Phosphogenesis during the Cenozoic transition from greenhouse to icehouse conditions: Upper Oligocene to lower Miocene siliceous, phosphate, and organic-rich sediments near La Purísima, Baja California Sur, Mexico

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Abstract
Upper Oligocene and lower Miocene, siliceous, organic-, and phosphate-rich sediments are widespread in Baja California Sur (Mexico). A representative section at La Purísima was analysed for its sedimentology, stratigraphy, geochemistry, and mineralogy. A corresponding age model was obtained by dating zircons from ash layers (27.84 ± 0.33 to 21.21 ± 0.59 Ma). The sediments were deposited in an upwelling-dominated, hemipelagic setting, for which the presence of lamination, the scarcity of benthic organisms (except for in gravity-flow deposits), and redox-sensitive trace-element enrichments indicate oxygen-depleted conditions. Anoxic conditions were particularly strong around 27 and 24–22 Ma. Gravity-flow deposits are frequent and predominantly composed of phosphatic-coated grains. They were generated by seismic and volcanic activity, as is indicated by the close association with volcanic ash layers. The phosphatic-coated particles were formed in a more proximal, better-oxygenated shelf environment. They precipitated also in situ within the hemipelagic sediments, where they were often concentrated by subsequent winnowing. In situ phosphogenesis also partly cemented the gravity-flow deposits. At La Purísima, phosphogenesis occurred throughout the time interval investigated and was particularly important around 28–25.5 and 23.5–21.5 Ma. These two time
intervals correspond to the late Oligocene glacial maximum and the Oligocene–Miocene and early Miocene glacial intervals Mi1 and Mi1a. This provides evidence for the increasing importance of glacial denudation during the Oligocene, which led to an enhanced phosphorus flux into the ocean. Cooler climates also promoted the efficient transfer of phosphorus to thermocline waters by increased upwelling. Subsidiary phases of phosphogenesis during the intervening warm periods are explained by the weathering of glacial legacy sediments. These observations suggest that during the transition from greenhouse to icehouse conditions in the Oligocene and Miocene, new and radical changes in the global phosphorus cycle affected and partly inverted feedback mechanisms between climate, geochemical cycles and life, and profoundly influenced the biosphere and its evolution.

**KEYWORDS**

Baja California, Mexico, Miocene, Oligocene, palaeoceanography, phosphorites

1 | INTRODUCTION

The transition from greenhouse to icehouse conditions during the Cenozoic went hand in hand with fundamental changes both in continental weathering regimes and associated mobilization mechanisms of biophile elements, as well as in ocean circulation and nutrient distribution patterns. In tandem with important orogeny in the Himalayan and Alpine regions, the arrival of glacial denudation substantially increased weathering rates, leading to a largely increased flux of biophile elements to the ocean from the Oligocene onwards (Cermeño, Falkowski, Romero, Schaller, & Vallina, 2014; Edmond, 1992; Föllmi, 1995; Lear, Elderfield, & Wilson, 2003; Misra & Froelich, 2012). Furthermore, the initiation of the Antarctic Circumpolar Current and the progressive development in North Atlantic Deep Water Formation enhanced vertical water mixing, the latitudinal exchange of deeper waters, and the more efficient transfer of nutrients to low-latitude thermocline waters by increased upwelling (Berger, 2007; Cermeño et al., 2014). As such, the unfolding icehouse affected vital feedback mechanisms between geochemical cycles and life, and directed evolutionary patterns both on land and in the sea (Berger, 2007; Janis, 1993).

The evolution from greenhouse to icehouse conditions started with an initial and most important cooling step during the latest Eocene, which culminated in the early Oligocene glaciation episode (EOGM or EOT1; Figure 1; Miller, Wright, & Fairbanks, 1991; Pälike et al., 2006; Coxall & Wilson, 2011; Moore et al., 2014). Following a brief warming episode during the early Oligocene (at around 33–32 Ma), a protracted (~5 Ma) cooling phase occurred during the later part of the early Oligocene, which resulted in the early late Oligocene glacial maximum (OGM; Figure 1; at around 28–27 Ma; Wade & Pälike, 2004; Harzhauser et al., 2016). This glacial episode is followed by a long-term (~3 Ma) warming phase (LOW; Figure 1), which culminated in the late Oligocene climate optimum (at around 24 Ma). A renewed short (<1 Ma) and major cooling phase occurred near the Oligocene–Miocene boundary (Mi1; Figure 1; at around 23 Ma; Miller et al., 1991). The three successive cooling steps were sufficiently strong to extend the ice caps present in Antarctica and shift the Earth’s climate into a transient icehouse mode (Pälike et al., 2006; Zachos, Shackleton, Revenaugh, Pälike, & Flower, 2001a). The changes in climate and the environment are well expressed in benthic foraminiferal stable oxygen ($\delta^{18}O$) and carbon isotope ($\delta^{13}C$) records (Zachos, FLower, & Paul, 1997; Zachos, Pagani, Sloan, Thomas, & Billups, 2001b) such as those from ODP Site 1218 (equatorial Pacific; Pälike et al., 2006), which are used here to trace Oligocene palaeoenvironmental change in the Pacific realm. These records are of sufficient resolution to demonstrate that climate evolution during this time interval was predominantly paced by the long eccentricity cycle (405 ka) (Pälike et al., 2006; Wade & Pälike, 2004).

The long-term trends towards more positive $\delta^{13}C$ values during the Oligocene and near the Oligocene–Miocene boundary were generally interpreted as due to an increase in marine productivity and a correspondingly increased organic flux to the ocean floor (Diester-Haass, Billups, & Emeis, 2011; Mawbey & Lear, 2013; Stewart, James, Anand, & Wilson, 2017). Enhanced productivity during this time period is also suggested by modelled silica flux rates and calculated oceanic phosphorus accumulation rates, which both show an important increase from the early Oligocene onward (Cermeño et al., 2014; Föllmi, 1995). The enhanced silica and phosphorus flux to the ocean led to a widespread increase in opal accumulation and to a worldwide pulse in the deposition of phosphorite and phosphate-enriched
sediments during the Oligocene and early Miocene (Diester-Haass & Chamley, 1982; Riggs & Sheldon, 1990; Salamy & Zachos, 1999; Vanden Berg & Jarrard, 2004). The episode of increased phosphogenesis is well-documented from different settings, such as in southeast U.S.A. (Compton, Hodell, Garrido, & Mallinson, 1993; Mallinson & Compton, 1997), offshore South Africa (Compton, Wigley, & McMillan, 2004), and in the central Mediterranean realm (Baldassini & Di Stefano, 2015; Föllmi, Gertsch, Renevey, de Kaenel, & Stille, 2008). These authors proposed detailed depositional models and age constraints for most phosphorite deposits. Correlations with recent, high-resolution $\delta^{13}C$ and $\delta^{18}O$ stratigraphies are, however, often lacking, implying that precise relationships with overall climate and productivity changes are not yet established. This information is essential to understand the interdependencies among changes in weathering regimes, nutrient delivery and storage, and overall oceanographic change during this critical passage from greenhouse to icehouse conditions.

Baja California Sur (Mexico) hosts an important and economically viable occurrence of phosphorite associated with organic-rich and silica-rich sediments of late Oligocene to early Miocene age. These deposits open a window into the process of phosphate accumulation along the eastern side of the central Pacific during this time period, and have great potential to provide important information on climate, environmental, and trophic change in this region and in general. A key section through this lithological interval from an area near La Purísima was analysed and the results including an improved age model are presented here (Figures 2 and 3). The data show that phosphogenesis and phosphorite formation started during the Oligocene glacial maximum at around 28 Ma and ended during the Oligocene–Miocene glacial interval Mi1, at around 22 Ma. The continuity in phosphorite deposition during this time interval suggests links among surges in weathering regimes both during glaciation and deglaciation phases, a reinforced upwelling regime, and continuous high productivity rates along the western Mexican margin.

