



Oxygen isotope analysis of fossil organic matter by secondary ion mass spectrometry

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Received 15 September 2015; accepted in revised form 29 February 2016; available online 8 March 2016

Abstract

We have developed an analytical procedure for the measurement of oxygen isotope composition of fossil organic matter by secondary ion mass spectrometry (SIMS) at the sub-per mill level, with a spatial resolution of 20–30 μm . The oxygen isotope composition of coal and kerogen samples determined by SIMS are on average consistent with the bulk oxygen isotope compositions determined by temperature conversion elemental analysis – isotope ratio mass spectrometry (TC/EA-IRMS), but display large spreads of $\delta^{18}\text{O}$ of ~ 5 – 10% , attributed to mixing of remnants of organic compounds with distinct $\delta^{18}\text{O}$ signatures. Most of the $\delta^{18}\text{O}$ values obtained on two kerogen residues extracted from the Eocene Clarno and Early Devonian Rhy-nie continental chert samples and on two immature coal samples range between $\sim 10\%$ and $\sim 25\%$. Based on the average $\delta^{18}\text{O}$ values of these samples, and on the O isotope composition of water processed by plants that now constitute the Eocene Clarno kerogen, we estimated $\delta^{18}\text{O}_{\text{water}}$ values ranging between around -11% and -1% , which overall correspond well within the range of O isotope compositions for present-day continental waters. SIMS analyses of cyanobacteria-derived organic matter from the Silurian Zdanow chert sample yielded $\delta^{18}\text{O}$ values in the range 12 – 20% . Based on the O isotope composition measured on recent cyanobacteria from the hypersaline Lake Natron (Tanzania), and on the O isotope composition of the lake waters in which they lived, we propose that $\delta^{18}\text{O}$ values of cyanobacteria remnants are enriched by about $18 \pm 2\%$ to $22 \pm 2\%$ relative to coeval waters. This relationship suggests that deep ocean waters in which the Zdanow cyanobacteria lived during Early Silurian times were characterised by $\delta^{18}\text{O}$ values of around $-5 \pm 4\%$. This study, establishing the feasibility of micro-analysis of Phanerozoic fossil organic matter samples by SIMS, opens the way for future investigations of kerogens preserved in Archean cherts and of the O isotopic composition of ocean water at that period in time.

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1. INTRODUCTION

The temperature of Archean oceans has been a topic of great controversies for half a century since the recognition that the oxygen isotope composition of sedimentary cherts, expressed using the $\delta^{18}\text{O}$ notation ($\delta^{18}\text{O} = [^{18}\text{O}/^{16}\text{O}_{\text{sample}}/^{18}\text{O}/^{16}\text{O}_{\text{SMOW}} - 1] \times 1000$, where SMOW is the Standard Mean Ocean Water), increased by about

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15–20‰ from ~3.5 billion-year ago to the present-day (Perry, 1967; Knauth and Epstein, 1976; Knauth and Lowe, 1978). The oxygen isotopic composition of silica precipitated from a fluid is related to the isotopic composition of the fluid and to the temperature T at which precipitation occurred, according to the equation: $1000 \times \ln(\Delta^{18}\text{O}) = (3.09 \times 10^6 \times T^{-2}) - 3.29$ (Knauth and Epstein, 1976), where $\Delta^{18}\text{O} = \delta^{18}\text{O}_{\text{chert}} - \delta^{18}\text{O}_{\text{water}}$. This equation contains three variables: the temperature T of the fluid from which cherts precipitated, $\delta^{18}\text{O}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{chert}}$. Therefore, it is not possible to derive both the temperature and the isotopic composition of seawater based on measurements of $\delta^{18}\text{O}_{\text{chert}}$ without making an assumption on either the seawater T or its O isotope composition. As a result, and considering only Precambrian cherts with pristine O isotope composition not modified during secondary alteration (see for example the recent reviews by Perry and Lefcariu, 2014), two end-member scenarios (not mutually exclusive) have been proposed to explain the observed secular trend of the chert $\delta^{18}\text{O}$ values:

- (1) Archean oceans were characterised by temperatures up to around 50–70 °C higher than today, which implies that the O isotope composition of oceanic waters has remained globally constant around 0‰ throughout the Earth history (Knauth and Epstein, 1976; Knauth and Lowe, 1978, 2003; Knauth, 2005). This scenario is supported by other proxies, such as Si isotopes in cherts, which show variations consistent with a ~50 °C decrease in temperature from the early Archean (e.g., Robert and Chaussidon, 2006), or O isotope composition of serpentine in ophiolite rocks, and notably from those of the *ca.* 3.8 Ga Isua Supracrustal Belt (e.g., Pope et al., 2012).
- (2) Archean oceans were characterised by $\delta^{18}\text{O}$ values lower by about 10–15‰ compared to present day, in which case surface temperatures on the Earth have remained globally constant since ~3.5 Ga (e.g., Kasting et al., 2006; Jaffrés et al., 2007; Hren et al., 2009). This scenario is consistent with the proposed existence of major Archean and Proterozoic glaciations (e.g., Evans et al., 1997; Young et al., 1998), suggesting that surface conditions on the Earth were not drastically different to today during the Precambrian. This scenario is also in line with the lack of evidence for a high atmospheric pressure of CO_2 in Archean sediments that would have been required to maintain high surface temperature under a Sun much fainter than today (e.g., Lowe and Tice, 2004; Kasting et al., 2006; Jaffrés et al., 2007), even though recent modelling studies have suggested that fewer amounts of greenhouse gases (CO_2 and CH_4) are in fact required to counteract the “faint young Sun problem” (Charnay et al., 2013).

Recent *in situ* studies of the O and Si isotope composition variations at the micrometre scale in cherts have shown that transformation of amorphous silica precursors during diagenesis is accompanied by isotopic fractionation in

micrometre-scale domains (Marin et al., 2010; Marin-Carbonne et al., 2012). For the *ca.* 1.9 Ga Gunflint chert for example, this observation implies a lowering by ~20 °C of the seawater temperature (~37–52 °C) calculated from $\delta^{18}\text{O}_{\text{chert}}$, which, however, remains much higher than present day temperature (Marin et al., 2010; Marin-Carbonne et al., 2012).

These two end-member scenarios have fundamental implications, notably for understanding the early-Earth environmental conditions that promoted the appearance and evolution of life *ca.* 3.4–3.5 Gyr ago (e.g., Schopf, 1993; Tice and Lowe, 2004; Wacey et al., 2011; Brasier et al., 2015). Putative and *bona fide* early-life remnants, found as micrometre-size insoluble organic matter (OM) patches disseminated in cherts (e.g., Schopf, 1993; Tice and Lowe, 2004; Wacey et al., 2011; Brasier et al., 2015), can potentially provide us with an independent way of constraining the O isotope composition of Archean seawater. Indeed, the O isotope composition of organic compounds, such as cellulose or lipids, is thought to be primarily controlled by the isotopic composition of the water in which they formed, but seems to be relatively insensitive to the temperature of this water (e.g., DeNiro and Epstein, 1981; Sternberg and DeNiro, 1983; Silva et al., 2015). While the study of the C and S isotope characteristics of carbonaceous OM patches and associated sulphides, notably through *in situ* ion microprobe studies, has been used to argue for their biological origin and to show that they can preserve isotopic information throughout geological times (e.g., House et al., 2000; Ueno et al., 2001; Wacey et al., 2011; Bontognali et al., 2012; Williford et al., 2013; Fischer et al., 2014), their O isotope composition has never been investigated.

Here we present a detailed analytical approach establishing the feasibility of analysing the O isotope composition of fossil OM by secondary ion mass spectrometry (SIMS) on well characterised Phanerozoic samples, including the characterisation of a kerogen sample that can be used as a SIMS reference material for O isotope analysis. Carbonaceous remnants have low O abundances (~5–15 wt.%; e.g., Durand and Monin, 1980) and typically occur as small micrometre-scale patches disseminated in a O-rich quartz matrix. Therefore, analyses were carried out on insoluble OM residues isolated from the chert samples by acid digestion. However, extracted residues are not pure OM and contain many O-bearing micro-inclusions of diverse mineral phases. Our analytical approach thus includes a procedure allowing for filtering the O isotope data compromised by analysis of mineral micro-inclusions, based on measurements of the intensities of species such as ^{28}Si , ^{32}S and $^{56}\text{Fe}^{16}\text{O}$. We have applied this approach to five coal and kerogen samples ranging in age from Eocene to Silurian and on recent chert-hosted cyanobacteria remnants. Based on these results obtained on Phanerozoic samples, we have investigated (i) how does fossil OM preserve its O isotope signature, (ii) what is the bulk oxygen isotope fractionation between OM and water, and (iii) what are the potential implications for deriving the O isotope composition of paleo-waters from that of coeval OM. These results will be crucial for future studies applying

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