0	78.7	45.9	2.0	0.019	5.5	23.3	20.0	56.8	15.2	1.4	1.4	137.2	482	24.2	131.3
S10	FB	−0.31	0.02	41.1	1.9	12.6	12.2	7.8	81.1	72.2	1.6	0.211	6.4	24.0	21.4	47.7	13.0	0.8	1.8	100.3	539	24.5	134.5
S33	FB	−0.91	0.04	27.5	1.3	8.7	8.9	4.4	32.4	2.4	0.8	0.207	3.9	14.0	3.8	30.0	9.4	0.7	1.3	58.7	248	14.1	108.4
S34	FB	−0.73	0.03	72.5	2.8	30.6	14.3	8.5	93.2	49.2	3.0	0.022	5.8	24.5	22.8	56.7	16.7	1.6	1.7	173.7	286	14.4	137.7
S35	FB	−1.49	0.04	62.4	2.1	4.3	12.5	3.1	8.7	5.0	2.4	0.076	6.3	27.6	3.8	56.2	13.2	0.8	1.0	78.9	320	4.9	99.7
S36	FB	−0.08	0.01	64.4	2.2	12.8	7.3	7.0	78.4	31.8	1.9	0.010	3.9	20.6	13.5	39.8	12.3	1.1	3.9	133.7	277	14.9	117.6
S53	FB	−0.37	0.02	99.4	2.3	1.0	15.6	5.0	19.1	7.0	3.7	0.012	1.8	14.8	3.3	46.6	18.8	0.9	12.5	68.7	339	2.4	119.4
S54	FB	−0.30	0.02	39.7	2.6	16.0	12.6	4.1	82.6	26.1	1.6	0.018	3.2	18.2	10.6	37.3	13.9	0.8	18.0	146.3	494	11.7	100.2
S55	FB	−0.74	0.02	88.7	1.8	1.2	15.9	4.5	10.7	16.3	3.0	0.009	2.2	16.7	5.7	54.8	18.2	0.7	5.6	87.7	250	2.5	104.0
P34	TpB	−0.06	0.01	27.6	1.8	9.4	10.2	4.2	43.4	19.7	2.0	0.034	6.1	15.2	17.0	51.5	11.6	0.7	3.3	106.7	180	8.5	58.1
P64	TpB	−1.45	0.02	28.4	1.4	31.5	6.6	5.1	108.8	32.6	1.7	0.532	8.3	70.4	15.7	51.2	8.1	1.4	13.3	91.3	406	11.2	92.7
P65	TpB	−1.55	0.02	46.2	2.6	24.7	24.5	6.0	188.1	44.0	1.3	0.913	8.2	63.4	22.7	70.2	13.4	1.7	57.0	162.1	683	13.1	124.7
P68-1	TpB	−0.89	0.02	45.0	2.3	22.1	9.7	6.7	220.8	49.6	2.7	0.024	8.7	61.4	25.6	66.2	13.2	1.6	12.7	158.8	720	15.9	134.7
P68-2	TpB	−0.98	0.02	42.0	2.1	27.8	9.7	6.1	246.6	47.5	2.0	0.034	13.0	65.6	25.0	63.0	12.3	1.6	12.1	148.3	442	16.4	115.6

