Volcanism-Triggered Climatic Control on Late Cretaceous Oceans

Ruiyang Sun1,2, Hanwei Yao1, Changzhou Deng1, Stephen E. Grasby1, Chengshan Wang4, Xi Chen3, and Runsheng Yin1

1State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, 2University of Chinese Academy of Sciences, Beijing, China, 3State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing, China, 4Geological Survey of Canada, Calgary Natural Resources Canada, Calgary, AB, Canada

Abstract During the Late Cretaceous, Earth’s climate oscillated between warm and cool states, and global oceans changed between anoxic and oxic conditions, resulting in black(gray) shales and oceanic red beds (ORBs) deposition, respectively. To understand such climate/ocean dynamics, this study investigated bulk Hg and Hg isotopes, total organic matter (TOC) concentration and organic carbon (OC) distribution, respectively. In both areas, black(gray) shales show much higher Hg concentrations than ORBs, indicating enhanced Hg flux to global oceans during time of black(gray) shale deposition. Black(gray) shales show lower Fe2+/Fe3+ and positive Δ199Hg, suggesting a significant input of Hg into the anoxic/dysoxic ocean via atmospheric deposition. The isotopic ratios are consistent with a volcanic source for this excess Hg. ORBs show high Fe2+/Fe3+ and negative shifts of Δ199Hg, suggesting that the dominant source of Hg into the oxic oceans was via terrestrial runoff. This study suggests that volcanism was an important driver of the climate/ocean dynamics during the Late Cretaceous.

Plain Language Summary The Late Cretaceous ocean developed widespread black(gray) shales and oceanic red beds which were deposited in warm-anoxic/dysoxic and cool-oxic oceanic conditions, respectively. The driving force for such climate/ocean dynamics remains unclear. This study demonstrates distinct Hg concentrations and isotopic composition in black(gray) shales and oceanic red beds, which suggest that volcanism was a major trigger of the climate/ocean dynamics in the Late Cretaceous.

1. Introduction

During the Cretaceous, climate oscillated between warm and cool states, with widespread global deposition of black(gray) shales and ocean red beds (ORBs) respectively (Arthur & Sageman, 1994; Hu et al., 2012; Takashima et al., 2006). Black(gray) shales, which are organic-rich, reflect anoxic/dysoxic oceanic conditions (Arthur & Sageman, 1994; Jenkyns, 2010; Kuyper et al., 2002); whereas ORBs have low organic content but are rich in ferric (Fe3+) minerals, suggesting deposition under oxic oceanic conditions (Wang et al., 2009). The driving forces of these Late Cretaceous ocean/climate dynamics remain uncertain. Volcanism, which emits large amounts of atmospheric greenhouse gas (e.g., CO2) that modulate global temperature and oceanic productivity, may serve as a key trigger of the ocean/climate dynamics in the Late Cretaceous, however, geochemical evidence for this hypothesis remains rare. To test the potential role of volcanism as a driver of the dramatic changes in the Late Cretaceous ocean-climate system, we conducted analysis of bulk mercury (Hg) and Hg isotopes, total organic carbon (TOC), as well as Fe2+/Fe3+ in the Upper Cretaceous sediments deposited in southern Tibet and the North Atlantic (Figure 1).

Volcanism, the primary natural source of Hg to the environment, emits large amounts of Hg to the atmosphere (Grasby et al., 2019). This Hg can undergo global atmospheric transport prior to its worldwide deposition into terrestrial and oceanic ecosystems. Mercury enters the ocean via two pathways: atmospheric Hg deposition and terrestrial runoff (Amos et al., 2014; Zhang et al., 2015). In the ocean, Hg sinks to the seabed via an organic matter (OM) shuttle (Grasby et al., 2019; Saniei et al., 2012). Where examined over longer periods of geologic time, volcanic Hg emissions appear balanced by the OM shuttle in the ocean (Grasby et al., 2013, 2019). However, excessive Hg emissions occur during large igneous provinces (LIPs) eruptions, or enhanced terrestrial erosion, result in anomalously high Hg concentrations and Hg/TOC ratios in marine sediments (Grasby et al., 2017, 2019;
Sanei et al., 2012; Shen et al., 2019; Them et al., 2019). Mercury isotopes, which undergo unique mass-dependent fractionation (MDF, represented by δ^{202}Hg) and mass-independent fractionation (MIF, represented by Δ^{199}Hg and Δ^{201}Hg), provides refined information on Hg cycling (Blum et al., 2014). In particular, Hg-MIF can provide clear source constraints, as it occurs mainly during photochemical processes with little contribution from other reactions (Kwon et al., 2020). Therefore, spikes of Hg concentration or Hg/TOC ratio combined with Hg isotope data can be useful proxies of large volcanism and its environmental effects in geological history (Grasby et al., 2019; Percival et al., 2021).

