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Research paper

# Paleo-redox depositional conditions inferred from trace metal accumulation in two Cretaceous-Paleocene organic-rich sequences from Central Egypt



GFOLOGY



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## ABSTRACT

Cretaceous-Paleocene organic-rich sediments in Egypt occur as an east-west trending belt extending from the Quseir-Safaga district (Red Sea) to the Kharga-Dakhla (Western Desert) region. They are associated with the Duwi Formation (phosphate-bearing) and the overlying Dakhla Formation (deeper epicontinental shale/marl). This study aims to reconstruct the paleo-redox conditions during deposition of these thermally immature organic-rich sediments using carbon-sulfur-iron systematics and trace metal proxies in two cores, one each from the Quseir and Abu Tartur areas. Paleoproductivity, based on P content, seems to have been higher in the Quseir section than in the Abu Tartur section. The Quseir section also records a relatively greater occurrence of anoxic conditions during the accumulation of these sediments than the Abu Tartur section. This difference is indicated by its markedly higher total organic carbon (TOC) content as well as higher contributions of redox-sensitive and sulfide-forming metals (Mo, U, Ni, V, and Co). A weak correlation exists between S and TOC, and a positive S intercept  $(>1)$  was observed in most of the rock units of the study sections. A high consistency between the TOC-S-Fe relations and trace metals findings was found. The uppermost Duwi and the lowermost Dakhla strata, which have the highest TOC and represent a maximum sea transgression during the Late Cretaceous, have the highest contents of redox-sensitive trace metals. The carbonate-dominated transgressive Baris and Beida members of the Dakhla Formation record relatively stronger oxygen-depleted conditions during their accumulation than others, which led to relatively higher TOC contents and redox-sensitive metal accumulations. A scenario for the environmental conditions that existed during the deposition of these organic-rich successions, based on compiled trace metals and TOC-S-Fe implications, is reconstructed here.

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### 1. Introduction

Under anoxic oceanographic conditions, the fluxes and transfer rates of organic matter and some trace metals to the seafloor are high and can result in significant drawdown of trace metal concentrations in seawater ([Ross and Bustin, 2009](#page--1-0)). The resulting organic-rich sediments are often enriched in redox-sensitive metals such as U, Cu and Ni and in insoluble sulfides of Mo, V, Cd, Zn and sometimes Co (Brumsack, 2006; März, 2007; Hetzel et al., [2009\)](#page--1-0). The sources and delivery of trace metals are often difficult to differentiate because of the multilinked mechanisms, such as

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bio-concentration, terrestrial input and diagenetic enrichment, that affect trace metal accumulation in organic-rich sediments ([Brumsack, 2006; Ross and Bustin, 2009](#page--1-0)). However, the distributions of co-occurring major elements such as Al, Ti, Fe, and S, which are relatively stable during diagenesis, can help to explain trace metal enrichments with regard to their sources and depositional settings ([Brumsack, 2006](#page--1-0)).

Both biotic and abiotic processes participate in the removal of trace metals from the water column and their accumulation in sediments ([Tribovillard et al., 2006\)](#page--1-0). Biotic processes comprise the uptake of trace metals by phytoplankton as a nutrient. Abiotic processes usually occur in sub-to anoxic media through diffusion of dissolved trace metals from the water column, across the sediment- Corresponding author. The corresponding author. Water interface, and through post-depositional remobilization.

Trace metal compositions are commonly used in paleoceanographic research to evaluate past redox conditions in marine systems [\(Algeo and Maynard, 2004; Brumsack, 2006; Algeo and Rowe,](#page--1-0) [2012](#page--1-0)).

Many marine basins existed along a broad marine continental shelf across northeast Africa during the Late Cretaceous-Paleocene time period. Their sedimentation processes were influenced by global warming that favoured development of anoxic conditions, leading to the deposition of organic-rich sediments [\(Robinson and](#page--1-0) [Engel, 1993](#page--1-0)). These sediments are excellent oil source rocks; their thermal maturation has produced gigantic oil fields in the Middle East (e.g., [Saleh, 2011\)](#page--1-0). However, some of these rocks have not experienced adequate catagenesis, and as a consequence massive immature black (oil) shale sequences exist in Egypt ([El-Shafeiy](#page--1-0) [et al., 2014\)](#page--1-0). The Late Cretaceous-Paleocene black shales occur as an east-west trending belt extending from the Quseir-Safaga district along the Red Sea to the Kharga-Dakhla landscape and the Abu Tartur Plateau in the Western Desert, passing through the Nile Valley (Fig. 1). They are associated with the phosphate bearing Duwi Fm. and the overlying epicontinental shale/marl of the Dakhla Fm.