**FIGURE 1** From left to right: Ten-point average trends of the $\delta^{18}O$ and $\delta^{13}C$ records (both in ‰ vs. VPDB) measured on benthic foraminifera from ODP Site 1218 (Leg 199, Clipperton Fracture Zone, central Pacific; Pälike et al., 2006) with glacial episodes after Pekar et al. (2006) and Wade and Pälike (2004), global average phosphorus burial record (Föllmi, 1995), and temporal distribution of phosphates at San Juan de la Costa (Schöllhorn, 2016) and La Purísima. EOGM = Early Oligocene Glacial Maximum; OGM = Oligocene glacial maximum; LOW = Late Oligocene Warming. Blue and red arrows indicate cooling and warming trends. The green arrows trace positive trends in the $\delta^{13}C$ record. Uninterrupted black vertical lines to the right indicated the occurrence of phosphorites as dated by U/Pb radiometric ages; the interrupted black vertical line indicates the possible occurrence of phosphorites (not dated).
Upper Oligocene and lowermost Miocene phosphate-rich sediments are known from different localities in Baja California Sur. Overall, these sediments were deposited at different water depths in a forearc basin to the west of the Sierra Madre Occidental arc (Ferrari et al., 2013; Garrison, 1992; Hausback, 1984; Zanchi, Gelati, & Robba, 1991).

In the regions of San Hilario and San Juan de la Costa (Figure 2), the phosphate-rich sediments constitute the San Juan Member of the El Cien Formation (Heim, 1915; Dar- ton, 1921; Beal, 1948; Mina, 1957; Salas, 1978; Ojeda, 1979; Reyes and Rodríguez in López-Ramos, 1982; Alatorre in López-Ramos, 1982; Hausback, 1984; Applegate, 1986; Alatorre, 1988; Galli-Olivier, Garduño, & Gamiño, 1990; Galli-Olivier, 1993; Piper, 1991; Fischer, Galli-Olivier,
The San Juan Member is composed of mudstone, siltstone, and sandstone, which are intercalated with granular, phosphate-rich layers, and volcanic tuff. Phosphate from this unit is exploited at the Rofomex mine near San Juan de la Costa (Figure 2). The San Juan Member rests unconformably on sandstone, siltstone, and mudstone of the Upper Cretaceous—Eocene Tepetate Formation and is overlain by lower Miocene conglomerate, sand-, and siltstone of the Cerro Colorado Member of the El Cien Formation (Applegate, 1986; Fischer et al., 1995).

The age of the San Juan Member is constrained by a radiometric K-Ar age of 25.5 ± 0.4 Ma on biotite from a tuff layer in the middle of this member near El Cien, in the area of San Hilario. Calcareous nannofossils and preserved shark teeth from the same area concur with this age (Bukry, in Hausback, 1984; Applegate, 1986). Using diatom biostratigraphy, Kim and Barron (1986) dated the section at San Hilario as late Oligocene (vigilans and veniamini zones). Schöllhorn (2016) provided five new LA-ICP-MS U-Pb ages dates obtained on zircons from tuff...
layers in a core from the ROFOMEX mine in San Juan de la Costa, which range between 28.37 ± 0.45 and 26.75 ± 0.17 Ma, confirming the late Oligocene age of the San Juan Member. Schwennicke (1992, 1994, 1995) described the facies, sedimentology, and palaeontology of the San Juan Member in detail and concluded that phosphate precipitation was microbially mediated and that the zones of phosphogenesis were located both within the oxygen-minimum zone of an upwelling regime as well as in protected shallow-water areas. The thus formed phosphate particles were mostly reworked and transported in an offshore direction by storm-driven gradient flows.

Siliceous siltstone and mudstone including phosphate-rich and dolomite beds also crop out in the region of Timbabichi, where they occur in the Timbabichi Member of the El Cien Formation (Figure 2; Hausback, 1984; Grimm, 1992, 2000; Drake et al., 2017). The phosphate-rich beds were interpreted as reworked and transported, originating from a shelf area influenced by upwelling (Grimm, 1992, 2000). The age of the Timbabichi Member is poorly constrained, but interpreted to be coeval with the San Juan Member of the El Cien Formation (Grimm, 1992, 2000). A Rb–Sr age of 25.9 Ma obtained for the base of the overlying Comondú Formation provides a minimum, late Oligocene age for the Timbabichi Member (Drake et al., 2017; Schwennicke & Plata-Hernández, 2002, 2003).

In the vicinity of La Purísima (Figures 2 and 3)—the area considered in this contribution—the presence of siliceous and organic-rich sediment has been known since the pioneering work of Heim (1915, 1921, 1922) and Darton (1921). Darton (1921) mentioned the presence of “strata closely resembling the Monterey Formation of southern California”, which he called “Monterey Beds” and assumed to be Miocene in age. Heim (1922) described the same succession of “siliceous shale” containing foraminifera and fish debris, which he also considered to be equivalent to the Californian Monterey Formation. He interpreted the sediments as “a deposit of cold ocean water .... on a rather deep ocean bottom” (p. 539 in Heim, 1922). Interestingly, neither author identified the important phosphate-rich deposits associated with the “Monterey shale”. Beal (1948) renamed the diatomaceous and siliceous sediment in the area of La Purísima as the San Gregorio Formation. This lithostratigraphic unit lies above shelf sandstone, siltstone, and mudstone of the Eocene Bateque Formation, and is overlain by the lower to middle Miocene, shallow marine coquina and silty sandstone deposits of the Isidro Formation (McLean, Hausback, & Knapp, 1987). Hausback (1984) provided a K–Ar age of 27.2 ± 0.6 Ma on glass from a rhyolithic tuff 92 m above the base of the San Gregorio Formation at San Gregorio, ca. 20 km west of La Purísima (Figure 2). At La Ventana, ca. 10 km SW of La Purísima, the same author obtained K–Ar ages of 23.9 ± 0.4 Ma and 23.4 ± 0.3 Ma on biotite and glass from two rhyolithic tuff layers at 2 and 9 m above the base of the section. He published a further K–Ar age of 25.3 ± 0.3 Ma on biotite from a rhyolithic tuff in the “pump house” area of La Purísima. Kim and Barron (1986) used diatom stratigraphy to date two sections analysed by Hausback (1984) at San Gregorio and La Ventana as late Oligocene (vigilans zone) and latest Oligocene to earliest Miocene (veniamini and gelida zones), respectively.

McLean et al. (1987) described the same series as a succession composed “predominantly of diatomite and containing subordinate phosphatic sandstone, vitric tuff, and porcelanite”. Based on calcareous nanofossil biostratigraphy and K–Ar ages (27–22 Ma) from the tuff, they attributed a late Oligocene to early Miocene age to this succession. Piper (1991) analysed selected phosphate samples from La Purísima for their chemical and stable isotope composition and considered upwelling and related primary productivity rates as important in phosphogenetic processes in this area. Grimm (1992) provided detailed descriptions of six sections near La Purísima, including the river section described here, which he interpreted with regard to their facies, sedimentology, and palaeontology. Ledesma (1992) investigated the petrography of the phosphatic particles in detail and described their complex nature, which she related to initial phosphogenesis in a shallow marine environment, followed by reworking due to gravity flow and continued phosphogenesis in a deeper marine environment. A general description of the Oligocene to Pleistocene sedimentary succession near La Purísima and their relationships with the regional tectonic regime was provided by Fischer, Ganz, and Jungblut (1997). Kracht and Ganz (1998) published a detailed log of the section considered here and confirmed the allochthonous character of the phosphorite beds. Using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), they deduced that the phosphate-hosting siliceous mudstone was formed in a nutrient-enriched and oxygen-reduced, upwelling-dominated, marine shelf-slope environment.