2. Geological Background

2.1. Chuangde Section, South Tibet

Southern Tibet is composed of five distinct tectonic zones (Figure S1 in Supporting Information S1): the Higher Himalayan Crystalline Belts, the Tethyan Himalaya tectonic zone, the Indus-Yarlung Zangbo suture, the Xigaze forearc basin, and the Gandese Arc (Gansser, 1991). Cretaceous marine deposits in southern Tibet are mainly exposed in the Tethyan Himalaya tectonic zone, which formed at the northern margin of the Indian continent (Hu et al., 2009). The Tethyan Himalaya sedimentary sequence is generally subdivided into southern and northern zones, separated by the Gyirong-Kangmar thrust (Ratschbacher et al., 1994). Cretaceous strata in the northern Tethyan Himalaya zone were deposited mainly on the deeper part of the continental margin.

The Chuangde section crops out in the northern zone of the Tethyan Himalaya (Figure S1 in Supporting Information S1), consisting of the upper part of the Cenomanian-Santonian Gyabula Formation and the Santonian-early to middle Campanian Chuangde Formation (Figure 2). The upper part of the Gyabula Formation (~50 m thick) is composed of gray calcareous shales. The Chuangde Formation (~17 m thick) consists of ORBs.
2.2. ODP Site 641A, North Atlantic

The ODP site 641A core was collected from a well located at the Galicia margin of western Spain, North Atlantic Ocean (Figure S2 in Supporting Information S1). This core reflects bathyal to near-abyssal sedimentation (Moullade et al., 1988), consisting of the Cenomanian–Turonian Hatteras Formation which consists of black shales and the Turonian–Campanian Plantagenet Formation which consists of ORBs (Figure 3).

3. Methods

Fresh samples were collected from the Chuangde section \((n = 23)\) and the ODP core \((n = 17)\). The samples were air-dried, crushed, powdered, and sieved at 200 mesh, before chemical analyses at the Institute of Geochemistry, Chinese Academy of Sciences.

TOC, wt.% was analyzed using the potassium dichromate method (Schumacher, 2002). Briefly, OM in samples was oxidized to \(\text{CO}_2\) in potassium dichromate solution. Contents of TOC were calculated according to potassium dichromate consumption. The detection limit of TOC in this method is 0.1 wt.%. Total Fe (TFe) content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian® Vista-MPX, America), and \(\text{Fe}^{2+}\) was analyzed using Fe-VOL05 titration method (Gao et al., 2018). \(\text{Fe}^{3+}\) content was calculated by subtraction of \(\text{Fe}^{2+}\) from TFe.

Total Hg (THg) concentration was measured using a direct combustion system followed by atomic absorption spectroscopy analysis (Milestone DMA-80). Measurements of standard reference material (GSS-4, soil) showed recoveries of 90% and 110%, and coefficients of variation for triplicate analyses were <10%. The samples were prepared for Hg isotope analysis, following the double-stage thermal combustion and pre-concentration protocol (Zerkle et al., 2020). The preconcentrated solutions were diluted to \(\sim 0.5\) ng/mL Hg and acid concentration of <20% and then measured by Neptune Plus multi-collector-inductively coupled plasma mass spectrometry (Yin et al., 2016). Standard reference material (GSS-4, soil) was prepared and measured after every 10 samples. Hg concentrations and acid matrices in the bracketing NIST SRM 3133 solutions were matched with 10% of the neighboring samples. Mercury isotopic compositions were reported following convention (Blum &
Bergquist, 2007). MDF is expressed in $\delta^{202}$Hg notation in units of ‰ referenced to the NIST-3133 Hg standard (analyzed before and after each sample):

$$\delta^{202}\text{Hg}(‰) = \left(\frac{^{202}\text{Hg}_{\text{sample}}}{^{198}\text{Hg}_{\text{sample}}} / \frac{^{202}\text{Hg}_{\text{standard}}}{^{198}\text{Hg}_{\text{standard}}} - 1\right) \times 1000$$  \hspace{1cm} (1)

MIF is reported in $\Delta$ notation, which describes the difference between the measured $\delta^{xxx}$Hg and the theoretically predicted $\delta^{xxx}$Hg value, in units of ‰:

$$\Delta^{xxx}\text{Hg} \approx \delta^{xxx}\text{Hg} - \delta^{202}\text{Hg} \times \beta$$  \hspace{1cm} (2)