P69-1	TpB	−1.05	0.01	50.9	2.7	37.0	11.2	8.0	296.0	55.8	2.6	0.037	12.3	66.3	29.3	73.0	14.9	2.5	9.4	184.3	568	18.0	136.8
P69-2	TpB	−1.07	0.02	43.9	2.4	27.1	11.3	8.3	265.8	52.3	2.3	0.040	13.3	75.0	31.1	66.6	14.1	2.2	13.1	175.0	369	20.0	120.7
P70	TpB	−0.71	0.02	25.4	2.4	22.0	8.0	4.8	146.0	35.8	2.1	0.013	4.4	35.7	18.3	42.0	14.1	1.0	13.3	120.6	559	13.0	99.2
P74-1	TpB	−1.37	0.02	107.7	1.9	1.5	15.9	2.8	5.9	0.4	4.1	0.034	3.1	30.7	4.5	50.2	22.0	0.9	4.4	51.6	228	4.3	127.6
P86	TpB	−0.68	0.02	39.4	2.5	27.7	12.3	8.3	262.5	62.7	3.2	0.016	7.4	46.6	36.4	88.3	16.3	1.7	20.5	218.4	169	21.8	145.7
P92	TpB	−1.34	0.02	38.8	2.1	29.2	11.8	9.0	166.9	59.3	3.3	0.018	6.5	40.2	25.5	60.1	16.6	1.3	13.2	205.9	345	16.5	151.6
P99	TpB	−1.69	0.02	14.5	1.5	2.0	18.5	6.9	61.5	44.8	6.5	0.065	14.3	46.0	15.1	74.0	18.4	1.1	56.0	135.3	1359	7.3	141.1
P100	TpB	−1.05	0.01	36.5	3.1	29.9	13.3	7.5	168.3	54.0	2.2	0.019	5.1	23.0	18.2	52.5	19.2	1.4	6.2	195.4	531	21.9	137.2
P105	TpB	−1.48	0.02	20.4	2.8	9.0	16.0	5.1	54.6	38.6	2.9	0.024	7.1	22.8	14.8	64.4	17.7	0.9	8.6	142.0	1266	16.6	184.7
P112	TpB	−1.41	0.01	42.1	2.2	22.7	11.7	9.5	232.5	65.9	2.8	0.047	20.9	55.8	23.1	57.9	15.9	1.8	12.5	201.6	332	25.2	133.2
P120	TpB	−2.02	0.02	17.2	1.7	4.7	19.4	3.7	61.5	40.0	2.0	0.026	11.7	31.1	11.9	57.8	15.6	1.1	17.2	139.9	996	6.6	150.4
P130	TpB	−1.80	0.02	17.0	2.5	7.8	17.1	7.7	88.5	55.0	5.2	0.057	18.9	47.5	19.8	102.3	18.3	1.0	15.6	74.6	1799	7.4	158.3
P131	TpB	−0.87	0.01	31.2	1.8	25.6	11.9	7.0	167.5	48.7	2.5	0.015	4.4	24.3	23.5	42.6	15.2	1.4	10.0	189.0	319	12.0	134.0
P138	TpB	−2.50	0.02	23.6	4.8	15.7	15.0	7.1	67.3	50.4	2.6	0.021	2.3	21.4	10.1	59.6	15.1	1.0	7.9	119.2	1400	21.7	276.3
P139	TpB	−1.98	0.01	68.4	2.5	3.2	16.9	8.5	9.0	3.9	5.0	0.020	1.2	17.2	4.2	51.7	19.9	1.2	6.9	76.9	226	17.1	552.3
SHT-15	volcanic	+0.90	0.03	28.5	2.1			26.0	182.6	838.1			85.8	205.3	58.7	73.2	16.6			63.0	935	23.0	166.1
SHT-25	volcanic	+1.22	0.05	47.7	2.3			28.3	189.1	919.7			48.1	211.2	48.4	78.6	17.3			58.0	809	22.0	175.5
SHT-28	volcanic	+0.09	0.06	48.3	2.4			29.4	186.6	936.3			44.0	231.9	74.9	75.8	17.4			58.0	809	23.0	156.4

Notes: TpB = Tetrapod Beds; FB = Fish beds; NFB = Non-Fossiliferous Beds.

