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Iron availability as a dominant control on the primary composition and diagenetic overprint of organic-matter-rich rocks

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ABSTRACT

Iron is known to stimulate surface ocean productivity, as well as intervene with bacterially-mediated processes of organic matter remineralization, during early diagenesis. In this paper, we examine the influence of iron supply on the geochemistry (trace metals, $\delta^{34}S$, organic matter) of sedimentary rocks deposited in a clastic-dominated marine ramp environment. To this end, we studied two Late Jurassic formations of the Boulonnais area (North-France). Both formations were deposited under quite similar conditions, but they differ in the reactive-iron supply they received. Only one of the two formations was affected by the particulate iron shuttle process. Our results indicate that 1) the iron shuttle may be recorded through concomitant enrichments in P, Mo, As and Sb; 2) a limited reactive-iron supply will allow the sulfurization of organic matter, even in a context of moderate productivity. Thus sulfurization can be a factor favoring a noticeable accumulation of organic matter: iron may thus be an important agent in the C cycle.

1. Introduction

The geological rocks of the Late Jurassic times (Kimmeridgian–Tithonian), cropping out along the Boulonnais shore (Strait of Dover, Northern France; Fig. 1), represent a proximal, lateral equivalent of the Kimmeridge Clay Formation (when used with a proper name, the word Formation will be abbreviated as Fm.), famous as a major petroleum source rock. These formations accumulated in a clastic-dominated ramp environment where the sedimentary succession is made up of an alternation of marlstone-dominated formations (called "Argiles") and sandstone-dominated formations (termed "Grès") reflecting a range of water depths from lower offshore to shoreface settings, respectively (e.g., Wignall, 1991; Ramanampisoa et al., 1992; Proust et al., 1995; Deconinck et al., 1996; Wignall and Newton, 2001; Williams et al., 2001; Al-Ramadan et al., 2005). In the present paper we compare two formations, namely the Argiles de Châtillon Fm. and the Bancs Jumeaux Fm. that accumulated in similar conditions: a relatively rapidly rising sea level (Taylor et al., 2001; Williams et al., 2001) and "normal" marine productivity in the sense that it was calculated that surface-water productivity was in the range of present-day open shelves (Tribovillard et al., 2001). Both formations show a comparable marly facies with relatively abundant marine organic matter (OM), but they also yield marked differences. Horizons within the Argiles de Châtillon Fm. contain abundant OM that is rich in sulfur (sulfurized OM), whereas the Bancs Jumeaux Fm. does not yield such S-richOM, but is instead rich in phosphatized biogenic clasts, typically bivalve shells. The two formations show contrasting magnetic parameters. In this paper, we further explore the differences between these formations, notably through the examination of the trace-metal and S-isotope composition, and emphasize the role played during authigenesis/diagenesis. Our focus is on determining whether reactive-iron availability could be an important factor controlling OM storage.

2. Geological framework and previous results

The shoreface sandstones and offshore mudrocks of the Kimmeridgian–Tithonian times are located along the Boulonnais coast of the Dover Strait (Fig. 1) and were deposited on the northwest European epicratonic platform, forming an embayment into the shoreline. The mudstones and shales of the Argiles de Châtillon (*autissiodorensis* + *gigas–elegans* ammonite zones, straddling the Kimmeridgian–Tithonian boundary), and the transition between the Argiles de la Crèche Fm. and Argiles de Wimereux Fm. (the so-called Bancs Jumeaux Fm., *wheatleyensis* + *pectinatus* ammonite zones,

