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Mercury anomalies in upper Aptian-lower Albian sediments from the Tethys realm

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ABSTRACT

The upper Aptian-lower Albian stratigraphic interval documents important perturbations in the carbon cycle associated with the Oceanic Anoxic Event 1b (OAE 1b) tentatively connected with pulses in volcanic activity and the formation of the southern Kerguelen Plateau. However, uncertainties in existing age models for this interval preclude a robust and definitely convincing cause-effect connection between these two events. A sedimentary record from the Poggio le Guaine section, Umbria-Marche Basin, shows anomalously high levels of mercury during the upper Aptian-lower Albian interval. The persistence of the anomalies of [Hg] after normalization against TOC, Al, and Fe suggests that chemical and physical processes related to organic-matter scavenging, adsorption onto clay minerals, hydrous iron oxides and sulphur only played a secondary role as mechanisms for Hg accumulation in the sediments. In agreement with previous studies in which anomalous enrichments of Hg in sedimentary records were interpreted as monitors of enhanced volcanic activity, we speculate that the Hg enrichments documented in the Poggio le Guaine section reflect a rapid increase in atmospheric Hg content associated with a massive release of volcanic Hg, and possibly suggest a multi-phase emplacement of the southern Kerguelen Plateau (SKP) as a realistic source. Nonetheless, comparison of Hg profiles and micropalaeontological data from the Poggio le Guaine section reasonably excludes the possibility that the global biotic turnover horizon documented in the upper Aptian could be directly attributed to the volcanic pulses of the SKP emplacement.

1. Introduction

There are various hypotheses concerning the nearly synchronous events related to the formation of large igneous provinces (LIPs), mass extinctions and oceanic anoxic events (OAEs) (e.g., Rampino and Strothers, 1988; Courtillot and Renne, 2003; Saunders, 2005; Bond and Wignall, 2014; Bond and Grasby, 2017), but the mechanisms by which LIPs can trigger and sustain OAEs and biotic crises remain debated. Recent studies have suggested the use of mercury Hg-chemostratigraphy as an efficient tool for tracing distal volcanism and LIP activity during major paleoenvironmental perturbations (Sanei et al., 2012; Sial et al., 2016). Volatile emissions from passively or eruptive magmatic degassing volcanoes, fumaroles and geothermal fields, influence the composition of the atmosphere and the global climate (Robock and Oppenheimer, 2003; Wallace, 2005; Bond and Wignall, 2014). Volcanism may be an important natural contributor of Hg (Martin et al., 2012; Bagnato et al., 2014), and, specifically in volcanic plumes, gaseous elemental mercury (Hg^0) is the dominant species (Schroeder and Munthe, 1998; von Glasgow, 2010; Martin et al., 2011) with an atmospheric residence-time of ca. 0.5–2 yr (Lindberg et al., 2007; Ariya et al., 2008), allowing long-distance transport from the emission source. Mechanisms including gas-phase oxidation (by halogens and ozone) followed by particle and precipitation scavenging are the dominant processes for the removal of mercury from the atmosphere (Fitzgerald, 1989). Consequently, large-scale eruptions may be recorded in natural archives such as sediments and ice cores (Fitzgerald, 1989). Once in the water column, mercury forms exceptionally strong associations with natural organic matter which represents one of the most efficient Hg scavengers from the water column (Guentzel et al., 1996). This results in a nearly-constant Hg/TOC ratio in modern environments (Hg/TOC = 0.01–0.02 in recent sapropels; Benoit et al., 2001; Outridge et al., 2007; Liu et al., 2012; Ruiz and Tomiyasu, 2015). On the other hand, complexes of Hg-sulphides precipitate with rapid mercury burial (Benoit et al., 1999; Niessen et al., 2003).

Here we investigate the distribution of Hg contents in the Poggio le Guaine section from the Umbria-Marche Basin (Western Tethyan realm)

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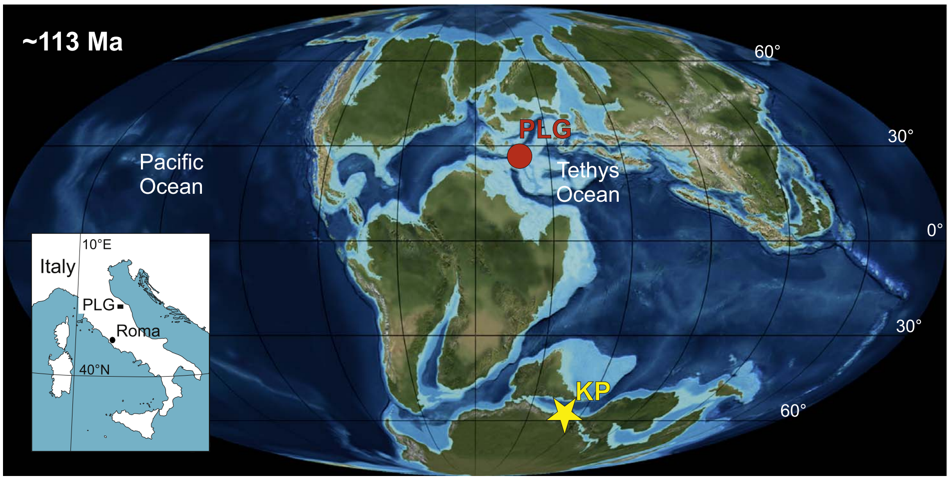

Fig. 1. Palaeogeographic map at ~113 Ma (modified after http:www.jan.ucc.nau.edu) showing the location of the Poggio le Guaine (PLG) section and of the Kerguelen Plateau (KP).

