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Carbon isotope records in a Mesoproterozoic epicratonic sea: Carbon cycling in a low-oxygen world

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ABSTRACT

Carbon isotope profiles of sedimentary strata are widely used as both a tool for stratigraphic correlation and as a mechanism for inferring important changes in Earth's biogeochemical cycles. Chemostratigraphic interpretations, however, often rely on the assumption that the isotopic composition of dissolved inorganic carbon (DIC) in the surface oceans is broadly homogeneous. At times of globally high sea level, when epicratonic (epeiric) environments dominate our sedimentary record, carbon isotope records reveal substantial lateral variability. Here we investigate lateral variability in the marine carbon isotope record from pericratonic to epicratonic environments of the Mesoproterozoic (~1.1 Ga) Atar/El Mreiti Groups of the Taoudeni Basin, West Africa. Restricted-marine epicratonic environments are consistently 2–4‰ lighter than open-marine pericratonic environments, suggesting input of an isotopically light carbon source that preferentially affected epicratonic environments. In contrast to epicratonic environments in the Paleozoic, where input of isotopically light carbon is generally attributed to input of terrestrial organic matter, we suggest that in situ remineralization of organic carbon via anaerobic microbial cycling drove observed isotopic variability. Within epicratonic El Mreiti Group strata, the extent of organic matter remineralization (and thus degree of ^{13}C depletion) is correlated with water depth, and associated with distinct differences in both total organic carbon (TOC) and pyrite concentration, suggesting a potential linkage to both the persistence of anoxia and the availability of sulfate within epicratonic environments. In such settings, the isotopic effects of organic carbon remineralization are potentially enhanced by either methane oxidation following methanogenic decomposition, or the intermittent oxidation of an enhanced dissolved organic carbon (DOC) pool.

1. Introduction

The isotopic composition of carbon has been measured on both carbonate minerals and organic matter and, particularly in ancient sedimentary rocks, is a primary dataset for inferring changes in the Earth's biogeochemical cycles (Kump and Arthur, 1999; Des Marais, 2001; Berner et al., 2003; Hayes and Waldbauer, 2006). Many of the important biospheric changes inferred from the fossil record are marked by distinct carbon isotope excursions (Anbar and Knoll, 2002; Rothman et al., 2003; Payne et al., 2004; Melezhik et al., 2005; Fike et al., 2006; Gill et al., 2011), suggesting an intimate link between perturbations to the global carbon cycle, oceanic ventilation, and biotic evolution (see Och and Shields-Zhou, 2012 for review). Carbon isotopes have also proven critical for stratigraphic correlation because dissolved inorganic carbon (DIC) in the oceans is generally well mixed and has a relatively short residence time, thus providing the opportunity for high-resolution isotopic signals. This correlation tool has proved particularly useful in the Proterozoic, where biostratigraphy is not a viable option, and changes in carbon isotopes are, at least in the latter Proterozoic, substantially large (cf. Halverson et al., 2005, 2010).

Despite broad agreement on the interpretation of marine carbon isotope records, several recent studies have suggested that traditional views may understate the complexity of marine carbon isotopes. The generally robust nature of the isotope record, for instance, has been used to argue against diagenesis as a mechanism for carbon isotope variation (see Knauth and Kennedy, 2009; Derry, 2010; Swart and Kennedy, 2012 for an alternative perspective), even in rocks that have clearly experienced at least some degree of diagenetic alteration. In another example, increased coupling of marine organic and inorganic carbon reservoirs, potentially driven by elevated marine carbonate saturation (Grotzinger and Kasting, 1993) and accentuated by nutrient-limited productivity (Anbar and Knoll, 2002), may result in reduced sensitivity of the marine carbon isotope record (Bartley and Kah, 2004). Similarly, decoupling of marine organic and inorganic carbon reservoirs, driven by low levels of biospheric oxygen—with or without the presence of oceanic stratification—may foster artificially large

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isotopic excursions (Rothman et al., 2003; see also Johnston et al., 2012).

Even the homogeneity of carbon isotopes in surface oceans of the geologic past has been called into question, particularly in the case of chemostratigraphic records derived from epicratonic (epeiric) seas that may have experienced restricted connectivity with the global ocean (Holmden et al., 1998; Cowen et al., 2005; Panchuk et al., 2005, 2006). Such environments can have substantial differences in both water volume and water residence times, which can magnify the influence of discrete (and potentially local) carbon sources (Patterson and Walter, 1994; Holmden et al., 1998; Panchuk et al., 2006). This particular observation may be critical when evaluating geologically ancient successions, many of which were deposited atop stable cratons during sea level highstand.

We suggest that at no time in Earth history should these potential effects on the marine carbon isotope record be more apparent than in the late Mesoproterozoic. Non-glacial climates of the Mesoproterozoic resulted in globally high sea levels and extensive epicratonic deposition (Kah et al., 2012). Under these conditions, a combination of continental elevation (i.e., substrate topography) and eustatic sea level may have been the controlling factor determining the degree of advective mixing between pericratonic shelves and broad expanses of epicratonic deposition. Furthermore, low oxygen conditions at the Earth's surface (Anbar and Knoll, 2002; Shen et al., 2002, 2003; Kah et al., 2004; Arnold et al., 2004; Brocks et al., 2005; Scott et al., 2008; Blumenberg et al., 2012) may have acted to enhance regional variability within the carbon cycle. In fact, existing carbon isotope data from this interval (cf. Fig. 10, Kah et al., 2012) reveal not only globally traceable stratigraphic excursions, but also substantial differences in the magnitude of these excursions between basins and between discrete depositional environments within single basins (Fig. 1).

