

# Mercury enrichments in lower Aptian sediments support the link between Ontong Java large igneous province activity and oceanic anoxic episode 1a

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## ABSTRACT

**The early Aptian recorded one of the most significant episodes of environmental change during the Mesozoic—the Selli oceanic anoxic episode (OAE 1a). It has often been suggested that magmatic activity related to the emplacement of the Greater Ontong Java large igneous province (LIP) triggered OAE 1a. A major challenge, however, resides in the establishment of precise temporal relationships between the environmental perturbations associated with OAE 1a and the phases of volcanic activity. In this study we evaluate the potential of mercury (Hg) as a proxy of volcanic activity and investigate lower Aptian sediments with different total organic carbon (TOC) contents, which are exposed at Roter Sattel (Briançonnais, Swiss Alps), Glaise (Vocontian Basin, southeast France), and La Bédoule (South Provencal Basin, southeast France). The intervals equivalent to OAE 1a are marked by significant increases in Hg contents, which are only partially dependent on TOC contents. This is shown by the Hg anomalies in the TOC-poor sediments of La Bédoule, the only moderate correlation of Hg and TOC contents in the TOC-enriched sediments of Roter Sattel ( $R^2 = 0.48$ ), and the persistence of the anomaly in Hg/TOC ratios in all sediments except for the TOC-enriched ones. These results suggest that the Hg anomaly not only is related to primary productivity, redox conditions, and organic-matter preservation, but has deeper roots. Volcanic outgassing related to Greater Ontong Java LIP activity is taken here as the main source of the Hg enrichment recorded in the western Tethyan sediments. Our Hg data indicate that magmatic pulses at the onset and during the OAE 1a triggered the early Aptian environmental perturbations.**

## INTRODUCTION

Oceanic anoxic episodes (OAEs) are periods of major environmental change marked by fluctuations in the global carbon cycle, which were accompanied by the widespread deposition of organic-rich sediments in deeper marine environments (Schlanger and Jenkyns, 1976). The early Aptian was a time of exceptionally profound changes and recorded one of the most significant OAEs of the Mesozoic—the Selli oceanic anoxic episode or OAE 1a (Jenkyns, 1980; Arthur et al., 1990). Its sedimentary hallmark consists of widespread organic-rich deposits referred to as the “Selli level” and equivalents (Coccioni et al., 1987; Bréhéret, 1997). The corresponding  $\delta^{13}\text{C}$  records in carbonates and organic carbon of marine and continental origin are characterized by a distinct negative shift (C3), with a minimum at the onset of the anoxic episode followed by a positive excursion (C4–C6; Menegatti et al., 1998). The OAE 1a is accompanied by a biocalcification crisis with a strong impact on pelagic and neritic ecosystems (Erba, 1994; Föllmi et al., 2006). Whole-rock and belemnite  $\delta^{18}\text{O}$  records and  $\text{TEX}_{86}$  data suggest an important warming phase during the negative carbon-isotope shift and a trend to cooler temperatures during the following

positive carbon-isotope excursion (Stein et al., 2011; Mutterlose et al., 2014).

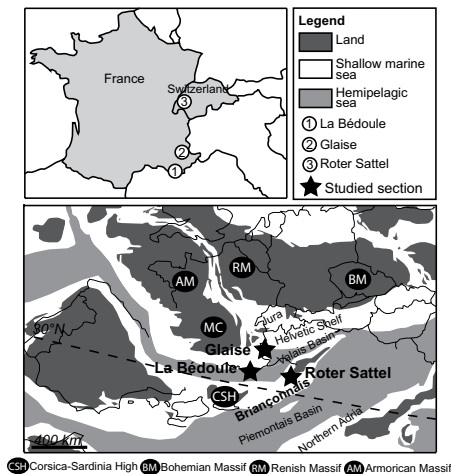
Intense volcanic activity related to the emplacement of large igneous provinces (LIPs) is considered as an important trigger of OAEs and related major environmental change (Coffin and Eldholm, 1994; Ernst, 2014). Based on age correlations and Pb and Os isotope records, it has often been proposed that the Greater Ontong Java episode (GOJE) of LIP activity leading to the formation of the Ontong Java, Manihiki, and Hikurangi Plateaus in the Pacific Ocean triggered the environmental perturbations related to OAE 1a (Méhay et al., 2009; Tejada et al., 2009; Kuroda et al., 2011; Bottini et al., 2012). The establishment of exact temporal relationships between OAE 1a–induced environmental perturbations dated by bio- and chemostratigraphy and phases of intensified GOJE LIP activity dated by radiometric means remains, however, a major challenge.  $^{40}\text{Ar}/^{39}\text{Ar}$  ages reported for the GOJE LIP range from 126 to 117 Ma (Ontong Java Plateau, 124–120 Ma; Manihiki Plateau, 124.6–117 Ma; Hikurangi Plateau, 118 and 96 Ma; Mahoney et al., 1993; Chambers et al., 2004; Timm et al., 2011). Uncertainties in these ages ( $\pm 1.6$  to  $\pm 1.8$  m.y.; Chambers et al., 2004; Timm et al., 2011) and in the stratigraphic time