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Sample	Layer	Nb	Mo	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
K09	NFB	13.4	0.9	0.07	0.05	2.0	0.27	0.02	6.2	423	35.2	65.6	7.4	26.4	4.7	0.87	3.5	0.54	3.0	0.61	1.53	0.26	1.61
K33	NFB	13.4	0.4	0.05	0.05	1.6	0.30	0.02	6.4	402	27.5	53.4	6.4	23.5	4.2	0.86	3.3	0.49	2.6	0.55	1.48	0.27	1.43
G22	NFB	7.9	1.2	0.06	0.02	6.0	0.24	0.02	3.3	303	26.9	48.4	5.1	17.6	3.0	0.57	2.3	0.35	1.9	0.39	0.99	0.17	1.05
F6	NFB	7.8	6.2	0.09	0.02	1.6	0.29	0.01	1.1	646	25.1	47.6	4.9	16.6	2.7	0.71	2.0	0.27	1.4	0.26	0.65	0.11	0.63
F7	NFB	11.3	3.8	0.05	0.03	0.7	0.26	0.04	4.7	310	44.4	80.3	10.2	35.6	6.2	0.98	4.7	0.69	3.6	0.74	1.97	0.35	1.86
F23	NFB	12.2	12.3	0.12	0.05	2.2	0.58	0.04	6.5	385	27.1	59.8	6.6	23.5	4.4	0.76	3.1	0.49	2.6	0.53	1.31	0.23	1.43
F30	NFB	12.6	5.4	0.09	0.04	2.0	0.26	0.02	7.5	375	26.1	50.1	5.9	20.8	3.7	0.68	2.6	0.41	2.3	0.46	1.14	0.20	1.25
F41	NFB	12.3	1.5	0.09	0.05	1.6	0.30	0.03	6.6	372	29.4	55.9	6.3	22.9	4.1	0.79	3.2	0.49	2.7	0.58	1.53	0.28	1.49
T14	NFB	12.3	0.5	0.08	0.05	2.1	0.20	0.03	5.6	400	50.4	99.1	10.7	37.6	6.7	1.07	5.1	0.78	4.3	0.87	2.08	0.34	2.03
T30	NFB	13.7	0.8	0.04	0.04	2.2	0.06	0.02	4.1	362	20.5	39.5	4.3	14.3	2.5	0.51	1.7	0.26	1.4	0.28	0.73	0.13	0.83
T54	NFB	15.1	0.3	0.10	0.04	2.2	0.11	0.05	5.6	322	27.4	57.5	6.3	22.3	4.0	0.69	2.9	0.47	2.5	0.52	1.31	0.23	1.47
S4	FB	13.7	0.6	0.06	0.04	1.9	0.14	0.03	6.2	587	40.1	74.1	9.1	32.7	6.0	1.03	4.6	0.72	3.9	0.81	1.99	0.34	1.95
