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Geochemical characterization of the Marinoan “Cap Carbonate” of the Niari-Nyanga Basin (Central Africa)

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ABSTRACT

Despite recent works on the Schisto-calcaire Group of the West-Congolian Supergroup in Central Africa, Neoproterozoic Cap Carbonate have not been well documented in the Niari-Nyanga basin that extends from Gabon to Angola. The couplet “Cap Carbonate (SCIa) and Upper Diamictite”, that is a marker of the “Snowball Earth event” was studied in 5 sections from the Niari-Nyanga basin and in one section from the external zone of the Mayombe folded belt (MFB). Our paper presents a high-resolution data set based on results from petrography, geochemistry, mineralogy and stable isotope studies performed on Cap Carbonate samples. The estimation of the illite crystallinity indexes indicates different degrees of post-sedimentary transformations evolving from deep diagenesis in the syncline basin to an epimetamorphism in the external zone of the MFB. Thin-sections of rocks sampled in this latter section display metamorphic features materialized by recrystallization of minerals in a S_1 cleavage plane. Despite such an observation, all our samples clearly show preservation of primary petrographic structures such as biolaminations, fenestrae and peloids. Geochemical data leads us to highlight that the Cap Carbonate is composed by a variety of carbonate types. These results support the fact that the Cap Carbonate was derived from a combination of biological and chemical processes: organomineralization and chemical precipitation from supersaturated solutions, with a negligible impact of post-depositional transformations. For all the studied sections, stable isotope profiles display a drop in $\delta^{13}C$ values, from about −2.6‰ to −4‰, associated with $\delta^{18}O$ values ranging from −6‰ to −10‰. Moreover, the similarity of the isotopic profiles of the studied Cap Carbonate (from the Niari-Nyanga basin and the MFB) and the close fit to the expected Neoproterozoic $\delta^{13}C$ and $\delta^{18}O$ seawater values constitute a strong indication of a weak impact of a diagenetic to epimetamorphic evolution on the carbon isotopic signature of the SCIa Cap Carbonate. In the light of this data set, our isotopic records must be considered as a reliable tracer of the Marinoan Glaciation within the West-Congolian Supergroup.

1. Introduction

Most Neoproterozoic glaciations that have led to the “Snowball Earth Hypothesis” are documented at a global scale by glacial deposits overlain by carbonate sequences considered as “Cap Carbonate” (Kirschvink, 1992; Kennedy, 1996; Kennedy et al., 1998; Hoffman et al., 1998). Such glacial deposits are defined as tillites or diamictites comprising debris from various sources, e.g. from continental, glacio-fluvial or even marine origin. The carbonate sequences referred to as typical “Cap Carbonate” or Cap Carbonate *sensu stricto* are generally less than 35 m-thick (Kennedy, 1996; Kennedy et al., 1998; Hoffman and Schrag, 2002; Corkeron and George, 2001; Hoffman, 2011). Sometimes, upper carbonate sequences are associated with Cap Carbonate *s.s.*, which leads to consider them together as Cap Carbonate *s.l.*, with larger thicknesses, of many tens or hundreds of meters (Hoffman and Schrag, 2002; Sial et al., 2010). The Cap Carbonate *s.s.* are made up of various lithofaciès, including typical dolostones and limestones of shallow marine environments with, sometimes, microbial origin (Kennedy, 1996; Hoffman et al., 1998; Nédélec et al., 2007). These carbonates are linked to the marine transgression due to the Neoproterozoic

