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# Microstructure-specific carbon isotopic signatures of organic matter from ∼3.5 Ga cherts of the Pilbara Craton support a biologic origin

Navot Morag[a,*], Kenneth H. Williford[a,b], Kouki Kitajima[a], Pascal Philippot[c], Martin J. Van Kranendonk[d], Kevin Lepot[a,e], Christophe Thomazo[c,f], John W. Valley[a]

[a] NASA Astrobiology Institute, WiscSIMS, Department of Geoscience, University of Wisconsin, 1215 W. Dayton St., Madison, WI 53706, USA
[b] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA
[c] Institut de Physique du Globe de Paris, CNRS and Université Denis Diderot, 4 place Jussieu, 75005 Paris Cedex, France
[d] School of Biological, Earth and Environmental Sciences, and Australian Centre for Astrobiology, University of New South Wales Australia, Kensington, NSW 2052, Australia
[e] Laboratoire Géosystèmes, Université Lille 1, CNRS UMR8217, 59655 Villeneuve d'Ascq, France
[f] UMR CNRS/uB5561 Biogéosciences UFR Sciences Vie Terre Environnement, Université de Bourgogne, 6 Bd. Gabriel, 21000 Dijon, France

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ABSTRACT

The ∼3.5 Ga Dresser Formation from the North Pole Dome of the Pilbara Craton (Western Australia) contains some of the oldest evidence for life on Earth. Here, we present a detailed study of microstructure-specific carbon isotopic composition of organic matter (OM) preserved in Dresser Formation bedded cherts and hydrothermal chert vein using in situ Secondary-Ion Mass Spectrometry (SIMS). The OM in these rocks occurs mainly as clots that, together with minor fine OM layers and laminae, are considered primary textures formed prior to host rock lithification. Other than rare OM-rich stylolites, no evidence was found for later OM migration beyond the micrometer scale. Average $\delta^{13}C$(OM) values in specific microstructural types range between −33.6‰ and −25.7‰. No correlation is seen between measured $\delta^{13}C$ values and H/C ratios in the studied OM microstructures. This lack of correlation and the low metamorphic grade of the rocks studied argue against significant modification of OM isotopic composition by later metamorphic alteration. It is thus concluded that the range of $\delta^{13}C$ values found in the samples represents primary OM isotopic variability. Within some individual samples variable $\delta^{13}C$(OM) values are correlated with specific microstructural types. This observation is not consistent with solely abiotic OM formation via Fisher-Tropsch type reactions. When compared with associated $\delta^{13}C$(ankerite) values, average $\delta^{13}C$(OM) values indicate C isotopic fractionation [$\Delta^{13}C$(Ank–OM)] of 25–33‰, which translates to dissolved $CO_2$–OM isotopic fractionation [$\Delta^{13}C(CO_2$–OM)] of 20–30‰. This range of $\Delta^{13}C(CO_2$–OM) is consistent with enzymatic C fixation via the Calvin cycle utilized by photoautotrophs and the reductive acetyl-CoA pathway utilized by chemolithoautotrophs. Photosynthetic OM formation is supported by the relatively shallow water depth inferred for the Dresser environment and the restricted occurrence of stromatolites to shallow water deposits in this unit, whereas chemolithosynthesis is supported by the abundance of OM in sub-seafloor hydrothermal chert veins. The range of $\delta^{13}C$(OM) values observed in the samples may therefore represent the remains of different organisms utilizing different C-fixation pathways. Other biologic effects, such as the growth rate and density of microbial communities, and further heterotrophic overprinting of the autotrophic biomass may have also contributed to the observed range of $\delta^{13}C$(OM) values.



## 1. Introduction

The North Pole Dome of the Pilbara Craton in Western Australia is well-known as the site of Earth's oldest putative stromatolites and microfossils occurring in ca. 3.5 Ga bedded chert-barite deposits of the Dresser Formation of the Warrawoona Group (Awramik et al., 1983; Walter et al., 1980). Although the biogenicity of these early structures have been debated (Buick, 1984, 1990; Buick et al., 1981), there is ample evidence in support of the existence of an early biosphere in the Dresser Formation, including the link between alleged biogenic structures and organic matter (OM) distribution (Glikson et al., 2008; Harris et al., 2009; Ueno et al.,

* Corresponding author.
*E-mail address:* morag@wisc.edu (N. Morag).

