



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Earth and Planetary Science Letters 217 (2004) 237–244

EPSL

www.elsevier.com/locate/epsl

U-rich Archaean sea-floor sediments from Greenland – indications of > 3700 Ma oxygenic photosynthesis

Minik T. Rosing^{a,b,*}, Robert Frei^{b,c}

^a *Geologisk Museum, Øster Voldgade 5–7, 1350 Copenhagen K, Denmark*

^b *Danish Lithosphere Center, Øster Voldgade 10, 1350 Copenhagen K, Denmark*

^c *Geologisk Institut, Øster Voldgade 10, 1350 Copenhagen K, Denmark*

Received 19 March 2003; received in revised form 18 September 2003; accepted 21 October 2003

Abstract

> 3700 Ma metamorphosed pelagic shale from West Greenland contains up to 0.4 wt% reduced carbon with $\delta^{13}\text{C}$ values down to -25.6‰ [PDB, PeeDee Belemnite]. The isotopic signature and mode of occurrence suggest that the carbon derived from planktonic organisms. The Pb isotopic composition shows that the shale had high primary U/Th. This indicates that organic debris produced a local reducing environment which precipitated U transported to the site of sedimentation by oxidized ocean water. The existence of highly productive plankton that fractionated C isotopes strongly and set up oxidation contrast in the environment suggests that oxygenic photosynthesis evolved before 3700 Ma.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Isua; oxygenic photosynthesis; carbon; Archaean; Pb isotopes; U; Th

1. Introduction

The most important evolutionary step for the proliferation of life on Earth was the development of oxygenic photosynthesis. The advent of this metabolic strategy marked the beginning of global atmospheric management by life, and the determinant influence of life on Earth climate. This node on the tree of life is thus one of the most important geological events to date.

Living organisms generally display decreasing

levels of structural complexity the deeper they are rooted on the phylogenetic tree. Life forms that existed during deposition of the oldest sediments on Earth left no morphological fossils that could sustain the strong metamorphic recrystallization and deformation that have affected all rocks older than 3600 Ma. Early life must thus be identified and characterized by its metabolic interaction with Earth's chemical environments. The interaction of life with its environment causes characteristic geochemical fractionations, which can be identified in geologic deposits. Metabolic processes can also cause isotope fractionations that are diagnostic of specific enzymatic catalysts. Characterization of pre-3600 Ma life must thus be based on the identification and interpretation of

* Corresponding author. Tel.: +45-3532-2345;

Fax: +45-3532-2325.

E-mail address: minik@savik.geomus.ku.dk (M.T. Rosing).

biogenic element- and isotope fractionations preserved in the rock record.

The earliest evidence for life on Earth has been identified by the presence of abundant ^{13}C -depleted carbon in >3700 Ma pelagic sediments from Isua, West Greenland. These sediments contain up to 0.4 wt% carbon derived from planktonic organisms [1]. The high content of organic material in the protolith sediments suggests a high rate of metabolic activity of the organisms, which might have enabled them to influence other geochemical parameters in the sedimentary environment to an extent that we can identify today. In the following we will present geochemical data that reflect some of the metabolic strategies of the >3700 Ma biosphere.

One of the most profound influences of the activity of life is the oxidation of the environment associated with sequestering of organic material. The oxidation state of the atmosphere and hydrosphere is mainly controlled by the balance of oxygenic photosynthesis relative to the consumption by biologic respiration and geochemical redox processes such as continental weathering and oxidation of volcanic emanations and hydrothermal fluids. The presence of free oxygen in the atmosphere represents a state of disequilibrium that would be highly transient in the absence of continuous oxygen production. The oxygen level, on the other hand, is not to first order indicative of the flux of oxygen through the system. When oxygen production locally or globally exceeds the oxygen consumption oxidizing environments develop, while reducing conditions do not necessarily indicate the absence of photosynthetic oxygen production. The compelling evidence for a reducing atmosphere from some Archaean and Proterozoic geologic deposits [2] cannot therefore be taken as evidence against an early emergence of oxygenic photosynthesis. In fact, most evidence suggests that oxygenic photosynthesis was present during time periods from which there is evidence for a non-oxygenic atmosphere [2–6]. In the following we will examine the available evidence from >3700 Ma metasedimentary rocks from Isua in West Greenland as a separate data point for one aquatic setting, which we regard as not constrained by atmospheric conditions docu-

