Chemical Geology 428 (2016) 59–76

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

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

Lian Zhou [a,*], Thomas J. Algeo [a,b,c,**], Lanping Feng [a], Rixiang Zhu [d], Yongxin Pan [d], Shan Gao [a], Laishi Zhao [a], Yuanbao Wu [a]

[a] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China
[b] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China
[c] Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA
[d] Palaeomagnetism and Geochronology Laboratory (SKL-LE), Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

ARTICLE INFO

Article history:
Received 22 August 2014
Received in revised form 27 February 2016
Accepted 29 February 2016
Available online 2 March 2016

Keywords:
Molybdenum isotopes
Boron
Vertebrates
Fossil lagerstätte
Lacustrine facies
Maar

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 (δ^{98}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 (δ^{98}Mo $= -0.29 \pm 0.04$‰) 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.

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

* Corresponding author.
** Correspondence to: T.J. Algeo, State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China.
E-mail addresses: zhcug@163.com (L. Zhou), Thomas.Algeo@uc.edu (T.J. Algeo).

http://dx.doi.org/10.1016/j.chemgeo.2016.02.029
0009-2541/

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 volcaniclastic 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 δ^{98}Mo ($=\delta^{98/95}$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 δ^{98}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 δ^{98}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 δ^{98}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 δ^{98}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 δ^{98}Mo of soil and ground water (Archer and Vance 2008; Pearce et al. 2010). On the other hand, hydrothermal sources yield markedly lower δ^{98}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 δ^{98}Mo depends mainly on benthic redox conditions. For euxinic watermasses in which aqueous sulfide (H_2S_{aq}) exceeds ~11 μM, sediments acquire δ^{98}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 H_2S and/or SO_2 may be released into the water column, potentially exceeding the threshold for thiomolybdate formation and scavenging. For oxic and suboxic watermasses, sediment δ^{98}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, 2008b; 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 volcaniclastic 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 km^3 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 km^2 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; Funiciello et al. 2003). Maars can be subject to frequent explosive hydromagmatic eruptions as well as episodic crater collapse (Lorenz, 1986; Begét et al. 1996; Funiciello 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 volcaniclastic 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*