$\beta$ is equal to 0.2520 for $^{199}$Hg, 0.5024 for $^{200}$Hg, and 0.7520 for $^{201}$Hg. Analytical uncertainty was estimated based on replication of the NIST-3177 standard solution, and full procedural analyses of GSS-4. The overall average and uncertainty of NIST-3177 ($\delta^{202}$Hg: $-0.58 \pm 0.13$‰; $\Delta^{199}$Hg: $0.01 \pm 0.07$‰; $\Delta^{201}$Hg: $-0.02 \pm 0.07$‰, 2SD, $n = 8$) and GSS-4 ($\delta^{202}$Hg: $-1.67 \pm 0.14$‰; $\Delta^{199}$Hg: $-0.34 \pm 0.08$‰; $\Delta^{201}$Hg: $-0.35 \pm 0.07$‰, 2SD, $n = 3$) agree well with comparable with previous studies (Blum & Bergquist, 2007; Deng et al., 2021; Yin et al., 2016). The larger values of standard deviation (2SD) for either UM-Almadén or SRMs are used to reflect analytical uncertainties.

4. Results

Analytical results of this study are summarized in Table S1 in Supporting Information S1. In the Chuangde Section (Figure 2), the Gyabula Formation (gray shales) shows TOC values of $0.28 \pm 0.08$ wt.% (SD), much higher than the Chuangde Formation (ORBs) that have TOC values below the 0.1 wt.% detection limit. The Gyabula Formation shows THg of $78.4 \pm 57.7$ ppb (SD), significantly higher than that of the Chuangde Formation ($24.5 \pm 22.5$ ppb, SD). The Gyabula Formation shows higher Hg/TOC ratios ($370 \pm 588$ ppb/wt.% , SD). The Hg/TOC ratios of the Chuangde Formation cannot be accurately calculated, due to the low TOC levels (Grasby et al., 2019). The $\delta^{202}$Hg values of the Gyabula Formation ($0.05 \pm 0.45$‰, SD) are higher than that of the Chuangde Formation ($-1.48 \pm 0.62$‰, SD). A negative shift in $\Delta^{199}$Hg is observed from the Gyabula Formation ($-1.48 \pm 0.62$‰, SD) to the Chuangde Formation ($-0.03 \pm 0.09$‰, SD). The Fe$^{3+}$/Fe$^{2+}$ ratios increase...
from the Gyabula Formation (0.53 ± 1.10, SD) to the Chuangde Formation (5.62 ± 7.27, SD).

The ODP 641A core shows similar trends to the Chuangde Section (Figure 3). The Hatteras Formation shows TOC concentrations of 13.5 ± 9.0 wt.% (SD), higher than that of the Plantagenet Formation (0.39 ± 0.2 wt.%, SD). The Hatteras Formation also has higher Hg concentrations (288 ± 221 ppb, SD) and Hg/TOC ratios (23.1 ± 7.3 ppb/wt.%, SD) than the Plantagenet Formation (Hg: 2.3 ± 0.9 ppb; Hg/TOC: 6.8 ± 2.6 ppb/wt.%). The Hatteras Formation shows an average δ\(^{202}\)Hg value of −0.69 ± 0.42‰ (SD), which is higher than that of the Plantagenet Formation (−1.26 ± 0.53‰, SD). A negative shift of Δ\(^{199}\)Hg is observed from the Hatteras Formation (0.11 ± 0.09‰, SD) to the Plantagenet Formation (−0.04 ± 0.07‰, SD), whereas Fe\(^{3+}/Fe^{2+}\) ratios also increase from the Hatteras Formation (0.88 ± 0.96, SD) to the Plantagenet Formation (37.7 ± 40.5, SD).

5. Discussion

5.1. Volcanism Triggered Climate/Ocean Dynamics in the Late Cretaceous

Spikes of Hg concentration and/or Hg/TOC ratio indicate enhanced Hg loading to the marine environment (Grasby et al., 2019). The much higher Hg concentrations and Hg/TOC ratios in gray/black shales in the Gyabula Formation and Hatteras Formation, compared respectively to that in ORBs in the Chuangde Formation and Plantagenet Formation (Figures 2 and 3), suggest enhanced Hg flux associated with times of black/gray shales deposition, in contrast to low background Hg flux during ORBs deposition. The Hg isotope data helps to resolve the sources of Hg during these two periods.