mented in the geologic record a half billion years or more later in Earth history [2,7,8]. The concept of ‘the Archaean ocean’ is in our opinion meaningless, as it would have to embrace all possible aquatic environments with all possible lateral and vertical variations during more than 1300 Ma. The low diffusivity of oxygen and the slow mixing of the oceans allows for considerable lateral and vertical redox variations. By comparison with the modern world, we contend that diverse environments might have existed on Earth during the early Archaean, and that the evidence for the presence of reduced environments in one geographical area at one time does not preclude the existence of relatively oxidized environments in other areas at other times, in the same way as the existence of the Black Sea sedimentary environment does not preclude the existence of the Pacific or the Dead Sea. It should be borne in mind that the Isua supracrustal package may well cover up to 200 Ma of depositional time, and that there is no evidence that all rocks in the belt belong to a single depositional sequence [9–11].

The oxidation state and the presence or absence of redox contrasts in the atmosphere and hydrosphere through geologic time are recorded in the concentrations of redox-sensitive chemical components in sedimentary rocks. The concentrations of redox-sensitive components are susceptible to alteration during metamorphism, and their present-day concentrations in metasedimentary rocks may not be directly related to the sedimentation processes. In the following we will use the behavior of uranium relative to thorium as a monitor of redox conditions in an oceanic environment at the time of deposition of early Archaean sediments. These two elements have the benefit that the timing of their fractionation is recorded in the lead isotopic composition of their host rocks because the relative rates of uraniumogenic ^{206}Pb to ^{207}Pb production have changed dramatically through Earth history, due to the short half-life of ^{235}U relative to the age of Earth. Uranium is highly redox-sensitive and occurs in tetravalent and hexavalent oxidation states in nature [12], while thorium only occurs in the tetravalent state in nature. In their tetravalent states uranium and

thorium are geochemically similar, and are not fractionated during most geochemical processes. The Pb isotopic composition of a rock formation will therefore carry a Pb isotopic memory of past U/Th ratios regardless of later mobilization of these elements.

Uranium can be transported in the sedimentary environment in solution or as suspended particles. In oxidized environments U is dominantly transported as dissolved uranyl complexes, because U-rich minerals are unstable under high oxygen fugacity and because hexavalent U and its complexes are highly soluble in aqueous solutions. Th is practically insoluble in water at Earth surface conditions. Under reducing conditions U is dominantly transported together with Th in mineral particles. In general, U is not fractionated from Th during magmatic processes or during surface processes under reducing conditions. These properties of U and Th and their different modes of transport form the basis for the common assumption that uranium that exceeds the amount necessary to balance the Th concentration to meet the crustal average U/Th ratio is introduced to sediments by reduction of dissolved uranyl complexes, i.e. $U_{\text{autigenic}} = U_{\text{tot}} - (U/Th_{\text{crust}} \times Th_{\text{tot}})$ [13–17].

2. Geology

In this study we have analyzed carbon and lead isotopic compositions of > 3700 Ma pelagic sediments from the Isua supracrustal belt in West Greenland [1,18,19]. These sediments were deposited as pelagic mud interspersed with detrital mass flows, volcanic ash layers and pillow lavas. The rocks used in the present study have been recrystallized under amphibolite facies conditions, but have largely escaped penetrative deformation or metamorphic segregation. They are exceedingly well preserved for early Archaean metasedimentary rocks, and preserve primary sedimentary bedding. Carbon occurs as 2–5 μm globular graphite grains. The distribution of these grains is controlled by the sedimentary bedding. High concentrations of ^{13}C -depleted reduced carbon in the pelagic layers and absence of carbon from sub-mm-

thin volcanic ash layers indicate that the carbon was pelagic in origin and probably derived from plankton [1]. Additional evidence for the primary origin of the carbon is the presence of graphite inclusions in their stratigraphic context included in rare mm-size feldspar, biotite and garnet porphyroblasts. There is thus little possibility that the carbon can be derived from secondary infiltrating fluids. Isotopic age determinations indicate that the rocks were affected by a metamorphic event at ca. 2800 Ma [20,21]. Although these metasedimentary rocks are not perfectly preserved, they are at present unparalleled as a source of information about the early Earth surface environments [22]. No pristine rocks from the early Archaean are known on Earth today. All available sample materials have been subjected to high-grade metamorphic recrystallization, and most lithologies are strongly deformed. The samples selected for this study are probably the best available material and there is consensus that the rocks are sedimentary in origin and preserve primary sedimentary features [22].