S10	FB	11.2	1.1	0.11	0.04	1.3	0.07	0.03	3.0	520	46.1	77.4	8.6	30.6	5.2	1.20	4.1	0.59	3.3	0.70	1.77	0.30	1.68
S33	FB	2.9	0.4	0.20	0.03	1.0	0.05	0.01	0.7	385	38.8	69.5	6.5	19.5	3.0	0.53	2.4	0.38	2.3	0.50	1.35	0.27	1.87
S34	FB	14.0	0.5	0.07	0.05	1.8	0.25	0.05	6.6	476	26.4	51.4	6.2	22.7	4.1	0.76	3.1	0.49	2.6	0.54	1.46	0.27	1.49
S35	FB	6.1	0.2	0.19	0.03	2.0	0.08	0.01	0.8	543	19.1	33.4	3.3	10.1	1.4	0.40	1.1	0.15	0.8	0.17	0.45	0.09	0.61
S36	FB	14.2	1.0	0.05	0.04	1.3	0.21	0.06	4.5	467	28.0	56.4	6.9	24.3	4.5	0.72	3.4	0.51	2.7	0.56	1.51	0.27	1.45
S53	FB	6.3	6.3	0.05	0.03	2.3	0.23	0.01	0.7	571	25.2	43.4	4.3	13.2	1.5	0.44	1.3	0.12	0.5	0.09	0.30	0.06	0.35
S54	FB	20.4	21.9	0.12	0.04	2.5	0.33	0.02	4.7	772	21.6	42.3	5.1	17.9	3.4	0.59	2.4	0.41	2.3	0.48	1.23	0.23	1.53
S55	FB	9.3	3.5	0.04	0.03	2.0	0.19	0.01	0.8	391	12.1	20.8	2.2	7.3	1.0	0.30	0.8	0.10	0.5	0.10	0.29	0.06	0.34
P34	TpB	4.3	2.5	0.07	0.03	0	0.09	0.02	4.9	429	17.1	30.6	3.8	13.9	2.4	0.56	1.8	0.28	1.5	0.32	0.85	0.15	0.82
P64	TpB	6.8	8.2	0.13	0.03	1.1	0.38	0.02	4.9	536	15.8	31.3	3.3	12.2	2.3	0.50	1.8	0.31	1.8	0.38	0.96	0.17	1.06
P65	TpB	11.8	18.1	0.14	0.04	1.7	0.68	0.04	8.2	945	21.9	43.9	4.9	17.7	3.4	0.67	2.5	0.40	2.3	0.48	1.21	0.22	1.39
P68-1	TpB	11.9	9.4	0.16	0.04	1.7	0.47	0.04	8.7	907	28.4	55.1	6.2	22.4	4.1	0.78	3.0	0.50	2.7	0.58	1.43	0.25	1.55
P68-2	TpB	10.7	10.4	0.15	0.04	1.7	0.46	0.04	8.3	586	29.1	53.7	5.9	21.5	4.0	0.71	2.9	0.47	2.7	0.56	1.42	0.25	1.53

