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A sedimentological model of organic-matter preservation and phosphogenesis in the Miocene Monterey Formation at Haskells Beach, Goleta (central California)

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ABSTRACT

At Haskells Beach, west of Santa Barbara (CA, U.S.A.), the upper part of the Miocene Monterey Formation is predominantly composed of organic-rich mudstone, which is interstratified with phosphatic laminae and lenses. Minor lithologies consist of dolomite, volcanic ash, porcelanite, chert and condensed phosphate. These sediments date from the end of the Serravallian and almost the entire Tortonian (11.05–7.85 Ma) based on calcareous nannofossils and the $\delta^{13}C_{org}$ record, which correlates well with the global record. Sediments have total organic-carbon values between 2.75 and 9.15 wt.% (average value = 6.48 wt.%; n = 61). Rock-Eval analyses show the dominance of type-II kerogen. The sediment accumulation rate varied between 5.9 and 84.7 m/Ma. Correspondingly, organic-carbon accumulation rates range between 0.08 and 1.43 g/cm^2/ky (average value = 0.48 g/cm^2/ky). Total phosphorus contents in the organic-rich mudstone vary between 0.001 and 3.48 wt.% and C_{org}/P_{org} ratios show high values of up to 4727 (average value = 2232), whereas C_{org}/P_{total} values are low (up to 185; average value = 52). This indicates that early diagenetic organic-matter degradation was a source of phosphate in phosphogenesis. In addition, other sources of phosphate were necessary in order to explain the abundance of phosphate relative to organic matter such as the transfer of dissolved inorganic phosphate into the sediments. Slumps, angular unconformities, erosive surfaces, reworked clasts and nodules, and condensed phosphatic layers suggest that hydrodynamic conditions were important and likely variable, leading to frequent erosion and sediment reworking. Under these circumstances, organic-matter was predominantly delivered during gravity-flow events, which were followed by longer periods of low sediment accumulation and phosphogenesis of the uppermost sediment layer. Associated pore occlusion by phosphate minerals may have considerably enhanced the preservation of organic-matter. During the early Late Miocene, a progressive change is observed from the mixed accumulation of organic, phosphate, biosilica and carbonate sediments, to the predominant accumulation of biosilica-rich sediments. This change is related to more intense upwelling, a shift of the upwelling center to the Californian coastline, and a leveling out of basin topography leading to a more even spread of biosilica.

1. Introduction

The Middle to Upper Miocene Monterey Formation of the central Californian coastal area is composed of a hemipelagic to pelagic succession, which contains sediments rich in organic matter, carbonate, phosphate and biosilica and diagenetic transformations such as dolomite, porcelanite and chert. The Monterey Formation is important for various reasons, as it represents (1) the prime oil source rock in California (Behl, 1999; Isaacs, 2001), (2) a model for diagenetic mineralization and transformation (e.g., phosphate, silica, carbonate, clay minerals; Baker and Kastner, 1981; Garrison et al., 1987; Compton, 1991; Behl and Garrison, 1994; Behl, 2011; Hoffmann-Sell et al., 2011; Berndmeyer et al., 2012), and (3) a corner stone in theories on Mid-Miocene climate change ("the Monterey hypothesis"; Vincent and Berger, 1985; Föllmi et al., 2005). Excellent exposures of the Monterey Formation occur along the Pacific coast west of Santa Barbara, and they were described in numerous publications (Arends and Blake, 1986; Flower and Kennett, 1993, 1994; Föllmi et al., 2005; Garrison et al., 1994; Hornafius, 1994; Isaacs, 1981, 2001; John et al., 2002).

Here we provide a detailed description of the outcrop through the upper part of the Monterey Formation and the overlying Sisquoc Formation, exposed at Haskells Beach, Goleta, and propose a new, detailed stratigraphy, which is based on calcareous nannofossils and carbon-isotope stratigraphy (Fig. 1). We furthermore investigated the sedimentology in detail and measured TOC and P contents in a systematic way,

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in order to verify and improve a sedimentary model in which organic-matter preservation and phosphogenesis are explained and reconciled. Of interest with this respect is an analysis of C_{org}/P_{tot} and C_{org}/P_{org} ratios in the organic-rich mudrock, which reveal that organic matter was a source of authigenic phosphate, but that additional sources of phosphate must be invoked in order to explain the abundance of phosphate relative to preserved organic matter. In general, it results that organic-matter preservation remains important following the Mid-Miocene cooling episode and that rates of organic-carbon preservation are comparable to those calculated for the Middle Miocene (Föllmi et al., 2005). Furthermore, the dynamic sedimentary regime already invoked to explain organic-carbon preservation and phosphogenesis for the Middle Miocene part of the Monterey Formation, continued to play a comparable role during the early Late Miocene.