5.2. Hg-MIF Constrains Hg Sources to the Late Cretaceous Ocean

Changes in δ\(^{202}\)Hg and Δ\(^{199}\)Hg values between black/gray shales and ORBs at both sites (Figures 2 and 3) imply changing Hg sources in the Late Cretaceous ocean. However, the variation of δ\(^{202}\)Hg is triggered by a large number of physical, chemical, and biological processes that induce Hg-MDF (Blum et al., 2014 and references therein). Due to the lack of complete understanding of all these MDF processes in deep reservoirs, we find that δ\(^{202}\)Hg is not diagnostic of Hg source.

Unlike δ\(^{202}\)Hg, Δ\(^{199}\)Hg provides direct constraints on Hg sources, as Hg-MIF mainly occurs during photochemical processes rather than during complex biogeochemical cycling. The Δ\(^{199}\)Hg/Δ\(^{201}\)Hg ratio of ~1 for our samples (Figure 4) is consistent with that observed during aqueous Hg\(^{2+}\) photoreduction (Bergquist & Blum, 2007). Photochemical processes on Earth’s surface results in positive Δ\(^{199}\)Hg values in the atmospheric Hg(II) species and negative Δ\(^{199}\)Hg values in gaseous Hg(0) species (Bergquist & Blum, 2007). Gaseous Hg(0) is preferentially uptaken by vegetation and readily deposited to terrestrial soil via litterfall, therefore, terrestrial soil mainly shows negative Δ\(^{199}\)Hg values (Biswas et al., 2008; Demers et al., 2013; Yin et al., 2013). In contrast, atmospheric Hg(II) species with positive Δ\(^{199}\)Hg values are water-soluble and are more readily deposited into the ocean via wet deposition (Rolison et al., 2013; Strok et al., 2015; Yin et al., 2015). Therefore, Hg-MIF signals are particularly useful for constraining the two major sources of Hg in the ocean: atmospheric Hg(II) deposition and soil runoff (Grasby et al., 2019).

In this study, black/gray shales from the Gyabula Formation and Hatteras Formation display positive Δ\(^{199}\)Hg values (0.08 ± 0.04‰ and 0.11 ± 0.09‰, respectively), which are consistent with that observed in atmospheric Hg(II) species (Rolison et al., 2013), suggesting that Hg was predominantly sourced from atmospheric Hg(II) deposition. In contrast, the Δ\(^{199}\)Hg values of the Chuangde and Plantagenet formations ORBs are negative, −0.03 ± 0.09‰ and −0.04 ± 0.07‰, respectively. These negative values could suggest either: (a) an increased input of terrestrial soil given soil has negative Δ\(^{199}\)Hg (Biswas et al., 2008; Demers et al., 2013; Yin et al., 2013), or (b) a decrease in atmospheric Hg(II) deposition and hence a proportionate increase in soil Hg. A previous study...
by Chen et al. (2011) reported Chemical Index of Alteration values of the Gyabula Formation (66.1 ± 3.9, SD) and the Chuande Formation (69.6 ± 4.8, SD, SD) are similar, suggesting that a significantly increased input of terrestrial material seems unlikely. Weakened volcanic activity better supports the observed data. We therefore suggest that the periods of black shale deposition were dominated by excess volcanic derived Hg, whereas ORB deposition occurred during decreased atmospheric Hg deposition into the ocean.

If correct, our model implies that during black/gray shale deposition, frequent volcanic activity occurred which would have also released large amounts of greenhouse gases, mainly CO$_2$, as well as bio-limiting elements into the atmosphere-ocean system. Such volcanic emissions would have driven the global climate into a warm mode along with enhanced primary productivity in the oceans (Kuypers et al., 2002; Jenkyns et al., 2017; Sinninghe Damsté et al., 2010). High primary productivity and elevated deoxygenation due to the high atmospheric CO$_2$ concentrations (pCO$_2$) in the ocean would have then resulted in enhanced OM burial, which can explain the relatively higher TOC levels in black/gray shales at both sites. OM burial exhausted the dissolved O$_2$ in deep seawater, causing anoxic/dysoxic conditions to develop (Jenkyns, 2010), as supported by the low Fe$^{3+}$/Fe$^{2+}$ ratios in the black/gray shales at both sites (Figures 2 and 3). Enhanced volcanic activity during this time is consistent with a documented period of subaerial eruptions of the High Arctic Large Igneous Province (Naber et al., 2021), along with Boreal marine deposits with abundant ash beds (Grasby et al., 2021), as well as the timing of maximum extent of continental arcs (Lee et al., 2018).