scale ( $\pm 1$  m.y. for the Aptian; Gradstein et al., 2012) influence correlations between OAE 1a and GOJE LIP activity.

The recent development of mercury (Hg) as a proxy of distal volcanic activity offers the possibility to investigate potential relationships between environmental perturbations and LIP activity in detail (Nascimento-Silva et al., 2011; Sanei et al., 2012). Hg is characterized by an atmospheric residence time of 1–2 yr, which permits its global distribution in the form of gaseous elemental mercury ( $\text{Hg}^0$ ) (Pyle and Mather, 2003; Percival et al., 2015). Hg is deposited in the continental and marine environment during rainfall, mostly in the form of reactive  $\text{Hg}^{2+}$  (Percival et al., 2015). Under natural conditions, Hg is largely scavenged by organic matter (Sanei et al., 2012), and in modern and ancient sediments Hg and total organic carbon (TOC) are mostly positively correlated (Outridge et al., 2007; Gehrke et al., 2009). Volcanic emissions are considered as the major contributor of natural Hg. Sanei et al. (2012) were the first to suggest a relationship between Hg anomalies in uppermost Permian sediments and volcanic eruptions associated with the Siberian Traps (cf. also Grasby et al., 2013, 2016). Notable increases in Hg concentrations were also associated with the volcanic eruptions of the Karoo-Ferrar LIP (early Toarcian OAE; Percival et al., 2015) and the Decan Traps (Cretaceous-Tertiary [K-T] boundary extinction event; Nascimento-Silva et al., 2013; Sial et al., 2013, 2014; Font et al., 2016). The enrichment of Hg in sediments results from relatively complex processes (Krupp, 1988) such as adsorption onto organic matter and/or clay minerals (Sanei et al., 2012; Grasby et al., 2013; Sial et al., 2013; Percival et al., 2015). A careful evaluation is therefore needed in order to separate Hg anomalies related to higher TOC contents and the presence of clay minerals from those related to increased volcanic activity (Sanei et al., 2012; Percival et al., 2015).

Here we investigate the distribution of Hg contents in three sections in different basins of the western Tethyan Ocean, each of which includes an interval equivalent to the early Aptian OAE 1a. They are located at Roter Sattel (Briançonnais domain, Switzerland), Glaise (Vocontian

Basin, southeast France), and La Bédoule (South Provencal Basin, southeast France) (Menegatti et al., 1998; Moullade et al., 1998; Strasser et al., 2001; Stein et al., 2012; Westermann et al., 2013; Figs. 1 and 2). These sections are correlated by their carbonate carbon-isotope records and characterized by high, intermediate, and low TOC contents, respectively (maximum TOC contents of 5.45, 2.02, and 0.4 wt%, respectively), which allow testing of potential relationships between Hg and TOC contents (e.g., Percival et al., 2015). Furthermore, they are rich in claystone, which permits an evaluation of potential interdependencies between Hg and clay contents.



**Figure 1. A:** Study area (west Switzerland and southeast France). **B:** Paleogeographic map of Tethyan Realm (Aptian) showing location of Roter Sattel (Briançonnais domain, modern-day Swiss Alps), Glaise (Vocontian Basin, southeast France), and La Bédoule (South Provencal Basin, southeast France) sections. (Modified from R. Blakey: <https://www2.nau.edu/rcb7/>).