(Fig. 1), one of the most complete and undisturbed upper Aptian-lower Albian sedimentary records (Coccioni et al., 2014; Sabatino et al., 2015) where all the sub-events of the OAE 1b are exceptionally well-exposed. This section is recognized as a reference record for the Aptian–Albian throughout the Umbria-Marche Basin and with its excellent biochronological control provides an opportunity to explore the global oceanographic, climatic and evolutionary changes linked to the OAE1b.

2. Geological setting

The Cretaceous pelagic succession of the Umbria-Marche Basin was deposited in a complex basin and swell topography along the continental margin of the Apulian block, which moved with Africa relative to northern Europe (Fig. 1; Channell et al., 1979; Centamore et al., 1980). The basement of the Umbria–Marche Apennines is continental, and the Upper Jurassic through to Paleocene pelagic succession overlies a subsiding Triassic to Early Jurassic carbonate platform.

The Poggio le Guaine section is located on the Monte Nerone ridge of the Umbria–Marche Basin of central Italy, 6 km west of the town of Cagli (Marche Region, lat. 43°32′29.06″N, long. 12°34′51.09″E) (Fig. 1). The section offers a complete stratigraphic record for the upper Aptian-lower Albian interval, with 21 m of pelagic sediments from the “Marne a Fucoidi” Formation (Fig. 2). The sedimentary succession is characterized by pale olive to dark reddish brown argillaceous limestones, and calcareous to argillaceous marlstones with organic-rich black shales and mudstones (Fig. 2). The sediments become more reddish and argillaceous with dark shales in the Monte Nerone interval (from 11 to 14 m, Fig. 2). Some of the organic-rich (Fig. 2) horizons have previously been attributed to a regional expression of the global OAE 1b sub-events (Coccioni et al., 1990, 2012; Coccioni, 1996; Leckie et al., 2002; Trabucho Alexandre et al., 2011; Petrizzo et al., 2012, 2013; Coccioni et al., 2014; Sabatino et al., 2015). Specifically, these events are the upper Aptian 113/Jacob level equivalent (at 3.48 m, with 8 cm-thick black shales), the uppermost Aptian Kilian level equivalent (at 7.98 m, with 38 cm-thick poorly laminated black shale), the Albian Urbino/Paquier level equivalent (at 16.12 m, with 25 cm-thick well laminated black shale), and the Leenhardt level equivalent (at 17.7 m, with 26 cm-thick black shale). Intercalated with the four levels described above, 40 thin levels of dark to black shales have been identified, particularly through the Monte Nerone interval. They are generally characterized by very low values of TOC (Coccioni et al., 2014; Sabatino et al., 2015).

Following the documentation of a major planktonic foraminiferal turnover across the Aptian–Albian interval (Huber and Leckie, 2011; Huber et al., 2011), the first occurrence of planktonic foraminiferan *Microhedbergella renilaevis* (Huber and Leckie, 2011) was proposed as the biomarker which defines the base of the Albian (Petrizzo et al., 2012, 2013; Kennedy et al., 2014; Kennedy et al., 2017). On this basis, in the Poggio le Guaine section, the Aptian/Albian boundary can be reasonably placed at 7.6 m (Fig. 2).

According to the inferred ages of Huang et al. (2010) and on the basis of the GTS 2012 and GTS 2016 (Ogg and Hinnov, 2012; Ogg et al., 2016), the OAE 1b is ~4 Myr-long, ranging from the 113/Jacob (the first black shale level documented in the late Aptian) to the Leenhardt (the last significant thick black shale level in the early Albian). Thus, at Poggio le Guaine, the average sedimentation rate can be estimated 0.22 cm/kyr from the stratigraphic interval spanning from the 113/Jacob level to the Aptian/Albian boundary and 0.47 cm/kyr from that spanning from the boundary stage to the Leenhardt level.

3. Materials and methods

The studied pelagic section was sampled with a resolution of 10–30 cm (for Hg, TOC and metals contents) for the entire upper Aptian-lower Albian stratigraphic interval, and 138 selected samples have been analyzed. The analyses were carried out at the IAMC-CNR geochemistry laboratory of Capo Granitola. Data are shown in the Supplementary Tables 1 and 2.

3.1. Micropaleontological analysis

Planktonic and benthic foraminiferal and radiolarian abundances were calculated in the > 63 μm fraction of samples from Poggio le Guaine section. Data from the stratigraphic interval 0–19 m are by Coccioni et al. (2014). In this study, the microfauna assemblage composition was analyzed only from −2 m to 0 m. Samples were treated following the cold acetolysis technique of Lirer (2000) by sieving through a 63 μm mesh and drying at 50 °C. The cold acetolysis method enabled extraction of generally easily identifiable foraminifera even from indurated limestones. This technique offered the possibility of accurate taxonomic determination and detailed analysis of foraminiferal assemblages. Tests showing > 50% fragmentation were excluded from the specimen counts. The abundance counts are shown in the Supplementary Table 1.

3.2. Carbon and oxygen isotopes

Coccioni et al. (2014) and Sabatino et al. (2015) report the stable carbon e oxygen isotope composition of 489 bulk samples from 0 to 19 m of Poggio le Guaine section. In this study bulk sample stable isotope analyses were carried out in samples from −2 m to 0 m (Supplementary Table 1). They were measured by an automated continuous flow carbonate preparation GasBench II device (Spötl and Vennemann, 2003) and a Thermo Electron Delta V Advantage mass spectrometer.