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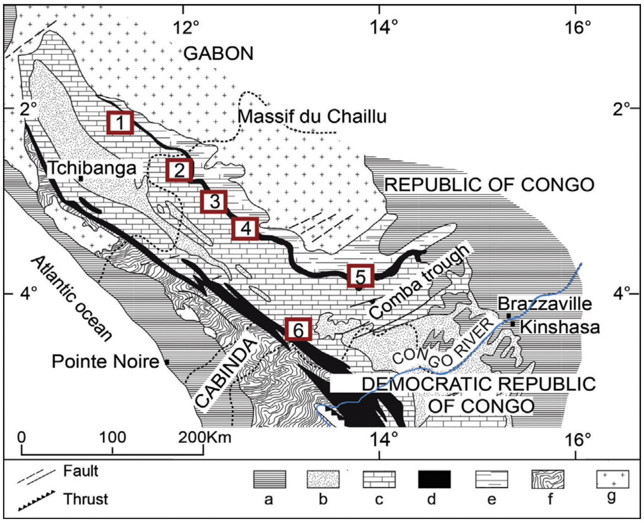

Fig. 1. Geological map of the MFB and the Niari-Nyanga basin with location of studied sections (from Dadet, 1969). (a) Meso-cenozoic; (b) Schisto-gréseux group; (c) Schisto-calcaire group; (d) Diamictite and grès group; (e) Bouenzian Formation; (f) Mayombian Supergroup; (g) Basement complex; 1: Lébamba section; 2: Dimani section; 3: Léboulou section; 4: Matalila section; 5: Nkengué section and 6: Mouyengo section.

ice sheet melting and document changes in climate condition from "icehouse" to "greenhouse" (Hoffman et al., 1998; Hoffman and Schrag, 2002). The diamictite and Cap Carbonate couplets materialize the most important Neoproterozoic climate events, the Sturtian (716.33 ± 0.54 Ma) and Marinoan (635.5 ± 1.2 Ma) glaciations that have been already extensively documented (Hoffmann et al., 2004; Macdonald et al., 2010).

The Marinoan Cap Carbonate usually displays typical structures and textures, such as tubestones, tepees, biolaminations, hummoky structures and peloids, associated with upward decreasing $\delta^{13}C$ values from the base to the top of the sequence (Kennedy, 1996; Kennedy et al., 1998; Hoffman and Schrag, 2002; Corsetti and Lorentz, 2006). On the other hand, Sturtian Cap Carbonate are characterized by black laminated limestones, rich in organic matter or sulphide, peloid grainstones, roll-up structures and slumped and overhanging domes of microbial origin (Kennedy et al., 1998; Vieira et al., 2007). Moreover, their lithostratigraphic column exhibits $\delta^{13}C$ values with an upward increasing trend (Kennedy et al., 1998; Santos et al., 2000; Hoffman and Schrag, 2002; Halverson et al., 2005; Vieira et al., 2007; Giddings and Wallace, 2009; Alvarenga et al., 2014). When radiometric data are not available, it has been proposed to consider Neoproterozoic carbonate $\delta^{13}C$ profiles as a chemostratigraphical proxy to decipher tentatively which glaciation is involved (Kennedy et al., 1998; Nogueira et al., 2003; Xiao et al., 2004; Porter et al., 2004; Font et al., 2006). However, the reliability of $\delta^{13}C$ records for Neoproterozoic carbonates has been questioned (Melezhik et al., 2001; Frimmel, 2010; Macouin et al., 2012). Indeed, diagenetic as well as metamorphic processes might alter the primary geochemical signatures and thus prevent the use of $\delta^{13}C$ profiles as a chemostratigraphical tool.

In Central Africa, the Archean to Paleoproterozoic Congo Craton underlies a very thick cover of Neoproterozoic to Paleozoic age and defined as the West-Congolian Supergroup (Dadet, 1969; Poidevin, 2007) (Figs. 1 and 2). From Gabon to Angola, this mega cover constitutes the Niari-Nyanga basin that is partly involved in the Pan-African Mayombe Chain, the so-called Mayombe folded belt (MFB) (Fig. 2). Two distinct glacial deposits were recognized in the lower part of the mega cover sequence: they are considered as the Lower and the Upper Diamictites (Dadet, 1969; Boudzoumou, 1986). The thin sequence mainly made up of carbonates and lying unconformably on the Upper Diamictite is known as the SCIa member and usually defined as the Marinoan Cap Carbonate (Frimmel et al., 2006; Préat et al., 2011). High-resolution sedimentological and isotopic studies focusing on this "Cap Carbonate" are relatively sparse (Caron et al., 2010, 2011). They lack to complete the low latitude African Cap Carbonate characterization as performed in Namibia (Hoffman et al., 1998) and West Africa (Porter et al., 2004; Shields et al., 2007; Nédélec et al., 2007).