3 | ANALYSIS OF THE SAN GREGORIO FORMATION IN THE VICINITY OF LA PURÍSIMA, BAJA CALIFORNIA, MEXICO

3.1 | Location of the measured section, analytical methods

The section of the San Gregorio Formation analysed here is located along the northern side of the La Purísima River, east of La Purísima and west of San Isidro, immediately south of “El Pilón de la Purísima” (Figures 2 and 3; 26°11′55″N 112°03′25″W). It was described earlier by McLean et
al. (1987), Grimm (1992), Ledesma (1992), and Kracht and Ganz (1998). The section was measured and sampled during two field campaigns—a first one in December, 1988 and a second one almost 25 years later, in October, 2013.

Thin sections and powders were prepared from selected samples. Calcite-bearing samples were examined for their calcareous nanofossil contents using the settling method described in De Kaenel and Villa (1996). Geochemical and mineralogical analyses were exclusively performed on siltstone and mudstone samples, with the exception of the XRD analyses, which were obtained on a representative set of different lithologies. All analyses were carried out at the University of Lausanne.

The bulk mineralogy was analysed and semi-quantified by a Scintag XRD 2000 diffractometer using external standards with an accuracy of 5%, following the methods described by Kübler (1983) and Adatte, Stinnesbeck, and Keller (1996). Major and trace-element contents were measured by a X-ray fluorescence Philips PW2400 spectrometer with Rh-Kα radiations and a power of 2400 W. The detection limits are approximately 0.01% for major elements and 1 to 7 ppm for trace elements. The external reproducibility (1σ) varies between 0.5 and 5% depending on the element, using standard reference materials (NIM-G; SDC; BHVO; QLO). The total organic carbon content (TOC, wt%), hydrogen index (HI, mg HC/g TOC, where HC is hydrocarbons), oxygen index (OI, mg CO₂/g TOC), and T_max (°C) were measured by a Rock-Eval 6 (Behar, Beaumont, & Penteado, 2001; Espitalié, Deroo, & Marquis, 1985). The analytical error for the TOC content is <0.1%.

The carbon isotope composition of organic matter was determined by flash combustion on a Carlo Erba 1108 elemental analyser connected to a Thermo Fisher Scientific Delta V Plus (Bremen, Germany) isotope ratio mass spectrometer, which was operated in the continuous helium flow mode via a Conflo III split interface. The carbon isotope compositions were reported in the delta (δ) notation as the per mil (‰) deviations of the isotope ratio relative to Vienna Pee Dee Belemnite limestone (VPDB) standard (δ¹³C value in ‰ vs. VPDB). The repeatability and intermediate precision of the δ¹³C analyses, determined by the standard deviation of replicated analyses of laboratory organic standards and unknown samples, were better than ±0.1 ‰ (1 SD). The accuracy of the analyses was checked periodically by analyses of the international reference materials (USGS-24 graphite, IAEA-PEF1 polyethylene foil, and NBS-22 oil).

Zircons were extracted by wet sieving, and by heavy liquid (methyleneiodide) and magnetic (FRantz) mineral separation from a selection of volcanic tuff layers. They were treated by 10N cold HF to remove volcanic glass from the tuffs, mounted in epoxy resin, polished, and examined by cathodoluminescence on a CamScan MV2300 scanning electron microscope. Their ²⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶⁰⁶³
were interpreted as the product of crustaceans, which survived turbulent transport in gravity flows (Föllmi & Grimm, 1990; Grimm & Föllmi, 1994). Fish scales and skeletons are present in the siliceous mudstone and siltstone and enriched in the organic-rich sediments, and fish bones and shark teeth occur within the phosphatic beds. Microfossils include diatoms (Kim & Barron, 1986), calcareous nannofossils conserved in discrete levels (McLean et al., 1987), and locally numerous benthic foraminifera.

With regard to calcareous nannofossils, of all samples analysed, unfortunately only the samples in the interval between 9 and 23 m delivered a sufficiently well-preserved and age-diagnostic nannoflora. Samples at 9 m, 22 m, and 23 m include Dictyococites pseudolockeri (>10; last occurrence (LO) at 24.73 Ma; late NP25), Helicosphaera bramletti (LO at 24.68 Ma; late NP25), Reticulofenestra coenura (LO at 25.87 Ma; early NP25), Pontosphaera enormis (first occurrence (FO) at 26.85 Ma; late NP24), Triquetrorhabdulus carinatus (FO at 29.09 Ma; early NP24), and Pontosphera jonesii (FO at 29.45 Ma; late NP23) as age-diagnostic species. Based on these species, the interval between 9 m and 23 m is late Oligocene ( Chattian) in age, and dates between the late NP24 and the early NP25 nannofossil zones (between 26.85 and 25.87 Ma; Martini, 1971; De Kaenel & Villa, 1996; Bergen, De Kaenel, Blair, Boesiger, & Browning, 2017).

3.4 Microfacies of the siliceous, organic-rich, and phosphatic sediments

Microfacies analyses of thin sections of the siliceous mud and siltstone reveal that the coarse laminations are due to abrupt differences in organic matter and siliceous content and to the presence of thin peloidal phosphatic laminae and lenses separating the laminae (Figure 5A,B,D,G). The phosphatic components within the siliceous and organic-rich mudstone and siltstone are dominated by peloids of different sizes and morphologies (Figure 5C–G). They consist of fossil remains (e.g., foraminifera and fish debris; Figure 5H) and phosphatic or detrital grains, which are coated by single or multiple generations of phosphate (Figure 5D,F,G,I,K–P). Subsidiary phosphatic grains are homogeneous and lack an internal structure (Figure 5L,N,O).

The multiple coated peloids often resemble oncoids (Figure 5C,G). In other cases, they represent lenticular, eye-shaped (“augen”) particles (Figure 5D,E). Besides the peloids, larger particles and nodules (up to several cm) occur, which are mostly uniform and without any internal structure, or are composed of a macaroni-like structured phosphate, and which are likely coprolites and faecal peloids (Figure 5F,L–N). Peripherally phosphatized extraclasts occur as well but are generally rare (Figure 5J). The phosphatic particles are often enveloped by silica, and pores within the particles are equally occupied by silica (Figure 5E,K).

The phosphatic particles occur both as isolated grains within the siliceous and organic-rich sediments as well as highly concentrated within the phosphatic granular layers. Thin sections reveal all transitional stages between phosphate-free siliceous or organic-rich mudstone and siltstone to layers with a few scattered phosphatic grains or to sediments with high concentrations of phosphatic particles principally confined to mm- to cm-thick lenses and laminae, and up to 50 cm thick granular phosphatic layers, which lack a clayey or organic-rich matrix, and which are commonly cemented by phosphate and/or silica (Figure 5G,I–P).

3.5 Sedimentary structures

The section of La Purísima is rich in sedimentary structures, which occur in all lithologies. The fine-grained canogenic deposits are composed of uniform, homogeneous ash layers, which may be slumped (Figure 6F). They may include small to metre-sized, partly bored and perforated extraclasts, which are partly silicified along their margins (Figure 6A,E). This type of volcanogenic deposit can be lenticular and bear an undulated, ripple-like surface (Figure 6C). The more coarse-grained volcanoclastic deposits are in all cases normally graded (Figure 6B,E) and may include organic matter or a peloidal and nodular phosphatic interval at their base (Figure 5L).