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2004; Van Kranendonk, 2011; Van Kranendonk et al., 2008), the isotopic signature of sulfur in microscopic sulfides, which suggest sulfur-based metabolism (Philippot et al., 2007; Shen et al., 2001; Ueno et al., 2008), and the carbon isotopic composition of methane in fluid inclusions, which is similar to that of microbially produced methane (Ueno et al., 2006). One of the prominent features of the Dresser Formation, and the Warrawoona Group in general, is the common occurrence of black-gray OM-bearing cherts. These cherts occur both as layered cherts interbedded within the stratigraphic succession and as hydrothermal veins–sometimes referred to as 'silica dikes', which cut across the local stratigraphy before truncating abruptly at specific overlying stratigraphic horizons, interpreted as the fossil seafloor, where they usually interfinger with the bedded cherts (e.g. Lindsay et al., 2005; Nijman et al., 1999; Van Kranendonk, 2006; Van Kranendonk et al., 2008). The source of OM contained in these cherts is enigmatic and may have significant implications regarding the emergence of early Archean biosphere – is it biogenic, and thus indicative of early life (e.g. Ueno et al., 2004), or abiogenic, and perhaps serving as a source of prebiotic compounds that led to the appearance of life (e.g. Lindsay et al., 2005)? Previous studies have shown that OM in the chert veins and bedded cherts is low in $\delta^{13}C$ in a manner comparable to that of organic carbon fixed by autotrophic organisms (Hayes et al., 1983; Pinti et al., 2009a; Ueno et al., 2001, 2004). However, some studies have argued that similar low values of $\delta^{13}C$ may form during the production of organic compounds by abiotic processes similar to the industrial Fischer-Tropsch synthesis and thus concluded that the isotopic composition of the OM by itself does not provide conclusive evidence for a biogenic origin (Brasier et al., 2002; Lindsay et al., 2005; McCollom and Seewald, 2006).

OM in the Dresser Formation bedded cherts and associated hydrothermal chert veins shows variable bulk (mm- to cm-scale) $\delta^{13}C$ values, between −38‰ and −29‰ VPDB, interpreted as resulting from varying degrees of post-depositional metasomatic alteration (oxidation) (Ueno et al., 2004) or hydrothermal/metamorphic alteration (Pinti et al., 2009a). A detailed study of OM preserved in these rocks using organic petrology and scanning and transmission electron microscopy has revealed the occurrence of several morphologically-distinct OM populations, indicating potentially different sources and/or subsequent degradation/maturation processes (Glikson et al., 2008). These findings demonstrate the inherent difficulty in interpretation of bulk OM data and the need to consider the petrographic context of the carbonaceous microstructures. In situ (micron-scale) C-isotope analysis using Secondary-Ion Mass Spectrometry (SIMS) may provide further important data about the origin of OM since it is capable of distinguishing between different generations of OM in the cherts, whose unique isotopic composition may be averaged or completely obscured by conventional bulk analysis. Hitherto, in situ C isotope analyses of OM in the Warrawoona Group have targeted only rare carbonaceous filaments, which may represent fossil bacteria, and associated carbonaceous clots in two chert vein samples (Ueno et al., 2001). Furthermore, these analyses were standardized against a sample of crystalline graphite, which differs from the kerogenous OM found in the cherts, creating differences in the instrumental mass bias and thus potential errors in analysis (House et al., 2000; McKeegan et al., 1985; Williford et al., 2013).

This study presents a new, comprehensive data set of kerogen-standardized in situ SIMS $\delta^{13}C$ analyses of specific OM microstructures and associated carbonates for unweathered samples recovered from the PDP2b and 2c drillcores (Van Kranendonk et al., 2008) of the lowermost chert-barite unit of the ~3.5 Ga Dresser Formation, which represent Earth's oldest proposed fossiliferous sedimentary rocks (Ueno et al., 2001; Van Kranendonk, 2011; Van Kranendonk et al., 2008; Walter et al., 1980). Our data provide new insights as to the origin, migration and alteration of OM preserved in these rocks.