P69-1	TpB	12.9	10.4	0.15	0.05	2.0	0.63	0.03	10.1	789	31.5	58.5	6.5	23.3	4.4	0.83	3.2	0.53	3.0	0.63	1.57	0.28	1.74
P69-2	TpB	11.8	9.3	0.15	0.04	1.8	0.61	0.04	9.0	528	38.5	67.3	7.3	26.2	4.7	0.83	3.5	0.57	3.3	0.70	1.74	0.30	1.86
P70	TpB	10.8	4.4	0.12	0.03	1.4	0.32	0.04	5.3	781	26.1	50.7	5.4	17.9	3.1	0.56	2.3	0.38	2.2	0.49	1.27	0.24	1.58
P74-1	TpB	16.6	1.6	0.06	0.03	1.7	0.23	0.00	0.8	363	12.0	21.3	2.0	5.8	0.9	0.13	0.8	0.12	0.7	0.15	0.44	0.09	0.50
P86	TpB	13.2	19.9	0.16	0.05	2.1	0.67	0.05	8.6	427	42.0	79.9	9.2	32.9	5.9	1.05	4.3	0.68	3.8	0.76	1.89	0.33	1.96
P92	TpB	12.7	16.8	0.11	0.05	1.8	0.34	0.05	8.4	615	25.4	49.4	5.7	21.5	4.1	0.81	3.0	0.50	2.9	0.60	1.52	0.27	1.73
P99	TpB	8.2	34.3	0.18	0.04	0.7	0.68	0.01	0.8	1535	14.0	25.2	2.8	10.3	1.8	0.97	1.4	0.22	1.2	0.25	0.69	0.12	0.64
P100	TpB	14.6	6.9	0.06	0.04	1.9	0.36	0.02	7.5	963	53.4	101.7	11.4	39.7	6.9	1.13	4.9	0.73	3.8	0.77	1.94	0.34	2.07
P105	TpB	12.5	6.0	0.07	0.03	1.7	0.20	0.02	2.3	2410	32.0	61.9	6.6	22.6	4.0	0.99	2.9	0.51	2.9	0.62	1.60	0.30	1.87
P112	TpB	12.3	10.9	0.14	0.05	2.2	0.56	0.03	10.3	562	43.8	86.0	9.8	35.6	6.6	1.06	4.7	0.75	4.1	0.84	2.00	0.33	1.97
P120	TpB	6.6	8.7	0.06	0.03	0.9	0.42	0.03	1.7	1211	19.6	35.6	3.7	12.8	2.0	0.84	1.5	0.21	1.2	0.24	0.65	0.12	0.72
P130	TpB	8.0	14.2	0.11	0.04	1.2	0.36	0.02	1.3	2216	20.9	45.4	4.5	16.1	2.7	0.89	1.9	0.29	1.5	0.30	0.72	0.13	0.74
P131	TpB	12.8	13.5	0.16	0.05	1.8	0.50	0.03	7.4	669	18.3	35.4	4.2	15.0	2.9	0.66	2.1	0.37	2.2	0.46	1.20	0.22	1.46
P138	TpB	33.4	5.9	0.05	0.07	2.6	0.26	0.03	3.8	2942	48.2	100.9	11.6	40.6	7.5	1.49	5.1	0.85	4.7	0.93	2.29	0.42	2.65
P139	TpB	42.1	2.9	0.03	0.12	3.8	0.19	0.08	0.9	495	19.6	44.9	6.7	29.6	7.2	1.15	4.7	0.73	3.5	0.66	1.57	0.25	1.24
SHT-15	volcanic	9.0							2.7	2099	62.2	132.7	16.5	69.8	13.2	3.53	11.1	1.26	5.4	0.85	2.09	0.25	1.65
SHT-25	volcanic	9.3							3.5	1741	59.5	126.6	15.9	67.0	12.9	3.38	10.6	1.23	5.3	0.84	2.04	0.25	1.63
SHT-28	volcanic	8.9							2.8	1738	57.7	125.2	15.6	65.5	12.7	3.33	10.4	1.20	5.2	0.82	1.98	0.24	1.59