The peloidal and nodular phosphatic layers display in most cases a sharp and well-defined base, which may be marked by scours and load and gutter casts (Figure 7G,H). The bases are commonly restructured by bioturbation (Thalassinoides and Gyrolithes; Figure 7A–E), which in

**FIGURE 4** Photographs of the different lithologies present in La Purísima. Numbers correspond to sample numbers (Figure 3). (a) Sample interval SI 16–17: phosphatic peloidal bed with highly bioturbated base (17) on top of siliceous mudstone; (b) Interval SI 28–35: peloidal phosphatic layers (28, 31, 34) alternating with volcanic ash layers (between 29 and 30, and below 32), organic-rich mudstone (29, 32), and silty porcelanite (35); (c) Interval SI 35–38: well-bedded, finely laminated silty porcelanite, overlain by an alternation of organic-rich mudstone (poorly visible in photograph), thin volcanic ash layers, and peloidal phosphatic beds (36, 37); (d) Interval SI 70–73: alternating volcanoclastic beds (70), volcanic ash layers (above 72‘ and in lenses below 71), siliceous mudstone (between 72 and 72‘), organic-rich mudstone (above 70, below 73), and peloidal phosphatic layers (72, 73); (e) Interval SI 82VI–82VII: volcanic ash layers (e.g., 82VIII) alternating with siliceous mudstone and siltstone layers (e.g., 82VI, 82VII), and sparse, thin peloidal and nodular phosphatic layers (82XV); (f) Interval SI 120–123: alternation of siliceous siltstone (121), limestone (120, 122, 123), and a few thin volcanic ash layers (white arrows).
The average TOC content \((n = 121)\) in the sediments of the section of La Purísima is 1.32 wt\%, with a maximum value of 5.25 wt\% (Figure 8). The hydrogen indices (HI) values are positively correlated with TOC content and average 320 mg HC/gTOC, with maxima >1,100 mg HC/gTOC. Average oxygen indices (OI) values are around 165 mg CO\(_2\)/gTOC, with maxima >1,500 mg CO\(_2\)/gTOC (Figures 8 and 9). Sediments with low TOC content, low HI, and high OI values prevail in the first 20 m of the section, whereas the remainder of the section shows a rather evenly distributed scatter in TOC, HI, and OI, with generally higher TOC and HI values, and lower OI values (Figure 8).

The organic carbon isotope ratios evolve between approximately −26\% and −21\% (Figure 8), oscillating along a stable long-term trend centred between −22\% and −24\% for the first 70 m of the section. Above this interval, the \(\delta^{13}C_{\text{org}}\) data show a trend towards heavier values of around −21\% (Figure 8).

3.7 | Whole-rock composition and major and trace elements

The XRD whole-rock data show a dominance of quartz, feldspar, calcite, apatite, and phyllosilicate minerals (Figure 10). The contents of these minerals average around 12, 9.1, 13, 18.9, and 14.7\%, respectively \((n = 142)\). Pyrite, dolomite, and ankerite occur in minor quantities, with maximum values of 2.4, 1.3, and 1.1\%, respectively. The unquantified fraction varies around a mean value of 19.2\%. It includes poorly crystallized silica (crystobalite and tridymite (=opal CT); McLean et al., 1987; Ledesma, 1992), apatite, and organic matter.

Apatite is the most abundant mineral detected, reaching 71.4\% in the phosphate-rich beds. Phyllosilicate minerals are present in variable quantities throughout the section. The calcite content is very variable and maximum values of up to 88\% are limited to the carbonate beds and nodules, whereas it is minimal for most of the siliceous and organic-rich mudstone and volcanogenic deposits. Quartz content diminishes progressively in the upper part of the measured section. Feldspar content includes the sum of Na-plagioclase and K-feldspar abundances, which are more or less equal and both surprisingly high throughout the section (Figure 10).

Major and redox-sensitive trace elements (RSTE) were measured in siliceous and/or organic-rich mudstone samples. The SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), CaO, and P\(_2\)O\(_5\) contents vary between 16.8 and 85.78, 1.6 and 12.82, 0.44 and 4.23, 0.69 and 43.04, and 0.09 and 26.99 wt\%, respectively. Their average values are 64.88, 6.43, 2.10, 7.94, and 3.33 wt\%, respectively \((n = 73)\).
Vanadium, Mn, Co, Ni, Cu, Zn, Mo, and U contents range between 24 and 842 ppm, 41 and 1048 ppm, not detected (n.d.) and 16 ppm, 11 and 220 ppm, 1 and 53 ppm, 55 and 1769 ppm, 1 and 975 ppm, and n.d. and 121 ppm, respectively. Their average values are 240, 187, 6, 41, 24, 241, 54, and 18 ppm, respectively (n = 91; n.d. = not detected).

**FIGURE 6** Sedimentary structures in volcanic deposits at La Purísima. (a) Base of the section, interval SI 1–5: volcanic ash deposit (1–3) including spheroidal chert concretions (C) and disrupted layers (black arrows), overlain by a highly bioturbated porcelanite (between 3 and 4) and a peloidal and nodular phosphate bed (4–5). The phosphate bed includes up to m-sized calcareous extraclasts (white arrows); (b) Interval SI 74-74” : a sharply based (white arrow), normally graded, volcaniclastic sand and siltstone bed (74”) on top of volcanic ash, peloidal phosphatic (74), and siliceous siltstone layers; (c) Interval SI 22-23: organic-rich mudstone layer (22) overlain by a scoured volcanic ash layer, a peloidal and nodular phosphatic layer (23), and a suite of laterally continuous and discontinuous volcanic ash layers, which are each draped by organic-rich mudstone veneers. (d) Interval SI 88’-88”: finely bedded siliceous mudstone and siltstone, intercalated with cm-thin volcanic ash layers (white arrows), a coarse-grained volcaniclastic deposit (blue arrow), draping an undulated surface, and a nodular and peloidal phosphatic bed (88”). Carbonate concretions (88”) are present within the siliceous sediment; (e) Interval SI 91’-91”: a graded volcaniclastic sandstone and siltstone carrying phosphatic nodules and peloids, pebbles and boulders of tuffaceous and siliceous sediments, which show a reaction rim. The base of this bed is sharp and erosive; (f) Interval SI 95’-96: a slumped volcanic ash bed, which is underlain and overlain by siliceous siltstone and mudstone, and organic-rich mudstone (e.g., on top of 95”)
Figure 12). These contents were normalized against Al and the resulting ratios are shown in Figure 12. A Mo and Mo/Al enrichment factor (EF) versus U and U/Al EF cross-plot (Figure 13) and a V/Mo versus Mo diagram cross-plot (Figure 14) were compiled in order to reconstruct the degree of oxygenation, following Algeo and Tribovillard (2009) and Tribovillard, Algeo, Baudin, and Riboulleau (2012), and Piper and Calvert (2009), respectively.

3.8 | LA-ICP-MS zircon ages

LA-ICP-MS zircon ages were obtained on volcanic ash layers and correspond to 27.84 ± 0.33 Ma (sample Si 1, at the base of the section; Figure 3), 26.21 ± 0.26 Ma (sample Si 43; at 17.40 m; Figure 3), 24.42 ± 0.31 Ma (sample Si 91; at 52.00 m; Figure 3), 22.53 ± 0.25 Ma (sample Si 118; at 69.00 m; Figure 3), and 21.21 ± 0.59 Ma (sample Si 166; at the top of the section; Figure 3). The Concordia plots, ages of the individual zircons, and relative probabilities are shown in Figure 15. The ages are in chronological order and suggest that the analysed sediments date from the Chattian (late Oligocene) and the Aquitanian (early Miocene).

4 | DISCUSSION

4.1 | Biostratigraphy, chemostratigraphy, and radiogenic ages

The nannofloral assemblage preserved in the lower part of the section indicates the late Chattian (late NP24 and early NP25; Figure 16), with an age between 26.85 and 25.87 Ma. The LA-ICP-MS zircon age of 27.84 ± 0.33 Ma at the base of the section is 9 m beneath the first diagnostic nannofossil-bearing sediment. The zircon age of 26.21 ± 0.26 Ma at 17.40 m corresponds well to the age span indicated by the calcareous nannofossils of the same interval. The age of 24.42 ± 0.31 Ma at 52.00 m suggests that the NP 25 zone extends well into the upper part of the section, with an upper limit of this zone lying not too far above 52 m. By extrapolation from the radiogenic data alone, the Oligocene–Miocene boundary is likely located in the interval between 60 and 65 m in the La Purísima section.

The ages proposed here allow for the first time for consistent dating of a section through the San Gregorio Formation. The age model is compatible with the range of previous ages obtained on single samples from the same section or on coeval sections in the vicinity of La Purísima, which are based on K–Ar radiochronology (27–22 Ma; Hausback, 1984; McLean et al., 1987), and diatom and calcareous nannofossil biostratigraphy (Kim & Barron, 1986; McLean et al., 1987).