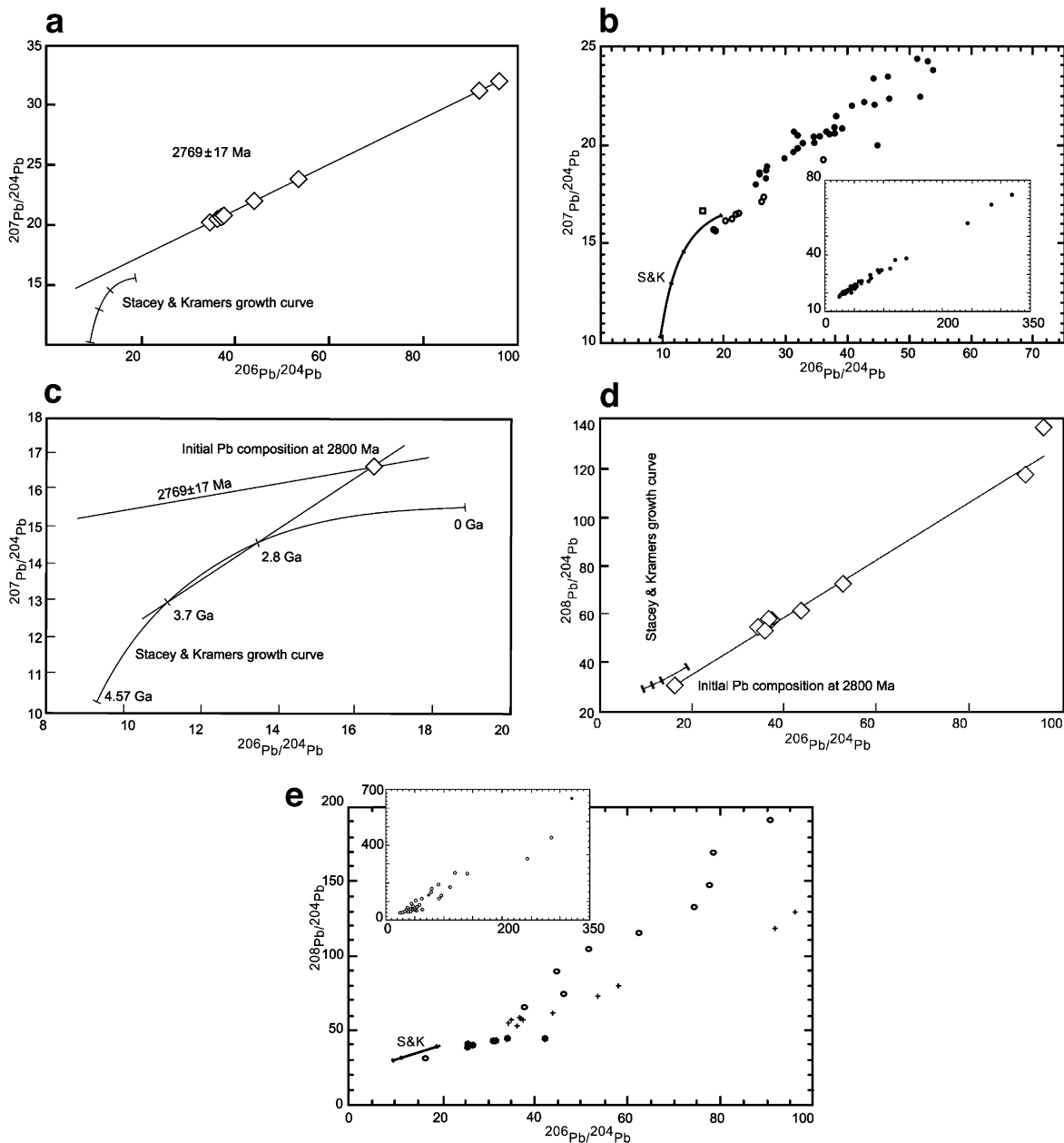
3. Pb isotope data

Eight samples of clastic metasediment were selected along a traverse covering ca. 20 m of stratigraphy and an additional four samples representing metabasalt and banded iron formation at the base of the section were included in this study. The samples were split and ca. 100 g material free of visible veins or weathering surfaces from each sample was powdered in agate. 200 mg aliquots were dissolved in HF. Pb was chromatographically separated, and analyzed on a VG 54 thermal ionization mass spectrometer following procedures described in [20] at the Danish Center for Isotope Geology. Age determination and error propagation were carried out in Isoplot [23]. Major and trace element geochemical analyses were carried out by SARM at CRPG, Vandoeuvre, France, by inductively coupled plasma (ICP) emission spectroscopy and ICP mass spectrometry (ICP-MS), respectively.

All the samples show very radiogenic Pb compositions that plot above the Stacey and Kramers

uranogenic $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ growth curve [24], which represents the Pb isotopic evolution of average crustal Pb (Fig. 1a,b). The data points define an errorchron with an age of 2769 ± 17 Ma (MSWD = 52), which indicates that the U–Pb system was perturbed during a metamorphic event at ca. 2800 Ma. The Pb isotopic composi-

tions of the sediments at the time of perturbation are defined by the intersection of the errorchron for the samples and an isochron originating at the Stacey–Kramers growth curve at 3700 Ma (the minimum age of the rocks) and projecting through 2769 Ma (the age of metamorphism). The initial composition at 2769 Ma calculated by this



model is $^{206}\text{Pb}/^{204}\text{Pb} = 16.4$ and $^{207}\text{Pb}/^{204}\text{Pb} = 16.7$ (Fig. 1c), which corresponds to a μ ($^{238}\text{U}/^{204}\text{Pb}$) value of 22 during the 3700–2800 Ma time span.

Systems that evolve from a common initial Pb isotopic composition will evolve to define a fan-shaped array in the $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. If samples evolve with identical U/Th but different Th/Pb they will define a linear array in the $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. The data points for the metasediments are well correlated, but