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Sample	Layer	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U	TOC	Th/Y	Zr/Y	Hf/F	La/Yb	La/Sm	Sm/Yb	CaCO ₃	ΣREE
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(%)							(%)	(mg/kg)
K09	NFB	0.24	4.0	0.95	1.21	0.67	17.0	0.28	9.8	2.3	0.22	0.55	7.9	0.22	21.9	7.5	2.9	14.1	151.3
K33	NFB	0.22	4.2	1.06	1.13	0.89	18.7	0.30	10.7	2.2	0.27	0.73	10.3	0.29	19.2	6.6	2.9	3.6	126.1
G22	NFB	0.16	2.3	0.56	0.71	0.79	16.1	0.20	6.2	2.8	0.08	0.53	6.9	0.19	25.6	9.0	2.9	0.1	108.9
F6	NFB	0.10	2.9	0.56	0.25	1.24	24.8	0.15	7.1	1.5	0.09	0.98	15.6	0.39	40.0	9.3	4.3	35.4	102.9
F7	NFB	0.28	2.1	0.53	0.69	0.63	13.7	0.22	6.1	8.6	0.24	0.32	4.3	0.11	23.8	7.2	3.3	0.2	191.9
F23	NFB	0.21	4.0	1.02	0.83	0.69	23.7	0.49	12.9	4.5	1.36	0.93	9.1	0.29	18.9	6.2	3.0	0.0	132.0
F30	NFB	0.19	3.3	0.83	1.07	0.70	15.9	0.30	9.5	4.4	1.36	0.78	9.1	0.27	21.0	7.1	3.0	6.6	115.8
F41	NFB	0.23	3.7	0.94	1.04	0.98	21.5	0.34	10.4	4.4	1.55	0.64	7.9	0.23	19.8	7.3	2.7	2.2	129.8
T14	NFB	0.30	3.9	0.87	1.11	1.07	19.4	0.37	10.6	4.3	0.44	0.39	4.8	0.14	24.9	7.6	3.3	3.8	221.3
T30	NFB	0.12	3.6	1.00	0.51	0.92	16.6	0.38	11.8	2.1	0.20	1.58	14.4	0.48	24.7	8.3	3.0	0.3	87.0
T54	NFB	0.23	3.9	1.00	0.79	1.08	24.2	0.38	11.6	3.2	0.39	0.83	8.7	0.28	18.7	6.8	2.7	1.0	127.9
S4	FB	0.30	3.7	0.88	1.17	1.10	13.4	0.33	9.3	3.7	1.26	0.39	5.4	0.15	20.6	6.7	3.1	5.3	177.6
S10	FB	0.25	3.2	0.66	1.62	0.91	9.3	0.16	5.0	1.9	0.34	0.21	5.5	0.13	27.4	8.9	3.1	30.1	181.7
S33	FB	0.30	3.3	0.65	0.18	0.61	26.6	0.22	9.9	2.2	0.09	0.70	7.7	0.24	20.7	12.9	1.6	51.0	147.3
S34	FB	0.23	3.9	1.02	0.97	1.29	18.6	0.38	12.2	3.4	1.30	0.85	9.6	0.27	17.8	6.5	2.8	4.1	121.8
S35	FB	0.10	3.6	1.14	0.15	0.76	32.5	0.25	11.4	0.8	0.09	2.35	20.5	0.73	31.3	13.2	2.4	18.0	71.1
S36	FB	0.22	3.2	0.82	0.65	1.16	16.9	0.30	11.1	6.3	1.59	0.75	7.9	0.22	19.4	6.3	3.1	1.2	131.4
S53	FB	0.06	4.5	1.43	0.09	0.26	17.8	0.31	10.9	1.2	0.11	4.60	50.2	1.88	72.2	17.1	4.2	0.1	90.7
S54	FB	0.24	3.5	1.01	0.63	0.68	21.6	0.56	13.4	6.0	0.72	1.14	8.6	0.30	14.1	6.3	2.2	0.5	99.7
S55	FB	0.06	3.8	1.32	0.10	0.24	18.4	0.49	11.9	2.1	0.09	4.80	42.0	1.53	35.3	12.1	2.9	0.1	46.0
P34	TpB	0.13	1.4	0.34	0.08	0.42	15.7	0.08	5.8	2.6	0.70	0.69	6.9	0.17	20.8	7.0	3.0	6.7	74.2
P64	TpB	0.16	2.4	0.44	0.76	3.87	10.2	0.14	4.6	2.9	1.46	0.41	8.3	0.22	14.9	6.8	2.2	29.2	72.0
P65	TpB	0.21	3.7	0.93	1.10	3.04	19.1	0.38	9.3	6.8	2.69	0.71	9.5	0.28	15.8	6.5	2.4	1.1	101.3
P68-1	TpB	0.24	3.7	0.82	1.16	2.64	16.5	0.32	8.9	9.0	2.82	0.56	8.5	0.23	18.4	6.9	2.7	1.7	127.4
P68-2	TpB	0.23	3.0	0.69	1.14	2.35	16.9	0.30	7.5	10.4	3.36	0.46	7.1	0.19	19.1	7.3	2.6	4.0	124.9