Of particular interest is the confirmation of the early Miocene age for the upper part of the San Gregorio Formation. This age is not known thus far for the San Juan Member of the El Cien Formation, the lithostratigraphic equivalent of the San Gregorio Formation further to the south in the region of San Hilario and San Juan de la Costa, nor for the Timbabichi Member at Timbabichi (Figure 2). The radiogenic ages from Drake et al. (2017) and Schöllhorn (2016) suggest that phosphogenesis and organic matter accumulation had already ceased in the latest Oligocene in this area, or that sediments equivalent to the upper part of the San Gregorio Formation are not preserved. This latter possibility is less likely since no major hiatuses were observed between the El Cien and overlying formations. The similarities in ages (28.37 ± 0.45 Ma at San Juan de la Costa; Schöllhorn (2016), and 27.84 ± 0.33 Ma at La Purísima) proposed for the bases of both lithostratigraphic units suggest a certain degree of synchronicity in the onset of deposition of the siliceous, organic-rich, and phosphate-rich sediments for both regions.

The correlation of the δ¹³Corg data with the central Pacific record of δ¹³C_carb values of IODP Site 1218 (Leg 199, Clipperton Fracture Zone; Pälike et al., 2006) is not without difficulties, even with the constraints provided by the radiogenic age dates (Figure 8). The long-term rise towards more positive values traversing the Oligocene–Miocene boundary, where it characterizes the Mi1 glacial event (Miller et al., 1991) appears to be present in the La Purísima record. The negative excursion following the Mi1 interval, however, is not observed in the La Purísima record. Altogether, the correlation is unfortunately too doubtful to obtain meaningful time control with orbital resolution.

4.2 | Sedimentary processes

The observed sedimentary structures indicate two significant depositional processes; first, the presence of at least episodically dynamic hydrological conditions at the site of deposition, and second, the importance of gravity-flow deposition. Dynamic conditions are indicated by the presence of uniform phosphatic peloids or fish debris, which are concentrated in lenses and laminae within the siliceous and organic-rich mudstone, suggesting that they were condensed by winnowing and the selective removal of finer-grained sediments (Figure 5E–I,K). In addition, the presence of several, superimposed, phosphate generations of different colour, composition, and texture within the same phosphatic particles indicates the effect of sediment reworking, which permitted the addition of new and distinct phosphatic layers (Figure 6C,D–G). The presence of irregular, wavy, and oblique bedding in the early-formed, non-compacted carbonates and starved ripples on top of
volcanogenic layers is a further indication of elevated dynamic depositional conditions in this hemipelagic environment (Figure 7I).

Gravity-flow deposition is particularly evident for the coarser-grained volcanogenic and phosphate-rich beds and laminae. The presence of (a) sharp and partly erosive bases, which are marked by load casts, scours, and gutter casts (Figure 7D–H,J); (b) normally graded beds (Figures 6C, E, and 7G–H); (c) mixtures of different types and generations of phosphatic particles within the allochthonous beds
FIGURE 7 Sedimentary and biogenic structures associated with phosphatic and carbonate deposits at La Purísima. (a) SI 17: base of peloidal and nodular phosphatic bed marked by bioturbation (Gyrolithes) into the subjacent siliceous mudstone (coin diameter is 26.5 mm); (b, c) SI 36: organic-rich mudstone (m) and volcanic ash (v) layers, which are both strongly bioturbated. The bioturbations are filled in by a peloidal phosphatic sediment derived from the phosphatic layer (p) covering the ash bed (coin diameter is 26.5 mm); (d) Just below SI 68: graded peloidal and nodular phosphatic bed marked by bioturbation into the underlying siliceous mudstone; (e) just above SI 39: Gyrolithes burrow at the base of a peloidal phosphatic layer, intruding into a siliceous mudstone; (f) SI 70: two sharply based and graded peloidal phosphatic beds (p) separated by a laminated siliceous mudstone. Upper phosphatic bed = SI 70; (g) SI 73: graded peloidal and nodular phosphatic bed in a silty siliceous mudstone, showing a gutter cast; (g) SI 76A: polished slab of a graded phosphatic and nodular phosphate layer cutting into and overlying an organic-rich mudstone and a volcanic ash layer (v); (i) SI 75B: nodular carbonate in an organic-rich mudstone, carrying dispersed phosphatic nodules (pn) and peloids. The carbonate was formed before compaction and preserves well the original sedimentary structures such as winnowed peloidal layers (w), oblique bedding (o), and wavy stratification; (j) SI 23: thinly bedded peloidal and nodular phosphatic layer with a well-defined base marked by bioturbation into the underlying volcanic ash layer. The phosphatic layer is overlain by a silty siliceous mudstone with coarse laminations composed of phosphatic peloids

(Figure 5M–O); (d) the presence of rip-up clasts of underlying volcanogenic and hemipelagic beds in the basal intervals of phosphatic beds; and (e) frequent traces of Thalassinoïdes and Gyrolithes at the bases indicating the activities of displaced crustaceans (Figure 7A–E). These features all serve as witnesses of gravity-flow deposition. They have not only been observed in coarse-grained beds and laminae, which were systematically transported by gravity flow, but partly also in fine-grained sediments. Those may likewise show sharp and erosive bases, along with the presence of rip-up clasts in their basal portions. The sporadic presence of slumped structures in the mudstone and volcanogenic deposits is a further indication of the presence of topographic conditions, which allowed the reworking of sediments by gravity flow. Hummocky cross stratification was not observed in the gravity-flow deposits, and this suggests deposition beneath storm-wave base.

A direct relationship between volcanogenic and allochthonous phosphatic peloidal beds is commonly observed. Volcanogenic deposits may include phosphatic peloidal layers in their basal intervals (Figure 5L). They may also appear directly below or on top of the phosphatic layers (Figures 6B and 7A–C,H,J). Volcanogenic deposits may equally include a layer enriched in organic matter at their base, which displays a sharp basal contact and a transition towards the overlying volcanogenic sediment (Figure 6C). This indicates the inclusion of organic matter into the volcanogenic gravity flows during their displacement. These associations suggest a direct and causal link between volcanic eruptions and the triggering of gravity flow (Ledesma, 1992; Schöllhorn, 2016).

4.3 | Phosphogenesis

The precipitation of phosphate, the formation of phosphatic particles, and their concentration by winnowing and gravity-flow transport were important processes throughout the deposition of the San Gregorio and equivalent formations. The resulting phosphate-rich sediments are widespread and occur in an area of approximately $2.5 \times 10^4$ km$^2$ in central southern Baja California (Figure 2). Phases of phosphogenesis and phosphate accumulation were particularly important in the time intervals of 28–25.5 Ma and 23.5–21.5 Ma.

In the section at La Purisima, the phosphate-rich beds represent gravity-flow deposits, whereas the thinner and more confined phosphate-enriched lenses and laminae within the siliceous and partly organic-rich mudstone and siltstone resulted from dynamic winnowing processes (Figures 4, 5, and 7). The phosphatic particles represent such a mix of allochthonous and autochthonous, condensed phosphatic particles and nodules, and biogenic phosphate (fish debris, coprolites). The allochthonous fraction is far more abundant. The transported grains are mainly composed of particles coated by both single and multiple layers of phosphate (Figure 5). The latter type is indicative of dynamic sedimentary processes during formation as the particles were repeatedly introduced into and removed from the early diagenetic zone of phosphogenesis. Reworking may have been induced by high-energy events such as volcanic eruptions, but may also have been linked to current activity, similar to what is indicated by the winnowed, phosphate-enriched horizons within the siliceous and partly organic-rich mudstone and siltstone. The original area of phosphogenesis for the transported particles was likely less deep than the site at La Purisima, and also better oxygenated, as is indicated by the presence of benthic foraminifera, fish debris, and the frequent association of gravity-flow deposits and allochthonous crustacean trace fossils (Föllmi & Grimm, 1990; Grimm & Föllmi, 1994; Schöllhorn, 2016).