## 2. Geologic setting and sampling

The Dresser Formation is a package of interbedded chert-barite units and pillow basalts within the lower part of the Warrawoona Group of the Pilbara Supergroup (Van Kranendonk et al., 2007). Exposed only in the North Pole Dome, the Dresser Formation is preserved as a ring of hills, about 14 km in diameter, centered around the younger North Pole Monzogranite that was emplaced into the core of the dome at ~3.46 Ga (Van Kranendonk et al., 2008) (Fig. 1). The potentially fossiliferous, bedded chert-barite unit at the base of the Dresser Formation varies between 4 and 60 m in thickness (Van Kranendonk et al., 2008). It is composed of predominantly bedded chert, thick units of coarsely crystalline barite, conglomerate, sandstone and carbonates (Buick and Dunlop, 1990; Hickman, 1983; Nijman et al., 1999; Van Kranendonk, 2006; Van Kranendonk et al., 2008). The bedded chert-barite unit is underlain by pervasively hydrothermally altered komatiitic basalt transected by numerous veins of black-gray chert, varying up to ~20 m wide and up to 2 km long, which are thought to represent conduits of hydrothermal circulation (Isozaki et al., 1997; Nijman et al., 1999; Ueno et al., 2004; Van Kranendonk, 2006).

Two Pb–Pb model ages of ~3.49 Ga on galena in barite were previously cited as the age of the formation (Thorpe et al., 1992a), but recent U–Pb zircon dating of a felsic volcaniclastic sandstone from the top of the lowermost chert unit of the formation has yielded a maximum depositional age of 3.481 ± 0.002 Ga, which is interpreted to represent the age of deposition of this unit (Van Kranendonk et al., 2008). $^{147}Sm$–$^{143}Nd$ data from hydrothermally-altered metabasalts and basaltic metakomatiites, stratiform barite and black chert veins (from the studied PDP drill cores) yielded an isochron age of 3.49 ± 0.10 Ga, confirming the U-Pb and Pb-Pb ages (Tessalina et al., 2010). Overlying volcanics and related intrusions in the North Pole Dome have been dated at between 3.46 and 3.44 Ga (Amelin et al., 2000; Thorpe et al., 1992b).

Regional studies of metamorphic assemblages in the North Pole metabasalts show a locally variable pattern of metamorphic overprint. Peak metamorphic temperatures range from ~150 °C up to ~350 °C and show a general repeated pattern of increasing temperature with stratigraphic depth within the sequences of basalt-chert packages that comprise the North Pole Dome section (Kitajima et al., 2001; Terabayashi et al., 2003). However, in places the metamorphic conditions also vary considerably horizontally, within the sedimentary beds and basalt flows in relation with the occurrence of hydrothermal veins. This style of metamorphism was interpreted to result from repeated episodes of hydrothermal circulation within volcanic packages separated by silicified sediments that acted as aquacludes to hydrothermal fluid circulation (Van Kranendonk, 2006).

The Raman spectra acquired for the OM in different OM-bearing chert units of the North Pole Dome are generally similar to those of kerogen from lower greenschist facies metasedimentary rocks (Marshall et al., 2012; Ueno et al., 2004; Wacey et al., 2011b), although lower-temperature hydrothermal conditions of ~100–300 °C have been reported from the study of mineral assemblages (kaolinite-quartz: Van Kranendonk, 2006; Van Kranendonk and Pirajno, 2004) and fluid inclusions in cherts and adjacent metabasalts (Foriel et al., 2004; Harris et al., 2009).

The samples studied here come from the drill cores of the Pilbara Drilling Project site #2 (PDP2) collected in 2004 as part of a scientific collaboration between the Institut de Physique du Globe de Paris and the Geological Survey of Western Australia (for details see Van Kranendonk et al., 2008). Six samples were selected from