show some scatter about a regression line (Fig. 1d). This indicates that the whole rock samples evolved with similar U/Th ratios since the time of metamorphisms at 2769 Ma. The initial Pb isotopic composition at that time can be constrained by the $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ regression line and the information from the uranogenic Pb system that all the samples shared the composition $^{206}\text{Pb}/^{204}\text{Pb} = 16.4$ at 2769 Ma. This allows the calculation of a model initial $^{208}\text{Pb}/^{204}\text{Pb}$ value for the metasediments at 2769 Ma. This model initial $^{208}\text{Pb}/^{204}\text{Pb}$ value is 30.9, which lies to the right of the Stacey and Kramers growth curve. This indicates that the metasediments evolved with a lower κ ($^{232}\text{Th}/^{238}\text{U}$) than the source of average crustal Pb. The scatter of the data points allows some uncertainty in this model

initial $^{208}\text{Pb}/^{204}\text{Pb}$ composition. If we accept $^{206}\text{Pb}/^{204}\text{Pb} = 16.4$ and $^{208}\text{Pb}/^{204}\text{Pb} = 31$ as the initial Pb composition at 2769 Ma, it would indicate that there was no production of thorogenic Pb in the time span 3700–2769 Ma during which the samples evolved with high μ and extremely low ω ($^{232}\text{Th}/^{204}\text{Pb}$). Regardless of the uncertainty in the exact values of ω and κ during the early Archaean evolution of the sediments, it remains clear that the sediments evolved with a Th/U ratio that was strongly fractionated relative to the source of common crustal Pb. In an effort to identify the host of Th in the metasediments and the timing of Th introduction, we have carried out leaching experiments in which powdered samples were leached in successively stronger acids (cf. [20]). These experiments reproduce the ca. 2800 Ma age of disturbance for individual samples and show that the main reservoir of thorogenic Pb is an easily leachable phase with a ‘normal’ crustal Th/U ratio of ca. 4–6. The most acid-resistant phases, which are probably dominated by feldspar, define a very shallow and relatively unradiogenic regression line in the $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 1e). This indicates that these residual phases are dominated by a Pb component similar to our model initial composition at