During ORBs deposition, our interpreted weakened volcanic activity would have reduced Hg and greenhouse gas (e.g., CO$_2$) emissions and decreased global temperature (Freiderich et al., 2012; Larson, 1991; O’Brien et al., 2017; Sinninghe Damsté et al., 2010). Global cooling generated cold and dense surface seawaters (O$_2$-rich), which sank into the deep ocean and shifted the deep ocean watermass to oxic conditions (Wang et al., 2009, 2011; Hu et al., 2012). Most dissolved Fe$^{2+}$ species in oceans at this stage would be oxidized to Fe$^{3+}$ (Zhang et al., 2008), leading to the formation of CORBs with extremely high Fe$^{3+}$/Fe$^{2+}$ ratios (Figures 2 and 3). As supported by the low TOC levels in ORBs, OM burial at this stage would have largely decreased due to decreased oceanic productivity, owing to the oxidation of the nutrient Fe$^{2+}$ to form insoluble Fe$^{3+}$ species and decrease of bio-limiting element supply during a period of volcanic quiescence.

6. Alternating Scenarios of Hg Inputs Into Late Cretaceous Ocean

Based on all data available, two scenarios of Hg inputs into the Late Cretaceous ocean, driven by alternating climate/ocean dynamics, can be proposed (Figure 5):

Scenario (1): During the deposition of the black/gray shales (Figure 5a), frequent volcanic activity, supported by high Hg concentrations or Hg/TOC ratios, released large amounts of greenhouse gases (e.g., CO$_2$) into the atmosphere. Rising CO$_2$ levels would drive the global climate into a warm state, promoting marine productivity and OM burial (Kuypers et al., 2002; Sinninghe Damsté et al., 2010). OM degradation exhausted the dissolved O$_2$ in deep seawater, causing anoxic/dysoxic conditions to develop (Jenkyns, 2010). Volcanic activity also emitted massive amounts of Hg to the atmosphere, which was altered by photochemical reactions, resulting in positive $\Delta^{199}$Hg in the atmospheric Hg(II) which was deposited into the ocean (Blum et al., 2014). Given OM has a strong affinity to Hg (Grasby et al., 2019), extensive OM burial could scavenge a large amount of seawater Hg to the seafloor (van Bentum et al., 2012), resulting in positive $\Delta^{199}$Hg values in black/gray shales.

Scenario 2: During ORBs deposition (Figure 5b), volcanic activity and emissions of volcanic CO$_2$ weakened, as supported by their low Hg concentrations or Hg/TOC ratios. In this scenario, oceanic productivity and silicate weathering would gradually exhaust atmospheric CO$_2$, driving the global climate to a cool mode. Global cooling facilitated the transport of cold, dense and O$_2$-rich surface seawaters into the deep ocean, leading to oxic conditions in the deep ocean (Wang et al., 2009, 2011; Hu et al., 2012). Most dissolved Fe species in the ocean would then be oxidized to Fe$^{3+}$, leading to ORBs deposition. Reduced dissolved Fe$^{2+}$, an essential nutrient, would decrease ocean productivity and limit OM burial into the deep ocean. Weakened volcanic activity during this stage would result in decreased atmospheric Hg(II) deposition into the ocean. A decrease in OM burial would also limit the scavenge of seawater Hg (atmospheric Hg(II) derived) to the seafloor. This would lead to a proportionate increase in soil Hg, which is responsible for the negative shift of $\Delta^{199}$Hg in ORBs.
7. Conclusion and Implications

Our study demonstrates that volcanism can be an important driving force of the climate/ocean dynamics during the Late Cretaceous, and such climate/ocean dynamics could have strong control on Hg sources in the Cretaceous ocean. Frequent volcanism triggered warm conditions, which enhanced marine productivity and caused sequestration of atmospheric-sourced Hg in black/gray shales in anoxic/dysoxic and eutrophic oceans. Weakened volcanism allowed for cooler conditions, which led to low productivity and less OM burial, as well as less sequestration of atmospheric Hg, and therefore, terrestrial Hg became the major source of Hg in oxic and oligotrophic oceans. Understanding the ocean-climate system during these past transitions between warm and cool climate modes is essential for the accurate prediction of future climate and environmental changes.
Data Availability Statement

Datasets of this research can be found in a public domain repository (https://figshare.com/articles/dataset/Volcanism_triggered_climatic_control_on_mercury_sources_in_the_Cretaceous_Ocean/16862920).

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