## MATERIALS AND METHODS

The hemipelagic sediments of the three sections consist of limestone, marly limestone, marl, and organic-rich marl. Precise stratigraphic correlation between the sections was obtained using the structure of the  $\delta^{13}\text{C}_{\text{carb}}$  curve and the associated C2–C7 isotope segments (Menegatti et al., 1998; Kuhnt et al., 1998; Strasser et al., 2001; Westermann et al., 2013; Fig. DR1 in the GSA Data Repository<sup>1</sup>). The total extent of the OAE 1a interval is defined by the  $\delta^{13}\text{C}_{\text{carb}}$  record and starts with the onset of a negative shift and ends on top of a positive excursion (Menegatti et al., 1998; Erba et al., 2015).

<sup>1</sup>GSA Data Repository item 2017016, detailed descriptions and correlations between the studied sections, methods, and correlations between Hg and TOC data, is available online at <http://www.geosociety.org/pubs/ft2017.htm> or on request from editing@geosociety.org.

A total of 178 samples were measured for their Hg contents using a Zeeman R-915F (Lumex, St. Petersburg, Russia) high-frequency atomic absorption spectrometer and certified reference material GSD-11 standard with a correlation coefficient of 0.99 and a standard residual deviation of 5%. TOC contents were obtained by Rock-Eval<sup>TM</sup> 6 analysis using an internal and the IFP 160000 standard, with a relative error <0.2%.

## RESULTS AND DISCUSSION

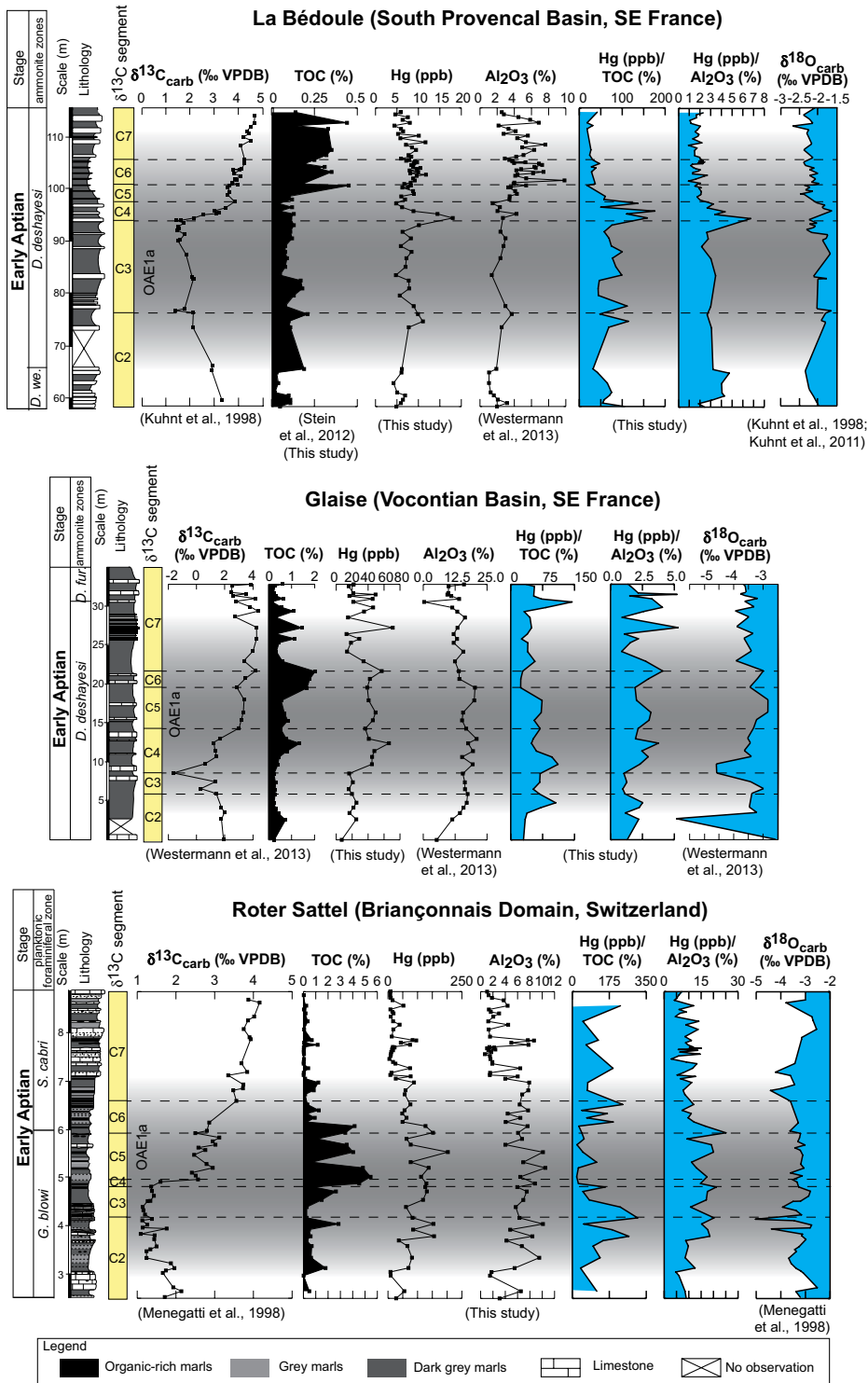
The Hg records at Roter Sattel, Glaise, and La Bédoule are generally elevated through the interval corresponding to OAE 1a (Fig. 2), with maximal values of 200.1, 64.2, and 18.0 ppb, respectively (Fig. 2). A first increase in Hg contents is observed in the interval in which the  $\delta^{13}\text{C}_{\text{carb}}$  record starts to decrease (segment C2), the first enrichments in TOC occur, and where the sections change from carbonate-dominated to marl-dominated sediments. These changes indicate the onset of OAE 1a. The Hg values are rather variable through the remainder of isotope segment C2 and C3 and remain generally elevated, with two local maxima near the C2–C3 boundary in the section of Roter Sattel. A further increase common to all sections is observed in the C3 and early C4 isotope segments, below the increase in the  $\delta^{13}\text{C}_{\text{carb}}$  record. In isotope segments C5 to the lower part of C7, the Hg records are variable between the three sections, but remain generally relatively high, before starting an irregular descending trend (Fig. 2). This descent goes along with a general decrease in TOC and the increasing presence of carbonate beds, thereby announcing the termination of OAE 1a.