The autochthonous phosphate fraction was formed within the partly organic-rich, siliceous mudstone and siltstone, which was deposited under more reducing conditions, as will be shown in the following section. Phosphogenesis either occurred around preformed phosphatic particles, which were partly covered by a new generation of phosphate, thereby producing lenticular, eye-
FIGURE 8 Total organic carbon (TOC) content, hydrogen and oxygen indices (HI and OI), and δ¹³Corg record of the section of La Purisima. The δ¹³C record of benthic foraminifera from ODP Site 1218 (Leg 199, Clipperton Fracture Zone, central Pacific; Pälike et al., 2006) to the right is shown for correlation purposes. Ten-point moving average trends are shown for both δ¹³C records, and a tentative correlation is suggested, using the longer term trends.
shaped (“augen”) particles (Figure 5D,E), or by phosphatic cementation within phosphate-rich lenses and layers (Ledesma, 1992). These processes are very similar to the processes observed in other localities of the San Gregorio and equivalent formations by Grimm (1992, 2000), Schwennicke (1992, 1994, 1995), and Schöllhorn (2016).

The abundance of particles and nodules of likely coprolitic origin (Figure 5F and L-N) underlines the dominance of fish and crustaceans, already suggested by abundant fish debris within the phosphate-rich deposits and crustacean traces at their base. A microbial component is also likely in the formation of phosphatic grains, as is indicated by the presence of oncoids (Figure 5C,G). Using scanning electron microscopy (SEM), Ledesma (1992) observed phosphatized filamentous and tubular microstructures in phosphate-rich beds of the San Gregorio Formation in sections near La Purísima. Schwennicke (1992, 1994, 1995) described the presence of cyanobacteria-like structures in phosphatic peloids in sections within the El Cien Formation near San Hilario and San Juan de la Costa, and Schöllhorn (2016) mentioned the presence of finely laminated phosphatic structures, which she interpreted as stromatolites in a core from the Rofomex mine in San Juan de la Costa. These observations suggest the importance of microbial activity in the precipitation of the phosphates (Arning, Briigel, Brunner, & Peckmann, 2009).

The chemical index of alteration (CIA) provides an indication of the degree of chemical weathering as a function of humidity (Nesbitt & Young, 1982; Schöllhorn, 2016). It is used here to evaluate climate conditions in the hinterland, in order to estimate if it constituted a direct source of phosphate. The CIA* was adapted from the original CIA and CaO was replaced by Na₂O because of the paucity of carbonates and its diagenetic mobility, and was calculated as follows:

$$\text{CIA}^* = \frac{\text{Al}_2\text{O}_3 + 3 \times 100}{(\text{Al}_2\text{O}_3 + 3 \times \text{Na}_2\text{O} + \text{K}_2\text{O}) \text{ (in molar proportion)}}$$

The CIA* shows a very stable stratigraphic evolution with values oscillating around 60 (Figure 11), indicating a semi-arid climate in the hinterland (Nesbitt & Young, 1982). These values are somewhat higher than those obtained by Schöllhorn (2016: 45–55), but are compatible with the notion that the phosphate flux directly from the Mexican continent was not significant.

### 4.4 The degree of oxygenation

The presence of partly laminated sediments enriched in TOC, the exclusive association between bioturbation and gravity-flow deposits, and the near absence of benthic macro-organisms in the autochthonous mudstone and siltstone are all indicative of oxygen-depleted bottom waters during deposition of the sediments associated with the San Gregorio Formation. The dominance of organic-rich, phosphate-rich, and siliceous sediments is typical for sedimentation in upwelling centres, and the role of upwelling and the presence of an associated oxygen-minimum zone have already been emphasized by previous researchers (Kracht & Ganz, 1998; Piper, 1991).
FIGURE 10  Relative abundance of major minerals in the section of La Purísima, as determined by XRD
FIGURE 11 Stratigraphic distribution of the quantitatively most important major elements (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, and P$_2$O$_5$) in the section of La Purisima, as determined by XRF exclusively on mudstone and siltstone samples. CIA* is the chemical index of alteration.
Redox-sensitive trace-element (RSTE) distributions of V, Mn, Co, Ni, Cu, Zn, Mo, and U, were analysed in order to evaluate the degree of oxygen depletion and temporal changes therein, as documented in the hemipelagic background sediments (Algeo & Maynard, 2004; Brumsack, 2006; Garnit, Boulhelm, & Jarvis, 2017; Tribovillard, Algeo, Lyons, & Riboulleau, 2006; Tribovillard et al., 2012). Enrichment factors relative to average shale (Wedepohl, 1971) for these RSTE are widely variable and are elevated (>10×) for Mo and U, whereas V and Zn contents are only slightly enriched (<10×), and Mn, Ni, Cu, and Co contents depleted (<1×) relative to average shale (Figure 12; Table 1). The highest enrichments in RSTE are observed in the levels around 10 m and 40–80 m (Figure 12). Correlation coefficients between these trace elements, and between RSTE and Al, TOC, and P contents are generally very low, with the exception of U and P, which are well correlated (Table 1).

Vanadium contents and V/Al ratios are not correlated with those of the other RSTE considered here, nor with Al, P, or TOC, and they are only moderately correlated with Cu and Ni (Table 1). This indicates that V is not preferentially adsorbed onto organic matter or associated with a sulphidic phase. The enrichment factor of V is comparable to that of dysaerobic settings in Toarcian sediments and at the lower end of upwelling centres (Brumsack, 2006; Fantasia, Föllmi, Adatte, Spangenberg, & Montero-Serrano, 2018). They are substantially lower than those associated with the Cenomanian–Turonian oceanic anoxic episode (C-T OAE; Brumsack, 2006). This all may indicate dysoxic rather than anoxic bottom waters (Algeo & Maynard, 2004; Calvert & Pedersen, 1993; Tribovillard et al., 2006).

Cobalt contents and Co/Al ratios lack correlation with all other RSTE considered here and also with P and TOC (Table 1). Only a slightly positive correlation is present with Al, suggesting that Co may be partly related to the detrital fraction and that the remainder is not associated with TOC but rather present in the form of sulphide. Its depletion relative to average shale implies that euxinic conditions were
|       | V   | V/Al | Mn  | Mn/Al | Co  | Co/Al | Ni  | Ni/Al | Cu  | Cu/Al | Zn  | Zn/Al | Mo  | Mo/Al | U   | U/Al | Al  | P   | TOC | EF range  | EF average |
|-------|-----|------|-----|-------|-----|-------|-----|-------|-----|-------|-----|-------|-----|-------|-----|------|-----|----|-----|----------|------------|
| V     | 1.00| 0.02 | 0.02| 0.23  | 0.43| 0.15  | 0.04| 0.01  | 0.02| 0.02  | 0.05| 0.1864| 0.05| 0.18–6.48| 1.84|
| V/Al  | 1.00| 0.03 | 0.02| 0.35  | 0.61| 0.31  | 0.07| 0.05  | 0.05| 0.34  | 0.01| 0.39–22.16| 5.65|
| Mn    | 1.00| 0.06 | 0.15| 0.00  | 0.12| 0.01  | 0.01| 0.00  | 0.00| 0.03  | 0.00| 0.05–1.23| 0.22|
| Mn/Al | 1.00| 0.17 | 0.37| 0.11  | 0.27| 0.01  | 0.05| 0.13  | 0.09| 0.16–3.23| 0.56|
| Co    | 1.00| 0.03 | 0.01| 0.00  | 0.00| 0.01  | 0.17| 0.03  | 0.01| 0.00  | 0.00| 0–0.85| 0.25|
| Co/Al | 1.00| 0.20 | 0.08| 0.08  | 0.00| 0.16  | 0.09| 0.15  | 0.00| 0–1.79| 0.48|
| Ni    | 1.00| 0.22 | 0.72| 0.00  | 0.03| 0.00  | 0.02| 0.03  | 0.00| 0–3.24| 0.61|
| Ni/Al | 1.00| 0.39 | 0.76| 0.00  | 0.09| 0.21  | 0.07| 0.07  | 0.21–8.09| 1.74|
| Cu    | 1.00| 0.17 | 0.07| 0.02  | 0.02| 0.00  | 0.04| 0.03–1.18| 0.54|
| Cu/Al | 1.00| 0.33 | 0.05| 0.27  | 0.35| 0.09  | 0.12–4.65| 1.49|
| Zn    | 1.00| 0.00 | 0.03| 0.00  | 0.01| 0.01  | 0.05| 0.58–18.62| 2.53|
| Zn/Al | 1.00| 0.00 | 0.04| 0.16  | 0.03| 0.07  | 1.31–46.44| 7.37|
| Mo    | 1.00| 0.00 | 0.00| 0.00  | 0.01| 0.17  | 0.96–375.00| 20.87|
| Mo/Al | 1.00| 0.00 | 0.00| 0.00  | 0.01| 0.16  | 2.36–812.61| 62.54|
| U     | 1.00| 0.03 | 0.87| 0.00  | 0.01| 0.51–32.78| 4.75|
| U/Al  | 1.00| 0.11 | 0.61| 0.00  | 0.00| 1.46–308.82| 16.80|
| Al    | 1.00| 0.05 | 0.01| 1.00  | 0.01|
| P     | 1.00| 0.01| 1.00|
| TOC   | 1.00| 1.00| 1.00|