To our knowledge, most of the previous geochemical studies on the Late Cretaceous-Paleocene organic-rich sediments of Egypt have focused on the unweathered black shale samples of the Duwi Formation accessible from phosphorite mines. In this study, we present organic and inorganic geochemical data for both the Duwi and Dakhla organic-rich sediments from the Abu Tartur and Quseir areas for comparison. Continuously cored samples were collected from bore holes drilled in 2007 and 2008 (Fig. 1). Because no single universal indicator for paleo-redox conditions is recognized, a study that used several proxies and evaluated the collective results was performed.

The purpose of this manuscript is four fold:

1. To present trace metal proxies for paleo-redox conditions of the thermally immature organic-rich sedimentary sequences.



Fig. 1. Satellite image for Egypt shows the two study locations (red boxes) with the boreholes marked as yellow circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

- 2. To evaluate factors influencing the deposition of these organicrich sediments, including productivity, bottom-water conditions, trace-metal sequestration, and post-depositional changes, within the cores. These factors will be compared between the two drilled sequences, more than 400 km apart, to yield a regional rather than a local picture of the paleo-depositional conditions and their variations.
- 3. To apply TOC-S-Fe ternary diagram to distinguish the paleoenvironmental conditions contributing to the differences in the organic-rich facies.
- 4. To reconstruct the paleo-environmental conditions leading to the deposition of key intervals from the studied sequences.

### 2. Stratigraphic setting

The **Duwi** Formation constitutes a part of the extensive Middle East to North African phosphogenic belt [\(Baioumy and](#page--1-0) [Tada, 2005](#page--1-0)). In addition to the phosphates, it is composed of organic-rich shale, glauconite and/or oyster limestone, chert, and silt-to sandstone (Bein and Amit, 1982; Tröger, 1984; [Germann et al., 1985; Mikbel and Abed, 1985; Notholt, 1985;](#page--1-0) [Ganz et al., 1987; Abed and Al-Agha, 1989; Glenn and Arthur,](#page--1-0) [1990; El-Kammar 1993](#page--1-0) and references therein). The marine Dakhla Formation is characterized mainly by foraminifera-rich shale and/or marl with limestone and subordinate siltstone intercalations.

[Baioumy and Tada \(2005\)](#page--1-0) subdivided the Duwi Formation into Lower, Middle, Upper, and Uppermost members. Deposition of the Duwi Formation represents a generally marine transgressive stage of the Late Cretaceous in Egypt (See [El-Shafeiy et al., 2014](#page--1-0) for details). Two transgressive cycles have been identified in the Duwi Formation. The first is recorded in the Lower member (transgressive system tract "TST"; [Table 1\)](#page--1-0) and reached a sea level maximum during accumulation of the Middle member organic-rich shale of the highstand system tract (HST; [Table 1\)](#page--1-0). A major regression, with lowstand system tract (LST), started at the boundary between the Middle and Upper members. The second transgressive cycle is recorded at the base of the Uppermost member, and continued into the overlying Dakhla Formation ([Table 1\)](#page--1-0).

The Dakhla Formation in the Red Sea area is subdivided into the Hamama and Beida members in ascending order that are separated by an unconformity representing the Cretaceous-Paleocene boundary ([Abdel Razik, 1972; Luger, 1988; Awad et al., 1992; Zalat](#page--1-0) [et al., 2008](#page--1-0)). [Zalat et al. \(2008\)](#page--1-0) subsequently subdivided the Dakhla Formation into two deepening upward cycles. The lower one corresponds to the Hamama member and is composed of a lime-mudstone and foraminiferal wackestone succession. The upper cycle corresponds to the Beida member and is represented by an intercalation of foraminiferal shale and lime-mudstone interbeds.

On the Abu Tartur Plateau, the Dakhla Formation has been subdivided by [Awad and Ghobrial \(1965\)](#page--1-0) into Mawhoob, Baris and Kharga members in ascending order. The lower part of the upper Kharga shale is replaced laterally by limestone with shale interbeds that is named the Kurkur Formation [\(Issawi, 1968\)](#page--1-0). The lower Mawhoob member (HST) was followed by a marine flooding that led to deposition of deep sub-tidal shales alternating with shallow sub-tidal wackestone/floatstones of the Baris member (TST; [El-](#page--1-0)[Azabi and Farouk, 2010\)](#page--1-0). Afterwards, the lower Kharga member (thin sub-tidal shale) was deposited in the beginning of regional uplift and relative sea level fall and represents the highstand system tract.

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