There is a general correspondence between the maximal values in the Hg records and the maxima in TOC contents. The sections with the highest, intermediate, and lowest TOC contents (maximum 5.45, 2.02, and 0.4 wt%, at Roter Sattel, Glaise, and La Bédoule, respectively) show the highest, intermediate, and the lowest Hg contents, respectively (maximum 202.6, 66.1, and 7.0 ppb). This, however, does not imply that every maximum in Hg contents corresponds to a maximum in TOC contents. This is especially true both for the isotope segments C2 and C3 in Roter Sattel as well as for the lowermost part of isotope segment C4 in Glaise and La Bédoule, where distinct maxima in Hg contents are identified in layers of relatively low TOC contents (Fig. 2). This is also shown by the Hg/TOC ratios, which remain high through the OAE 1a intervals in all three sections, except for the Selli level equivalent at Roter Sattel, where TOC values are ~4 wt% and higher. There, the generally high TOC values reduce the Hg/TOC ratios. Also, the correlation coefficients of the Hg and TOC records suggest that the relationship between the two parameters is not consistently linear ( $R^2 = 0.41$  and  $0.48, 0.12$  and  $0.32,$

and 0.17 and 0.15 for the isotope segments C2–C3 and C4–C6, for Roter Sattel, Glaise, and La Bédoule, respectively; Fig. DR2). This implies that not all Hg enrichments can be explained by TOC enrichments and corresponding fluctuations in primary productivity and redox conditions alone. The Hg anomaly has deeper roots, which go beyond the preservation of organic matter alone. We also tested if present clay minerals influenced overall Hg contents (Sial et al., 2013) and calculated the Hg/Al<sub>2</sub>O<sub>3</sub> ratio for each section (Fig. 2). These ratios correlate well with the overall Hg contents suggesting that the Hg fluctuations are not primarily controlled by changes in clay mineral contents.