←
 Fig. 1. (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for eight samples of >3700 Ma pelagic sediment from Isua, West Greenland, shown with open diamonds. Analytical uncertainty is less than the size of the symbols. The Stacey and Kramers growth curve for average crustal Pb [24] is shown for comparison. The age of the errorchron which has a MSWD=52 is calculated using Isoplot [23]. The high MSWD value indicates that the Pb isotopic composition of the sample suite was not perfectly homogeneous at 2800 Ma. (b) Pb isotopic data for the whole rock samples shown in panel a and their HCl leachates and leach residues in the range $^{206}\text{Pb}/^{204}\text{Pb} = 0\text{--}75$ and $^{207}\text{Pb}/^{204}\text{Pb} = 10\text{--}25$ (filled circles). The full dataset is shown in the inset. In open circles are data for banded iron formation and metabasalt samples from the same supracrustal segment as the carbon-rich metasediments. These samples plot along a parallel reference isochron, but originate at the Stacey and Kramers growth curve, which indicates that they evolved with ‘normal’ μ ($^{238}\text{U}/^{204}\text{Pb}$) values during the time span from 3700 to 2800 Ma. (c) Close-up of the region near the Stacey and Kramers growth curve showing the intersection of the errorchron defined by the metasediment samples and an isochron defined by all possible Pb compositions at 2800 Ma of systems derived from the Stacey and Kramers growth curve at 3700 Ma. This intersection is the model initial composition for the samples at 2800 Ma. The position above the growth curve indicates that the samples evolved with high μ ($^{238}\text{U}/^{204}\text{Pb}$) values of 22 during the time span from 3700 to 2800 Ma. (d) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the sample suite. The samples show some scatter about a regression line, which passes to the right of the Stacey and Kramers growth curve. This indicates that the metasediments evolved with low Th/U ratios. At the initial $^{206}\text{Pb}/^{204}\text{Pb}$ composition derived from panel b, the $^{208}\text{Pb}/^{204}\text{Pb}$ value at the regression line is 31, which is less radiogenic than the Stacey and Kramers model value at 3700 Ma. This indicates that the samples evolved with virtually no Th during the early Archaean. (e) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for whole rock samples, HCl leachates and residues. The residues are highlighted in filled diamonds, and are characterized by low thorogenic Pb and a shallow array indicative of a low Th/U ratio, while the leachates shown in open circles are extremely radiogenic, with high Th/U evolutions. Whole rock samples are shown with crosses. The model initial Pb composition at 2769 Ma is shown as the open square at the apex of the fan-shaped data array to the right of the Stacey and Kramers growth curve.

2769 Ma that can only be reached by an early Archaean high U/Pb evolution with a post-metamorphic evolution with a higher Th/U ratio. The whole rock isotopic composition is thus the combined result of an ancient high-U/Pb, low-Th reservoir and a high-Th/U phase introduced during late Archaean metamorphism.

4. Discussion

Highly radiogenic Pb compositions similar to those of the metasediments are not found in basaltic units associated with the sediments, or indeed in any other known lithologies from the region [21,25]. To our knowledge these Pb isotopic compositions are unique among terrestrial materials, which underlines that they evolved in a highly anomalous reservoir with a very early U/Pb enrichment. This rules out the possibility that introduction of externally derived radiogenic Pb during the 2769 Ma metamorphic episode is a possible cause for the isotopic composition of the metasediments. The isotopic composition of Pb in metasomatic veins in the region is extremely primitive and includes the least radiogenic terrestrial Pb analyzed [26]. Influx of such Pb during the 2769 Ma metamorphic event would lead to an underestimation of the early Archaean μ value in our model. Although the U–Th–Pb system of the rocks was perturbed during 2800 Ma metamorphism, we can conclude that the protolith sediments had high U/Pb which originated during sedimentation or diagenesis, while Th was first introduced to the metasediments during the late Archaean metamorphic event. Th and U mobility associated with fluid-controlled allanite and/or monazite mineralizations during the \sim 2800 Ma event is frequently observed in the region [21], and allanite is frequently observed as a late metamorphic phase in the most radiogenic samples of that study.