**TABLE 1** Correlation coefficients (R²) and enrichment factors (EF) relative to post-Archaean average shale (Wedepohl, 1971)
generally not present (Algeo & Maynard, 2004), with the exception of the sediments near 10 m and 40 m of the measured section (Figure 12).

Zinc is only moderately correlated with Ni, and to a much lesser degree with V, Mn, and Cu, whereas no correlation is observed with other RSTE, Al, and TOC (Table 1). This indicates that the Zn fraction is not associated with organic matter, but resides rather in a sulphide phase, similar to V, Ni, and Cu (Tribovillard et al., 2006). It is moderately enriched relative to average shale, and its enrichment is comparable to those in present-day upwelling centres and ancient sapropels, but much lower than in organic-rich sediments corresponding to the C-T OAE (Brumsack, 2006).

Molybdenum contents are not correlated with any of the other parameters considered here, except for a very slight correlation with TOC. Its enrichment is higher than those measured in Toarcian dysoxic sediments, is comparable to those in recent upwelling centres, but falls below those in sapropels and sediments related to the C-T OAE (Brumsack, 2006; Fantasia et al., 2018). As such, it indicates dysoxic to anoxic, but not yet euxinic conditions, with the possible exceptions of sediments around 10 m, 40 m, 55 m, and 75 m in the measured section (Figure 12).

Uranium shows a strong correlation with P, indicating that a large fraction resides in authigenic phosphate (Table 1). Its enrichment factor is comparable to those in Toarcian dysoxic sediments, at the low end of those in recent upwelling centres, and clearly below those associated with sapropel and C-T OAE sediments (Brumsack, 2006; Fantasia et al., 2018). As such it would indicate dysoxic to anoxic conditions (Algeo & Maynard, 2004; Tribovillard et al., 2006). However, its strong association with phosphate precludes a precise interpretation of past oxygen levels.

The depletion in Mn relative to average shale is comparable to that of other anoxic sites (Algeo & Maynard, 2004; Brumsack, 2006), indicating oxygen depletion in general, without any further precision.

Nickel contents show a rather good correlation with those of Zn, and only very moderate correlations with V, Mn, and Cu, suggesting that Ni is associated with a sulphide phase and not with the organic fraction. Its depletion relative to average shale is at the very low end of those in modern upwelling centres, and definitively different from the enrichments known from Toarcian, sapropel, and C-T OAE sediments (Brumsack, 2006; Fantasia et al., 2018).

Copper shows only weak correlations with V, Ni, and Zn, indicating that a part resides in the sulphide fraction. The lack of correlation with TOC contents excludes its association with an organic fraction (Table 1). Similar to Ni, it is depleted relative to average shale, and as such only comparable to the lower end of the EF in upwelling centres (Brumsack, 2006). Both Ni and Cu suggest that oxygen depletion was generally not too strong in the depositional setting of the San Gregorio Formation.

The MoEF and Mo/AlEF versus UEF and U/AlEF cross-plot shows a rather scattered distribution of ratios, with MoEF versus UEF ratios indicating dysoxic to anoxic conditions and Mo/AlEF versus U/AlEF ratios pointing to dysoxic to euxinic conditions (Figure 12). Both comparisons suggest at least partial participation of a particulate shuttle related to the presence of Fe and Mn (Algeo & Tribovillard, 2009; Tribovillard et al., 2012). The V/Mo diagram cross-plot indicates somewhat less strongly oxygen-depleted conditions, covering the areas of oxic–dysoxic to dysoxic–anoxic conditions (Figure 14; Piper & Calvert, 2009).
FIGURE 15 Concordia plots, age distributions, and histograms for $^{206}\text{Pb}/^{238}\text{U}$ ages of the three analysed volcanogenic intervals in the section at La Purísima.
The combination of all RSTE used here indicates the dominance of dysoxic rather than anoxic conditions throughout the studied time interval, possibly superimposed by shorter periods of more severely oxygen-depleted conditions, which may have even been euxinic, according to the Co and Mo contents. These periods occurred around 27 and 24–22 Ma, i.e., around the Oligocene glacial maximum and the Oligocene–Miocene glacial interval (OGM and Mi1 in Figure 1). They are associated with the longer time intervals of increased phosphogenesis and phosphate accumulation, which occurred around 28–25.5 and 23.5–21.5 Ma.

### 4.5 | Palaeoceanography

The range of radiometric ages established for the duration of phosphogenesis and phosphorite formation is between 28.62 ± 0.55 and 23.64 Ma for the occurrence in San Juan de la Costa (Drake et al., 2017; Schöllhorn, 2016), and 27.84 ± 0.33 and 21.21 ± 0.59 Ma for the La Purísima section. The onset of phosphogenesis at these two sites dates to approximately 28 Ma, if the overlapping value of the oldest dates is used. This age corresponds to the onset of the Oligocene glacial maximum (Oi2a; Wade & Pälike, 2004; Pekar, De Conto, & Harwood, 2006; Harzhauser et al., 2016), which resulted from a long-term cooling trend starting at around 32 Ma (Figure 1). It also coincides with a maximum in the record of δ¹³C values of benthic foraminifera at ODP Site 1218 (central Pacific), which is judged to be representative for the central Pacific realm (Pälike et al., 2006), and which follows upon a long-term trend towards more positive values, likewise beginning at 32 Ma (Figure 1). The time intervals characterized by particularly intense phosphogenesis and phosphorite deposition are around 28–25.5 Ma, and 23.5–21.5 Ma, as extrapolated from the radiochronological ages. The first interval broadly coincides with the Oligocene glacial maximum (Figure 1; Harzhauser et al., 2016), whereas the second interval corresponds to the glacial intervals Mi1 and Mi1a (Oligocene–Miocene boundary, early Miocene; Miller et al., 1991; Figure 1), and the intervening warm period of the earliest Miocene. It ended prior to the termination of Mi1a. The Mi1 interval coincides also with a broad maximum in δ¹³C_benthic values.
(Figure 1). The two episodes of reinforced phosphogenesis overlap with times of most severe oxygen depletion recorded in the La Purísima section at around 27 and 24–22 Ma. Phosphate-rich sediments also accumulated in the period between the two phases of increased phosphogenesis (around 25.5–23.5 Ma), albeit not in the same quantity and frequency (Figure 3).