Our paper presents a high-resolution sedimentological, mineralogical and geochemical characterization of the Marinoan Cap Carbonate (SCIa) sampled from five different sections of the Niari-Nyanga basin and one section of the (MFB). Our objectives are to determine the geochemical nature of the main components of this "Cap-Carbonate" and to estimate the degree of its post-depositional transformations, based on the illite crystallinity index. Finally, we discuss the impact of diagenetic processes on the isotopic signature of carbon ($\delta^{13}C$) and the use of the Cap Carbonate $\delta^{13}C$ as a tracer of the Marinoan Glaciation within the West-Congolian Supergroup.

2. Study area

2.1. Geological setting and lithostratigraphy

The Niari-Nyanga basin is a synclinal megastructure located at southwest of Central Africa and stretching from SW Gabon to NE Angola (Fig. 1). It includes mainly the Neoproterozoic cover and megasequences of the West-Congo craton and was defined as the West-Congolian Supergroup (Boudzoumou, 1986; Tack et al., 2001). Its eastern/north-eastern flank is subtabular and lies unconformably on the Archean to Paleoproterozoic basement complex known as the "Massif du Chaillu". Its western/southwestern flank is progressively folded southwards, before being involved in the MFB as its external zone (Fig. 1).

In Gabon and Congo, the lithostratigraphy of the West-Congolian Supergroup was described by several studies (Dadet, 1969; Boudzoumou, 1986; Boudzoumou and Trompette, 1988; Alvarez and Vicat, 1989) and recently reassessed by Prian et al. (2009) (Fig. 2). Two main glacial formations or diamictites called Lower and Upper Diamictite are defined within the West-Congolian Supergroup of the Niari-Nyanga basin. In absence of geochronological data, the Upper Diamictite was attributed to Marinoan glacial deposits (Frimmel et al., 2006; Poidevin, 2007; Préat et al., 2011). This diamictite unconformably overlies the Bouenzian Group and underlies the "Schisto-Calcaire Group". This group is 1500 m-thick and subdivided into four formations (SCI to SCIV; Dadet, 1969).

Our study focuses on the SCIa member of the SCI formation. This SCIa member, considered as the Marinoan Cap Carbonate *s.s.*, is 5–25 m-thick and unconformably overlies the Upper Diamictite, with smooth and/or sharp stratigraphic contact (Fig. 3a). For example, the sharp carbonate contact observed in the Lébamba section (Fig. 3a) is comparable to those of many other cap carbonate deposits portraying abrupt climate change (Nogueira et al., 2003; Sial et al., 2010; Hoffman, 2011). The cap carbonate SCIa corresponds to a thin-bedded carbonate sequence, with lenticular structure and plane to wavy laminations. Fine oblique stratifications, with oolitic and brecciated, as well as tepee and slump structures, can be observed in this sequence. In places, millimetric to centimetric interbeds of marls and siliceous shales, in which organic matter, opaque minerals and pyrite crystals can accumulate, characterize stylolite layers. This carbonate sequence is mainly made up of gray to pinkish dolostones, dolomitic limestones and limestones of centimetric to decametric thickness (Fig. 3a and b). A red to green sequence, comprising siltstones and shales, with lenses of marls, limestones and various sandstones, and defined as the SCIb member overlies the Marinoan Cap Carbonate (i.e. the