Transport of uranium into organic-rich sediments can be driven by contrast in oxygen fugacity across the seawater–sediment interface, or uranium can be scavenged from seawater by organic detritus. In either case, the high U/Th ratio of the primary sediment suggests that U was transported

in solution to the site of sedimentation and fixed by reaction with organic components in the sediments. Redox contrast in the sedimentary environment and the apparent transport of uranium as uranyl rather than particulate matter suggest that the oceans comprised relatively oxidized compartments > 3700 Ma. The evidence for U/Th fractionation may thus indicate that Isuan planktonic organisms released oxygen to their environment.

The total concentration of reduced carbon in the sediments reaches values up to 0.4 wt%. The variation in total carbon concentration and isotopic composition of the carbon is probably caused by a combination of variations in the composition of the original sediment and various degrees of interaction with metamorphic fluid which resulted in loss of total carbon and changes in $\delta^{13}\text{C}$ towards less negative values. For that reason, we would not expect any correlation between total C contents, $\delta^{13}\text{C}$ and Pb isotopic compositions. The high contents of reduced carbon must be caused by high primary biomass production. The rate of sedimentation cannot have been exceedingly low, because low concentrations of platinum group elements in the sediments [27] indicate that the cosmic contribution was comparable to that in modern ocean-floor sediments. This precludes a meteoritic origin of the carbon, and indicates that the rate of sedimentation was comparable to modern rates. The accumulated stratigraphic thickness of pelagic shale in the exposed section is ca. 20 m, suggesting that a steady sedimentation of pelagic organic material took place during hundred thousands to millions of years. This indicates a stable environment, and a steady, ample and abundant source of energy. The only known source that satisfies these requirements is sunlight. This suggests that the organic material was most likely produced by phototrophic plankton.

In theory, the production of biomass could have been coupled to oxidation of ferrous iron or other electron donors in a non-oxygenic metabolic cycle. However, there is no correlation between reduced carbon contents and the concentrations of iron, sulfur or other redox-active components in the metasediments (Fig. 2a). Total

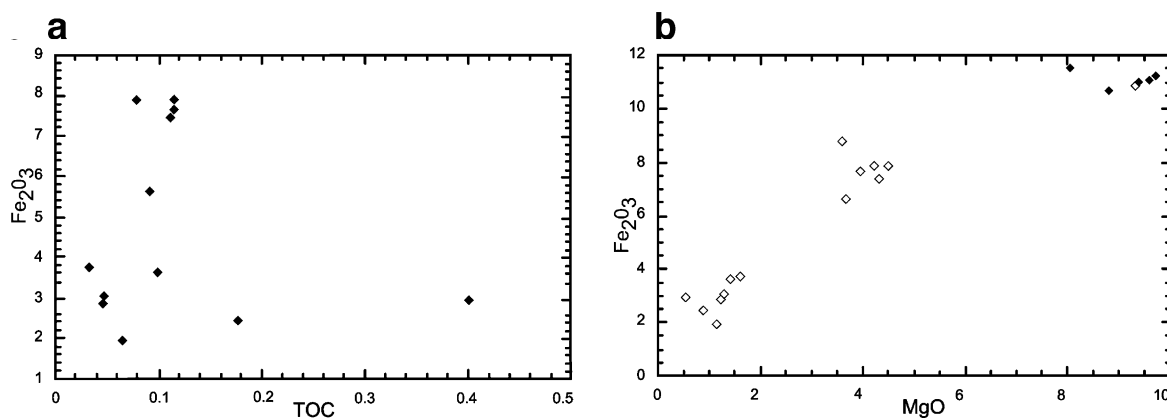


Fig. 2. (a) Total reduced carbon (TOC) wt% versus total iron given as Fe₂O₃ wt%. There is no correlation of the two variables, and the most C-rich metasediment sample is among the least Fe-rich samples. (b) MgO (wt%) versus Fe₂O₃ (wt%). Metasediments are shown as open diamonds and metabasalts as filled diamonds. The correlation suggests that the metasediments carry a large basaltic volcanogenic component, and that most Fe is supported by this component.

iron contents of the pelagic sediments are insufficient to support the reduced carbon, and Fe and Mg concentrations are strongly correlated (Fig. 2b), with Fe/Mg ratios comparable to those of intercalated metabasaltic rocks. This indicates that most Fe was part of the clastic component and probably derived from basaltic volcanic detritus. Chemotropic or non-oxygenic photosynthetic metabolism could thus not be responsible for the biomass production, and abiotic reactions between the sediment and metamorphic fluids is not a possible source of the reduced carbon.