P69-1	TpB	0.27	3.8	0.88	1.37	2.56	17.6	0.32	9.2	9.3	2.71	0.51	7.6	0.21	18.1	7.2	2.5	1.0	136.2
P69-2	TpB	0.29	3.5	0.83	1.25	2.51	18.7	0.35	8.5	12.0	3.93	0.43	6.0	0.17	20.7	8.2	2.5	1.4	157.1
P70	TpB	0.25	2.9	14.29	0.85	1.31	14.3	0.25	6.7	6.1	3.14	0.52	7.6	0.23	16.5	8.4	2.0	0.5	112.5
P74-1	TpB	0.07	5.7	1.90	0.12	1.30	24.9	0.19	16.6	2.1	0.08	3.85	29.7	1.33	24.0	13.6	1.8	0.1	44.8
P86	TpB	0.30	4.1	0.92	1.06	1.09	18.3	0.32	9.7	8.3	3.53	0.44	6.7	0.19	21.5	7.1	3.0	1.0	185.0
P92	TpB	0.27	4.2	0.83	0.93	0.75	19.0	0.26	8.7	7.0	2.88	0.52	9.2	0.25	14.7	6.2	2.4	1.4	117.6
P99	TpB	0.10	3.6	0.61	0.20	1.11	24.4	0.24	8.6	2.6	0.07	1.17	19.3	0.49	21.8	7.8	2.8	0.2	59.6
P100	TpB	0.32	4.1	0.92	0.90	0.86	13.8	0.26	10.4	6.0	0.71	0.48	6.3	0.19	25.8	7.7	3.3	1.5	229.1
P105	TpB	0.28	4.9	1.04	0.37	1.08	21.5	0.21	10.1	1.8	0.20	0.61	11.2	0.29	17.2	7.9	2.2	0.2	139.1
P112	TpB	0.30	3.7	0.79	1.19	1.61	15.3	0.27	8.8	5.4	0.21	0.35	5.3	0.15	22.2	6.7	3.3	46.4	197.8
P120	TpB	0.11	4.0	0.60	0.22	0.80	22.2	0.32	8.6	2.3	2.00	1.30	22.7	0.60	27.4	9.7	2.8	0.0	79.2
P130	TpB	0.12	4.1	0.58	0.15	1.21	23.6	0.25	8.0	1.9	0.10	1.09	21.5	0.56	28.2	7.8	3.6	0.2	96.2
P131	TpB	0.22	3.8	0.90	0.77	0.61	16.2	0.27	7.3	4.2	1.34	0.60	11.2	0.32	12.5	6.4	2.0	1.2	84.6
P138	TpB	0.40	7.3	1.74	0.47	0.71	12.8	0.18	8.9	5.0	0.29	0.41	12.7	0.33	18.2	6.4	2.8	0.3	227.6
P139	TpB	0.18	13.1	3.97	0.13	0.32	13.2	0.21	14.1	1.8	0.16	0.82	32.3	0.77	15.8	2.7	5.8	0.5	121.9
SHT-15	volcanic	0.24	3.9	0.44			12.8		7.7	1.7		0.34	7.2	0.17	37.7	4.7	8.0		320.9
SHT-25	volcanic	0.24	3.9	0.40			12.7		7.6	1.3		0.35	8.0	0.18	36.6	4.6	8.0		307.4
SHT-28	volcanic	0.23	3.6	0.39			12.3		7.4	1.5		0.32	6.8	0.16	36.3	4.6	8.0		301.7