2. Analytical methods

The section through the upper part of the Monterey Formation and the base of the overlying Sisquoc Formation at Haskells Beach was measured in detail and sampled at 1-meter intervals in the organic-rich mudstone for geochemical and mineralogical analyses and 3-meter intervals in all lithologies for thin sections. Collected samples were analyzed for their mineralogy and geochemistry at the University of Lausanne. Their bulk-rock mineral composition was obtained by X-ray diffraction (XRD) using a Scintag XRD 2000 Diffractometer following the procedures in Kübler (1983) and Adatte et al. (1996) with an accuracy of 5%. Major element concentrations were determined by X-ray fluorescence (XRF) using a XRF Philips PW2400 spectrometer with an accuracy between 1 and 7%. Total phosphorus analyses were conducted using the ascorbic and molybdate blue methods and employing a UV/Vis Perkin Elmer Lambda 25 spectrophotometer with an accuracy of 5% (Eaton et al., 1995; Mort et al., 2007). The TOC and C_{min} contents were analyzed by a Rock-Eval™6 device (Behar et al., 2001) with an analytical error of $<0.1\%$. The SEDEX sequential extraction procedure (Ruttenberg, 1992; Anderson and Delaney, 2000) was used to determine the content of different phosphorus species. The carbon-isotope composition of TOC ($\delta^{13}C_{org}$) was determined by the flash combustion method in a Carlo Erba 1108 elemental analyzer connected to a Thermo Fisher Scientific Delta V isotope-ratio mass spectrometer. The $\delta^{13}C$ values are reported in per mil (‰) relative to VPDB. Reproducibility and accuracy were better than ± 0.1‰ for $\delta^{13}C$. Calcite-containing sample aliquots were studied for their calcareous nannofossil contents using the settling method described in De Kaenel and Villa (1996).

3. Results

3.1. Stratigraphy

The Monterey Formation is subdivided into three members: (1) a lower calcareous member; (2) a middle carbonaceous and phosphate-rich member; and (3) an upper siliceous member (Bramlette, 1946; Isaacs, 1981, 1984, 2001; Pisciotto and Garrison, 1981; Garrison et al., 1987, 1994; Garrison and Kastner, 1990; Mackinnon, 1989; Hornafius, 1991; Behl, 1992, 1999; White, 1992; White et al., 1992; Chang and Grimm, 1999; Chaika and Williams, 2001; Surpless et al., 2009). The Haskells Beach section exposes the upper part of the middle member and the entire upper member, and both consist predominantly of mudstone and include secondary lithologies such as porcelanite and dolomite (Fig. 2). There is no clear contact between the middle and upper members and the transition is characterized by a gradual decrease in size and disappearance of dolomite beds, which is paralleled by an increase in porcelanite toward the top of the section, as shown by XRD analyses (see below). The Haskells Beach section is approximately 140 m thick and includes the contact with the overlying Sisquoc Formation. The quality of the outcrops varies from poor – mainly in the intertidal zone –, to very good, showing well-exposed small-scale sedimentological structures. In the middle part of the Haskells Beach section, an approximately 55 m deep incision into the sediments of the Monterey Formation was observed, which is infilled by slumped and conglomeratic sediments of the overlying Sisquoc Formation. Those sediments were interpreted as a conglomeratic infill of a large submarine channel or a canyon (Hornafius, 1994; cf. also Surpless et al., 2009). Otherwise, the contact between the Monterey and Sisquoc Formations is placed at the base of a series of three phosphatic conglomerate beds (Minor et al., 2009).

3.2. Sediment types and constituents

3.2.1. Minerals

The minerals identified in the measured section are authigenic, biogenic, detrital or secondary in origin. Authigenic minerals include phosphate, mainly as carbonate fluor-apatite (CFA, francolite), opal CT, quartz, dolomite, and pyrite. The main biogenic minerals are calcite, present in the form of calcareous nannofossils and foraminifera, and opal A, in the form of diatoms and radiolaria. Feldspar, phyllosilicates and a non-estimated part of quartz (mainly in agglutinated foraminifera) represent the detrital fraction and may have been transferred from the adjacent continent and/or originated from volcanic events. Secondary minerals include gypsum, probably derived from pyrite weathering and/or SO_4-rich fluids reacting with calcite, and sea salt.

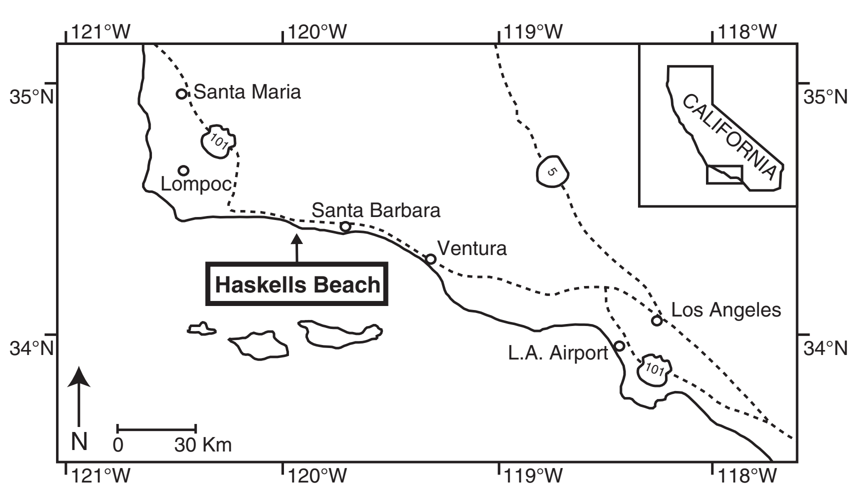

Fig. 1. Location of the Haskells Beach section.