The carbon in the least altered samples has $\delta^{13}\text{C}$ values of -25.6‰ [PDB, PeeDee Belemnite]. No contemporary sedimentary carbonate rocks that recorded the isotopic composition of the early Archaean CO₂ reservoir have been identified. However, metamorphic carbonate formed by infiltration metasomatism [18,28] in some of the rock formations that host the pelagic sediments have average $\delta^{13}\text{C}$ values of -1.5‰ [29]. This carbonate is most likely formed by redistribution of carbonate initially formed by reaction of sea-floor with oceanic bicarbonate, suggesting that this average value probably approximates the value for the CO₂ carbon source of the plankton. This suggests a biogenic fractionation of approximately 25‰, which is within the range of fractionations caused by the rubisco enzyme in phototrophic organisms [30]. The carbon isotopic

composition is thus consistent with phototrophic carbon fixation, but not unambiguously diagnostic of such organisms.

5. Conclusions

Planktonic organisms lived in the Isuan oceans where they produced large amounts of highly ¹³C-depleted organic matter. The aquatic environment of these organisms comprised relatively oxidized compartments, which allowed solute transport of U. The high biomass productivity of planktonic organisms, the strongly ¹³C-depleted carbon isotopic signature and the evidence for the presence of oxidized aquatic environments all suggest that oxygenic photosynthesis had developed before 3700 Ma.

Acknowledgements

The Carlsberg Foundation, The Greenland Homerule Government, The Danish National Research Fund and the Danish Center for Isotope Geology are thanked for support. E. Nesbit and D. Canfield are thanked for discussions. Constructive reviews by M.J. Whitehouse and an anonymous reviewer are gratefully acknowledged. [BOYLE]