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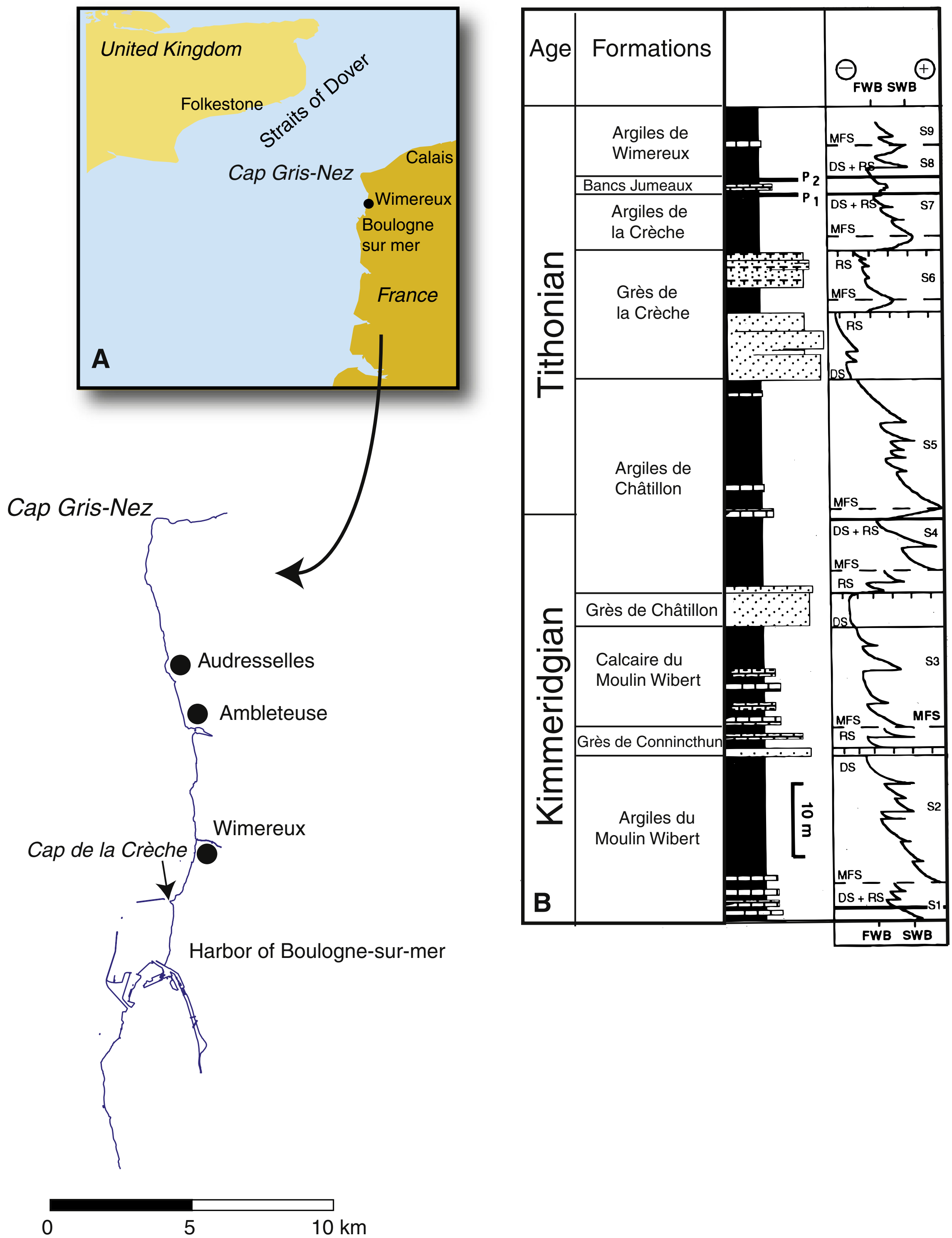

Fig. 1. Maps showing the location of the study area, between the Gris Nez Cape and the city of Wimereux. Right-hand side: simplified lithostratigraphic log of the Late Jurassic formations cropping alongshore the Boulonnais (after Deconinck et al., 1996). FWB and SWB stand for fair-weather wave base and storm-weather wave base, respectively. P1 and P2 stand for the two horizons rich in phosphatized shells.

Tithonian) represent a low-energy shelf facies deposited below fair-weather wave base, but with some storm influence expressed as thin shelly limestone interbeds and coquina beds (Wignall, 1991; Proust et al., 1995; Deconinck et al., 1996; Wignall and Newton, 2001; Williams et al., 2001). Similar to the more distal, time-equivalent, shales and mudstones of the Kimmeridge Clay Fm., exposed on the Dorset (UK) coast, these sediments are also organic-rich (Tribovillard et al., 2001). Detailed descriptions of the lithofacies and stratigraphy (including sequence stratigraphy) can be found in Proust (1994), Proust et al. (1993, 1995), Herbin et al. (1995); Deconinck et al. (1996); Wignall (1991); Wignall and Newton (2001); Williams et al. (2001), Al-Ramadan et al. (2005) and Braaksma et al. (2006).