The late Mesoproterozoic Atar/El Mreiti Group is a laterally extensive package of marine strata that was deposited in the Taoudeni Basin, which spans the West African craton. Existing isotopic and elemental data (Kah et al., 2012) indicate that chemically distinct water masses occurred at different times in pericratonic environments, suggesting the potential for interaction with isotopically distinct epicratonic and off-shore water masses (Kah and Bartley, 2011; Kah et al., 2012). Here we provide the first complete, high-resolution isotopic and elemental profile of carbonate from the El Mreiti Group deposited deep within the craton interior. Robust stratigraphic correlation has previously been established between Atar and El Mreiti group strata (Teal and Kah, 2005; Kah et al., 2012), allowing this study to directly compare isotopic and elemental trends across the epicratonic sea that covered the West African craton in the Mesoproterozoic. This is the first study to date to investigate the nature of potentially distinct water masses across time correlative units of a single Mesoproterozoic basin, with emphasis on relating isotopic records to processes capable of generating isotopic heterogeneity. Furthermore, our findings may provide important constraints on the environmental conditions that prevailed at a time of critical transition in the evolution of the Earth's biosphere.

2. Evolution of the Taoudeni Basin

2.1. Geologic background

The Taoudeni Basin is an areally extensive (>1,750,000 km^2) sedimentary basin formed atop crystalline basement of the West African craton. Basement rocks are exposed to both the north (Reguibat Shield) and south (Leo-Man Shield) of the basin, and consist of deformed Archean amphibolite and quartzo-feldspathic gneiss intruded by late Paleoproterozoic granite (Trompette and Carozzi, 1994; Villeneuve and Cornée, 1994; Schofield et al., 2006). The structural evolution of the Taoudeni Basin initiated via a series of NNE–SSW oriented basement normal faults and crustal thinning associated with formation of isolated horsts and grabens (Bronner et al., 1980). Proterozoic sedimentation began with continental to marine, dominantly siliciclastic strata of the Char (in Mauritania) and Douik (in Algeria) groups (Benan and Deynoux, 1988; Rahmani et al., 2009). Present-day exposure of these basal siliciclastic units is restricted to two prominent grabens that intersect the northern edge of the Taoudeni Basin. The thickness of these units varies dramatically, from 0 to >400 m in outcrop (Benan and Deynoux, 1988) and can be traced to an unknown extent at depth (Rahmani et al., 2009), reflecting deposition that was controlled by changes in basement topography during extension.

A basinwide unconformity marks the boundary between basal siliciclastic strata and the overlying Atar/El Mreiti Groups. Although of unknown duration, this period of non-deposition reflects cessation of earlier extensional tectonics, and formation of a regional peneplain (Bertrand-Sarfati and Moussine-Pouchkine, 1988; Benan and Deynoux, 1988). Resumption of sedimentary deposition is marked by lithologically varied siliciclastic and carbonate strata of the Atar/El Mreiti Groups, whose facies and thickness (see Section 2.4) were controlled predominantly by patterns of sea level and regional subsidence, with localized variation resulting from reactivation of basin normal faults (Moussine-Pouchkine and Bertrand-Sarfati, 1997). A second basinwide unconformity truncates predominantly carbonate strata of the upper Atar/El Mreiti Groups and is overlain by siliciclastic marine strata of the Assabet el Hassiane Group (Girard et al., 1989), glacio-marine to glacio-eolian deposition of the Jbéliat and Téniagouri groups (Deynoux, 1980; Deynoux et al., 1989; Alavaro et al., 2007; Shields et al., 2007), and marine to continental deposition of the overlying Nouatil Group (Alavaro et al., 2007). Proterozoic sedimentary strata of the Taoudeni Basin are then overlain by Early to Late Paleozoic continental strata (Deynoux, 1980).

2.2. Chronology of Proterozoic strata

Historically, the age of Proterozoic strata within the Taoudeni Basin was only poorly constrained by Rb–Sr analyses performed on sedimentary glauconite and illite (Clauer, 1976, 1981; Clauer et al., 1982). These analyses yielded ages ranging from 998 ± 32 Ma for deposition of the lowermost Char Group, to ~695 Ma for deposition of the Assabet el Hassiane Group. Geochronology of Atar/El Mreiti Group strata provide ages of 890 ± 35 Ma for unit I-5 (Atar/Touirist Formation), 874 ± 22 Ma for unit I-6 (Oued Tarioufet/Aguelt el Mabha and Gouamir formations), 866 ± 67 Ma for unit I-8 (Oued Terrarit Formation), and 775 ± 52 Ma for unit I-10 (Aouleigate Formation) (Clauer, 1976, 1981; Clauer et al., 1982). Although Rb–Sr ages clearly represent diagenetic mineralization, the consistent decrease in age through the stratigraphic column—as well as correlation of overlying glaciogenic units with global-scale Cryogenian glaciation—was long used to argue for early diagenetic stabilization of clay minerals and, thus, Neoproterozoic deposition for the majority of Taoudeni Basin strata.

More recently, a combination of chemostratigraphic and new geochronologic data have constrained the majority of Proterozoic deposition within the Taoudeni Basin (i.e. all deposition prior to the sub-Assabet el Hassiane Group unconformity) to be Mesoproterozoic in age (Rooney et al., 2010; Kah et al., 2012). Carbon isotope chemostratigraphy of Atar/El Mreiti Group strata (Teal and Kah, 2005; Kah et al., 2012) records moderately positive values (<4‰) punctuated by discrete, low-magnitude negative excursions (to approximately −2.5‰) that are consistent with global marine carbon isotope values between approximately 1.2 and 1.1 Ga (Kah et al., 1999, 2012; and references therein). These values are distinctly more positive and show greater isotopic variation than those