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1151 Table 3. Enrichment factors of redox-sensitive trace elements for the Sihetun section

Sample	Layer	Mo _{EF}	U _{EF}	V _{EF}	Zn _{EF}	Cu _{EF}	Ni _{EF}	Cr _{EF}	Co _{EF}	Pb _{EF}
K09	NFB	0.53	0.54	0.39	0.77	0.49	0.34	0.32	0.23	0.64
K33	NFB	0.20	0.48	0.39	0.67	0.54	0.31	0.34	0.25	0.65
G22	NFB	1.18	1.10	0.46	0.64	2.68	0.46	0.33	0.24	1.02
F6	NFB	3.93	0.39	0.26	0.73	0.27	0.56	0.05	0.24	1.03
F7	NFB	3.93	3.63	2.10	0.81	0.68	0.38	0.60	0.18	0.91
F23	NFB	6.48	0.97	0.80	0.85	0.55	0.47	0.25	0.27	0.81
F30	NFB	3.28	1.10	0.97	0.70	0.58	0.45	0.35	0.24	0.63
F41	NFB	0.85	1.04	0.73	0.62	0.59	0.43	0.30	0.38	0.80
T14	NFB	0.27	1.05	0.44	0.69	0.50	0.35	0.23	0.36	0.74
T30	NFB	0.44	0.49	0.25	0.55	0.32	0.16	0.14	0.18	0.61
T54	NFB	0.17	0.70	0.42	0.72	0.45	0.23	0.23	0.24	0.85
S4	FB	0.38	0.92	0.55	0.72	0.60	0.33	0.34	0.21	0.53
S10	FB	0.64	0.46	0.55	0.59	0.64	0.34	0.52	0.24	0.36
S33	FB	0.33	0.74	0.30	0.51	0.16	0.27	0.02	0.21	1.41
S34	FB	0.23	0.71	0.54	0.60	0.57	0.29	0.30	0.19	0.61
S35	FB	0.14	0.20	0.06	0.68	0.11	0.38	0.03	0.24	1.23
S36	FB	1.04	2.58	0.89	0.82	0.67	0.48	0.38	0.25	1.09
S53	FB	2.96	0.24	0.10	0.45	0.08	0.16	0.04	0.05	0.54
S54	FB	12.66	1.41	0.54	0.44	0.30	0.25	0.19	0.12	0.81
S55	FB	1.62	0.39	0.06	0.52	0.13	0.18	0.09	0.06	0.55
P34	TpB	1.80	0.75	0.35	0.76	0.60	0.25	0.17	0.28	0.72
P64	TpB	9.07	1.29	1.36	1.17	0.85	1.82	0.43	0.58	0.73
P65	TpB	5.39	0.83	0.64	0.43	0.33	0.44	0.16	0.16	0.37
P68-1	TpB	7.09	2.77	1.89	1.03	0.95	1.08	0.45	0.42	0.81
P68-2	TpB	7.88	3.21	2.12	0.98	0.94	1.16	0.43	0.62	0.83

P69-1	TpB	6.81	2.48	2.19	0.98	0.94	1.01	0.43	0.51	0.74
P69-2	TpB	6.00	3.16	1.95	0.89	0.99	1.14	0.41	0.55	0.78
P70	TpB	4.03	2.25	1.51	0.79	0.82	0.76	0.40	0.26	0.84
P74-1	TpB	0.71	0.39	0.03	0.48	0.10	0.33	0.00	0.09	0.74
P86	TpB	11.84	2.01	1.77	1.08	1.07	0.65	0.44	0.28	0.70
P92	TpB	10.36	1.77	1.17	0.76	0.78	0.58	0.45	0.26	0.76
P99	TpB	13.55	0.42	0.28	0.60	0.29	0.42	0.21	0.36	0.62
P100	TpB	3.79	1.35	1.05	0.60	0.49	0.30	0.36	0.18	0.49
P105	TpB	2.72	0.34	0.28	0.61	0.33	0.24	0.21	0.21	0.63
P112	TpB	6.82	1.37	1.64	0.74	0.71	0.81	0.50	0.83	0.62
P120	TpB	3.26	0.35	0.26	0.45	0.22	0.27	0.18	0.28	0.54
P130	TpB	6.08	0.33	0.43	0.90	0.42	0.47	0.28	0.51	0.65
P131	TpB	8.29	1.04	1.17	0.54	0.71	0.35	0.36	0.17	0.64
P138	TpB	2.90	1.00	0.37	0.60	0.24	0.24	0.30	0.07	0.40
P139	TpB	1.27	0.32	0.04	0.46	0.09	0.17	0.02	0.03	0.37
SHT-15	volcanic		0.38	1.16	0.84	1.62	2.69	5.60	3.05	0.46
SHT-25	volcanic		0.31	1.20	0.91	1.34	2.76	6.15	1.71	0.46
SHT-28	volcanic		0.35	1.18	0.87	2.07	3.04	6.26	1.57	0.45

Notes: TpB = Tetrapod Beds; FB = Fish beds; NFB = Non-Fossiliferous Beds;
Average upper crustal concentrations in EFs from Rudnick and Gao (2003).

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Figure 1

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Figure 3

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Figure 4

Figure 5

Figure 6

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Figure 7

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Figure 8

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Figure 9

Figure 10

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Figure 11

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Sihetun lakewater chemistry