In analogy to the interpretation of Hg anomalies being associated with massive volcanic activity during both the end-Permian and K-T extinction events as well as the Toarcian OAE (Sanei et al., 2012; Sial et al., 2013; Percival et al., 2015; Grasby et al., 2016; Font et al., 2016), we suggest that volcanic outgassing related to a phase of major GOJE LIP activity was the main source of the Hg anomaly recorded in the western Tethyan Ocean sections. The onset of the Hg anomaly documented here goes along with the negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion (segment C3) at the onset of OAE 1a. It correlates also with an important negative excursion in the  $\delta^{18}\text{O}_{\text{carb}}$  record (Menegatti et al., 1998; Kuhnt et al., 1998; Stein et al., 2011), a rise in the TEX<sub>86</sub> records (Mutterlose et al., 2014), and the onset of the nannoconid crisis (Erba et al., 2015). It slightly precedes the reconstructed gradual increase in  $p\text{CO}_2$  concentrations based on the  $\delta^{13}\text{C}_{\text{alg}}$  (alg—algae) record in Cau, Spain (Naafs et al., 2016), a negative shift in osmium-isotope records, and Pb isotope anomalies at Gorgo a Cerbara and Cismon (Italy; Tejada et al., 2009; Kuroda et al., 2011) and in the Pacific (Deep Sea Drilling Project Site 463; Kuroda et al., 2011; Bottini et al., 2012), all of which are attributed to isotope segment C3. This may be related to the sensitivity of the Hg record, which registers changes in volcanic activity on a much shorter time scale, related to the very short atmospheric residence time of Hg.

Our Hg record confirms a marked increase in GOJE LIP activity at the onset of OAE 1a. This increase led to the sustained release of volcanogenic CO<sub>2</sub> (Naafs et al., 2016), which itself triggered rapid global warming, elevated rates of silicate weathering, a biocalcification crisis, and thermal stratification of seawater at the onset of OAE 1a (Tejada et al., 2009; Mutterlose et al., 2014; Erba et al., 2015). During OAE 1a, feedback mechanisms contributed to the increase in preservation rates of organic matter on the seafloor and the positive shift in the  $\delta^{13}\text{C}$  record. The recording of the Hg anomaly offers a direct proxy of magmatism and provides new and promising clues to better calibrate the role of GOJE LIP activity during the environmental perturbations of the early Aptian.



**Figure 2.**  $\delta^{13}\text{C}$ , total organic carbon (TOC), Hg,  $\text{Al}_2\text{O}_3$ , Hg/TOC, Hg/ $\text{Al}_2\text{O}_3$ , and  $\delta^{18}\text{O}$  records from La Bédoule and Glaise (France) and Roter Sattel (Switzerland) sections. Precise biostratigraphic framework is based on planktonic foraminifera (Roter Sattel; Strasser et al., 2001) and ammonites (Glaise, La Bédoule; Bréhéret, 1997; Moullade et al., 1998). VPDB—Vienna Peedee belemnite. *D. fur.*—*Dorystoma furcata*, *D. we.*—*Deshayesites weissi*.

## CONCLUSIONS

We investigated Hg contents in three sections through sediments equivalent to the early Aptian OAE 1a, which are all rich in clay and characterized by different TOC contents (maximum 5.45,

2.02, and 0.4 wt% at Roter Sattel, Glaise, and La Bédoule, respectively). The three sections show consistent enrichments in Hg in the OAE 1a intervals. Whereas a direct relationship is lacking between clay and Hg contents, a partial

relationship between TOC and Hg contents is present in Roter Sattel, Glaise, and La Bédoule. This suggests that the Hg enrichments are only partly related to changes in primary productivity, redox conditions, and TOC preservation rates, and that a deeper cause is responsible for the Hg anomaly. We infer the increased emission of gaseous  $\text{Hg}^0$  due to a main pulse of volcanic activity during the formation of the GOJE LIP at the onset of OAE 1a to be the principal source of the Hg enrichment recorded in the western Tethyan Ocean sections. We confirm as such the utility of Hg in the sedimentary record as a direct proxy of volcanic and magmatic activity in support of the impact of GOJE LIP activity as a trigger of the early Aptian OAE 1a.

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