References

- [1] M.T. Rosing, C-13-depleted carbon microparticles in > 3700-Ma sea-floor sedimentary rocks from west Greenland, *Science* 283 (1999) 674–676.
- [2] D.E. Canfield, K.S. Habicht, B. Thamdrup, The Archean sulfur cycle and the early history of atmospheric oxygen, *Science* 288 (2000) 658–661.
- [3] J.J. Brocks, G.A. Logan, R. Buick, R.E. Summons, Archean molecular fossils and the early rise of eukaryotes, *Science* 285 (1999) 1033–1036.
- [4] J. Kasting, Earth history - The rise of atmospheric oxygen, *Science* 293 (2001) 819–820.
- [5] R. Buick, The antiquity of oxygenic photosynthesis: Evidence from stromatolites in sulfate-deficient Archean lakes, *Science* 255 (1992) 74–77.
- [6] E.G. Nisbet, N.H. Sleep, The habitat and nature of early life, *Nature* 409 (2001) 1083–1091.
- [7] H.D. Holland, R. Rye, Evidence in pre-2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota: Comment, *Geology* 25 (1977) 857–858.
- [8] R. Rye, H.D. Holland, Paleosols and evolution of atmospheric oxygen: A critical review, *Am. J. Sci.* 298 (1998) 621–672.
- [9] A.P. Nutman, V.C. Bennett, C.R.L. Friend, M.T. Rosing, similar to 3710 and > = 3790 Ma volcanic sequences in the Isua (Greenland) supracrustal belt; structural and Nd isotope implications, *Chem. Geol.* 141 (1997) 271–287.
- [10] J.S. Myers, Protoliths of the 3.8–3.7 Ga Isua greenstone belt, West Greenland, *Precamb. Res.* 105 (2001) 129–141.
- [11] A.P. Nutman, K.D. Collerson, Very early Archean crustal-accretion complexes preserved in the North-Atlantic craton, *Geology* 19 (1991) 791–794.
- [12] D. Langmuir, Uranium Solution-mineral equilibria at low-temperatures with applications to sedimentary ore-deposits, *Geochim. Cosmochim. Acta* 42 (1978) 547–569.
- [13] Y. Chung, W.C. Chang, Uranium and thorium isotopes in marine sediments off northeastern Taiwan, *Mar. Geol.* 133 (1996) 89–102.
- [14] J. Giridhar, D. Langmuir, Determination of E0 for the Uo2(2+)/U4+ couple from measurement of the equilibrium - Uo2(2+)+Cu(S)+4h+= U4++Cu2++2h2o at 25-degrees-C and some geochemical implications, *Radiochim. Acta* 54 (1991) 133–138.
- [15] K.J. Myers, P.B. Wignall, Understanding Jurassic organic-rich mudrocks - new concepts using gamma-ray spectrometry and palaeoecology; examples from the Kimmeridge Clay of Dorset and the Jet Rock of Yorkshire, in: J.K. Leggett, G.G. Zuffa (Eds.), *Marine Clastic Sedimentology*, Graham and Trotman, London, 1987, pp. 172–189.
- [16] P.B. Wignall, K.J. Myers, Interpreting benthic oxygen levels in mudrocks - a new approach, *Geology* 16 (1988) 452–455.
- [17] Q.J. Fisher, P.B. Wignall, Palaeoenvironmental controls on the uranium distribution in an Upper Carboniferous black shale (*Gastrioceras listeri* Marine Band) and associated strata; England, *Chem. Geol.* 175 (2001) 605–621.
- [18] M.T. Rosing, N.M. Rose, D. Bridgwater, H.S. Thomsen, Earliest part of Earth's stratigraphic record: A reappraisal of the > 3.7 Ga Isua (Greenland) supracrustal sequence, *Geology* 24 (1996) 43–46.
- [19] A.P. Nutman, J.H. Allaart, D. Bridgwater, E. Dimroth, M. Rosing, Stratigraphic and geochemical evidence for the depositional environment of the early Archean Isua Supracrustal Belt, southern West Greenland, *Precamb. Res.* 25 (1984) 365–396.
- [20] R. Frei, D. Bridgwater, T. Rosing, O. Stecher, Controversial Pb-Pb and Sm-Nd isotope results in the early Archean Isua (West Greenland) oxide iron formation: Preservation of primary signatures versus secondary disturbances, *Geochim. Cosmochim. Acta* 63 (1999) 473–488.
- [21] R. Frei, M.T. Rosing, T.E. Waight, D.G. Ulfbeck, Hydrothermal-metasomatic and tectono-metamorphic processes in the Isua supracrustal belt (West Greenland): A multi-isotopic investigation of their effects on the Earth's oldest oceanic crustal sequence, *Geochim. Cosmochim. Acta* 66 (2002) 467–486.
- [22] J.S. Myers, J.L. Crowley, Vestiges of life in the oldest Greenland rocks? A review of early Archean geology in the Godthabsfjord region, and reappraisal of field evidence for > 3850 Ma life on Akilia, *Precamb. Res.* 103 (2000) 101–124.
- [23] K.R. Ludwig, *Isoplot*, Berkeley Geochronol. Spec. Publ. 1 (1999) 47–66.
- [24] J.S. Stacey, J.D. Kramers, Approximation of terrestrial lead isotope evolution by a 2-stage model, *Earth Planet. Sci. Lett.* 26 (1975) 207–221.
- [25] B.S. Kamber, S. Moorbath, Initial Pb of the Amitsoq gneiss revisited: implication for the timing of early Archean crustal evolution in West Greenland, *Chem. Geol.* 150 (1998) 19–41.
- [26] R. Frei, M.T. Rosing, The least radiogenic terrestrial leads; implications for the early Archean crustal evolution and hydrothermal-metasomatic processes in the Isua Supracrustal Belt (West Greenland), *Chem. Geol.* 181 (2001) 47–66.
- [27] C. Koeberl, W.U. Reimold, I. McDonald, M. Rosing, in: K.C. (Ed.), *Lecture Notes in Earth Sciences* 91, Springer, Heidelberg, 1999, pp. 73–97.
- [28] N.M. Rose, M.T. Rosing, D. Bridgwater, The origin of metacarbonate rocks in the Archean Isua supracrustal belt, West Greenland, *Am. J. Sci.* 296 (1996) 1004–1044.
- [29] M. Schidlowski, P.W.U. Appel, R. Eichmann, C.E. Junge, Carbon isotope geochemistry of the 3.7×109-yr-old Isua sediments, West Greenland - Implications for the Archean carbon and oxygen cycles, *Geochim. Cosmochim. Acta* 43 (1979) 189–199.
- [30] M. Schidlowski, A 3,800-million-year isotopic record of life from carbon in sedimentary-rocks, *Nature* 333 (1988) 313–318.