In the time interval between 33 and 23 Ma, marine phosphorus burial rates more than doubled on a global scale, indicating a pronounced increase in the availability of oceanic phosphorus (Figure 1; Föllmi, 1995). This resulted in an episode of widespread phosphogenesis during the late Oligocene and early Miocene (Riggs & Sheldon, 1990). The beginning of phosphorite formation in Baja California coincides with the onset of this episode (Schöllhorn, 2016), indicating that its deposition is not only an expression of regionally favourable conditions such as reinforced upwelling but also equally the result of a globally accelerated phosphorus cycle. A possible mechanism to explain the increase in phosphorus supply is the general increase in weathering and phosphorus mobilization related to the arrival of glacial denudation during the Oligocene (Föllmi, 1995, 1996), together with orogeny in the Alpine and Himalayan collision zones (Garzione, 2008; Ruddiman & Kutzbach, 1991). Between these two weathering-increasing mechanisms, glacial denudation appears to be the main driver behind phosphorus mobilization from the Oligocene onward. This is deduced from (a) the generally positive coupling of benthic foraminiferal oxygen and carbon iso‐
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tope records on orbital timescales, suggesting direct ties between cooling, increased nutrient availability, and higher export production rates (Pälike et al., 2006); (b) the correlation between global increases in phosphorus burial and long‐term cooling from 32 Ma onwards (Föllmi, 1995); and (c) the surprisingly high amounts of dissolved phosphorus produced in present‐day glacial catchments (Föllmi, Hosein, Arn, & Steinmann, 2009; Hawkings et al., 2016).

A further circumstance that may have catalysed phosphorite formation during these time periods is the focused return of phosphorus‐enriched deep waters to the continental margin by an increase in the efficiency of coastal upwelling (Berger, 2007). This is often related to the isolation of the Antarctic continent and the onset of the Antarctic Circumpolar Current (ACC; Barker, Filippelli, Florindo, Martin, & Scher, 2007; Lyle, Gibbs, Moore, & Rea, 2007), in tandem with the progressive shift to North Atlantic Deep Water formation (NADW; Scher & Martin, 2008; Abelson & Erez, 2017; Coxall et al., 2018). These oceanographic changes may have led to an overall increase in bottom‐

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water circulation, which improved the exchange between high‐latitude and low‐latitude deep waters. This may have affected the load and distribution of biophile elements such as phosphorus and silica in ocean waters in general, and especially catalysed their focused transfer to the continental coast by upwelling (Berger, 2007; Coxall & Wilson, 2011).

Of interest is the observation that the OGM and Mi1 maxima are contemporary with maxima in the record of $\delta^{13}C_{\text{benthic}}$ values. The Oligocene and early Miocene benthic carbon isotope record is generally interpreted to result from changes in bottom‐water provenance and circulation patterns in general, changes in the ocean carbon budget and calcite compensation depth, and last but not least primary productivity (Pälike et al., 2006; Paul, Zachos, Flower, & Tripati, 2000). The $\delta^{13}C_{\text{benthic}}$ data set of ODP Site 1218 shows a strong 405 ky cyclical record, which is paced by long eccentricity (Pälike et al., 2006), with higher $\delta^{13}C_{\text{benthic}}$ values mostly coinciding with higher $\delta^{18}O_{\text{benthic}}$ values. This was interpreted as an expression of colder periods being associated with higher productivity and export of organic matter (Pälike et al., 2006). The interpretation of the long‐term trends in the $\delta^{13}C_{\text{benthic}}$ values is less clear. However, the synchronous long‐term evolution of $\delta^{13}C_{\text{benthic}}$ records in different basins (Billups, Channell, & Zachos, 2002; Diester‐Haass et al., 2011; Pusz, Thunell, & Miller, 2011; Wade & Pälike, 2004) indicates the global validity of the trends observed at ODP Site 1218. They are the likely expression of overall long‐term changes in carbon burial and primary productivity. Important in this respect is the observation that long‐term maxima in the $\delta^{13}C_{\text{benthic}}$ archive coincide both with long‐term cooling and warming trends (Figure 1).

Even if it is not possible to provide orbital‐scale time resolution for the periods of increased phosphogenesis and phosphorite accumulation at La Purísima, because of the rather poor correlation between $\delta^{13}C_{\text{org}}$ and the $\delta^{13}C_{\text{benthic}}$ data (Figure 8), it is possible to link these periods with long‐term cooling and glacial intervals of the late Oligocene and early Miocene. This observation is compatible with the above‐noted correlation between high in the $\delta^{13}C_{\text{benthic}}$ and the $\delta^{18}O_{\text{benthic}}$ records, as well as with the acceleration of the Oligocene and early Miocene phosphorus cycle due to glacial denudation. The notion that phosphogenesis and phosphorite accumulation did not completely cease during warming phases was already discussed by Schöllhorn (2016). She pointed out that increased phosphogenesis associated with both cooling and warming intervals during the Oligocene is not necessarily a contradiction, but likely related to the likelihood that glacial denudation may have induced a direct increase in (bio‐)chemical weathering by the increased production of very‐fine‐grained detrital material susceptible to (partial) dissolution, and that glacial legacy deposits may have been strongly weathered during subsequent warming phases (cf. Föllmi et al., 2009). These temporally separated increases in chemical weathering and phosphorus mobilization, especially during Oligocene cooling, but also during warming...
phases, were likely the main cause of increased phosphogenesis on a global scale and explain its association both with icehouse and greenhouse conditions.

This is an important deviation from the way in which the mobilization of biophile elements worked in an ice-free world such as during the Jurassic and Cretaceous, where higher temperature and humidity were the main responsible mechanisms for increased continental weathering and associated nutrient fluxes (Jenkyns, 2010). Feedback mechanisms between warming, more humidity, and more intense weathering under greenhouse conditions, and cooling and more intense glacial denudation under icehouse conditions were therefore different. The Cenozoic transition from greenhouse to icehouse conditions had therefore a decisive impact on the biosphere related to the more efficient transfer of nutrients to the oceans and within the oceans themselves, with a large influence on life and its evolution.

5 | CONCLUSIONS

The detailed stratigraphic, sedimentological, geochemical, mineralogical, and radiochronological analyses of a key section through upper Oligocene to lower Miocene organic-rich, siliceous, and phosphate-rich sediments at La Purísima, Baja California Sur (Mexico) reveal that phosphorite accumulation resulted largely from gravitational transport and concentration, aided by in situ phosphogenesis in an oxygen-depleted upwelling setting. The allochthonous, coated phosphatic grains were initially produced in a shallower and better-oxygenated environment. Their reworking was related to seismic and volcanic events, as implied by the close association between phosphate-rich turbidites and volcanic ash layers. LA-ICP-MS U-Pb dating of zircons extracted from the ash layers suggests that upwelling persisted between 27.84 ± 0.33 Ma and 21.21 ± 0.59 Ma, and was particularly strong around 27 and 24–22 Ma.

The Baja California phosphorites are representative of an episode of worldwide increased phosphogenesis, which started in the late Oligocene and lasted to the early Miocene. At La Purísima, they occur throughout the section, and the highest concentrations are observed for the time intervals between 28–25.5 Ma and 23.5–21.5 Ma, which correspond to the late Oligocene glacial maximum and the two glacial phases near the Oligocene–Miocene boundary (Mi1) and in the early Miocene (Mi1a). Their association with cooling episodes and glacial phases confirms the general observation that cooling was synchronous with more intense upwelling and the more efficient transfer of nutrients to the oceans, and within the oceans to thermocline waters by upwelling. The increased rates of nutrient mobilization on the continents are mainly related to the efficiency of glacial denudation processes and associated increase in nutrient mobilization and delivery. Subordinate episodes of phosphogenesis during the warmer phases are explained by intensified weathering of glacial legacy deposits during global warming.

The onset of glacial denudation during the Oligocene induced a new and more efficient way of nutrient mobilization and distribution, which was different from that in an ice-free world, where accelerations in nutrient fluxes were mainly related to rising temperature and humidity. These changes in weathering pattern and nutrient availability during the transition from greenhouse to icehouse conditions through the Oligocene and Miocene fundamentally changed feedback mechanisms between climate, geochemical cycles, and the evolution of life.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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