Early Archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life

Pons, Marie-Laure; Quitté, Ghylaine; Fujii, Toshiyuki; Rosing, Minik Thorleif; Reynard, Brune; Moynier, Frederic; Douchet, Chantal; Albarède, Francis

Published in:
Proceedings of the National Academy of Sciences USA (PNAS)

DOI:
10.1073/pnas.1108061108

Publication date:
2011

Document version
Publisher's PDF, also known as Version of record

Document license:
Other

Citation for published version (APA):
Early Archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life

Marie-Laure Pons,1 Ghylaine Quitté,2 Toshiyuki Fujii,3 Minik T. Rosing,4 Bruno Reynard,4 Frederic Moynier,4 Chantal Douchet,1 and Francis Albarede2

1Ecole Normale Supérieure, Université Claude Bernard Lyon 1, and Centre National de la Recherche Scientifique, 69007 Lyon, France; 2Research Reactor Institute, Kyoto University, Osaka 590–0494, Japan; 3Natural History Museum of Denmark, and Nordic Center for Earth Evolution, 1350 Copenhagen K, Denmark; 4Department of Earth and Planetary Sciences, Washington University, and McDonnell Center for the Space Sciences, St. Louis, MO 63130

Edited* by Mark H. Thiemen, University of California San Diego, La Jolla, CA, and approved September 15, 2011 (received for review May 20, 2011)

The Isua Supracrustal Belt, Greenland, of Early Archean age (3.81–3.70 Ga) represents the oldest crustal segment on Earth. Its complex lithology comprises an ophiolite-like unit and volcanic rocks reminiscent of boninites, which tie Isua supracrustals to an island arc environment. We here present zinc (Zn) isotope compositions measured on serpentinites and other rocks from the Isua supracrustal sequence and on serpentinites from modern ophiolites, midocean ridges, and the Mariana forearc. In stark contrast to modern midocean ridge and ophiolite serpentinites, Zn in Isua and Mariana serpentinites is markedly depleted in heavy isotopes with respect to the igneous average. Based on recent results of Zn isotope fractionation between coexisting species in solution, the Isua serpentinites were permeated by carbonate-rich, high-pH hydrothermal solutions at medium temperature (100–300 °C). Zinc isotopes therefore stand out as a pH meter for fossil hydrothermal solutions. The geochemical features of the Isua fluids resemble the interstitial fluids sampled in the mud volcano serpentinites of the Mariana forearc. The reduced character and the high pH inferred for these fluids make Archean serpentine mud volcanoes a particularly favorable setting for the early stabilization of amino acids.

Results and Discussion

The results are given in tabular form in SI Text and are plotted in Fig. 1. The data are reported in the conventional δ66Zn notation, which represents the fractional deviation in parts per one thousand of the δ66Zn/64Zn sample ratio with respect to the ratio of the Lyon JMC Zn standard. It is now well established (12, 20, 21) that the range of Zn isotope variations in the vast majority of igneous rocks and clastic sediments is fairly narrow (δ66Zn approximately 0.25–0.35‰). In contrast, Isua serpentinites are markedly depleted in the heavy Zn isotopes (δ66Zn = −0.40 to + 0.04‰), whereas most δ66Zn values for serpentinites from two of the other types investigated here, the Baja California and Alpine ophiolites and the Gakkel Ridge, fall within the normal range of igneous rocks and clastic sediments (20). δ66Zn in serpentinites from the Marianas are

www.pnas.org/cgi/doi/10.1073/pnas.1108061108

PNAS | October 25, 2011 | vol. 108 | no. 43 | 17639–17643


The authors declare no conflict of interest.

*This Direct Submission article had a prearranged editor.

1Present address: Géosciences Montpellier, 34095 Montpellier, France.

2To whom correspondence should be addressed. E-mail: albarede@ens-lyon.fr.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1108061108/-/DCSupplemental.

The discovery of oceanic black smokers and their unique fauna prompted the idea that life may have sprung from hydrothermal vent fields at the bottom of the ocean (1–3). The highly reducing conditions of the vent fields associated with midocean ridges fulfill one of the stringent conditions for the stabilization of biomolecules. These conditions are a consequence of the metamorphic hydration and oxidation of ultramafic rocks of the oceanic lithosphere—a series of reactions known as serpen
tination—that release highly reduced hydrothermal fluids with high concentrations of methane, ammonia, and hydrogen (4, 5). Serpentinitization also produces FeNi1, which catalyses formation of complex organic compounds (5). Serpentinitization thus provides both a source of reduced carbon and a potential energy source, which, together, create an environment suitable for the emergence of the first biomolecules. The vast majority of hydrothermal vent fields, however, especially those hosted by midocean ridges, spout solutions with pH well below the pK of amino acids, which makes them unsuitable for Streeker synthesis (6, 7). Attention therefore shifted toward high-pH hydrothermal vent sites (8, 9) and notably toward the modern vent fluids from the unusual midocean ridge locality of Lost City.

The search for an Archean environment in which reducing and high-pH conditions coexist at temperatures appropriate for supporting early life prompted us to investigate Isua serpent
tinites and their associated hydrothermal carbonates (10). Precipi
tation of large amounts of carbonates suggests that carbonate ions were abundant in the parent fluid and therefore signals that the pH of this fluid was at least in the range of the second dissociation constant of carbonic acids, which for seawater at ambient temperature is approximately 9 (11). Recent work on isotope fractionation of Zn complexes in solution (hydrates, or aqua ions, chlorides, sulfides, sulfates, carbonates) (12, 13) indicates that Zn carbonates efficiently fractionate Zn isotopes. Measurements of Zn isotopes for Isua serpentinites revealed anomalous values (14). Therefore, a more systematic investigation of Zn isotopes in samples from this locality seemed promising. Focusing on this particular metal was reinforced by the proposition that, because transition elements are less mobile than the volatile elements commonly considered as potential biomarkers, Zn isotope compositions may reflect the original properties of Archean rocks more accurately than the isotope concentra
tions of carbon, sulfur, and nitrogen.

The complex lithology of the Isua Supracrustal Belt, Green
dland (3.81–3.70 Ga old), includes metabasalts, which can be divided into an ophiolite-like unit and a second unit known as “Garbenschiefer,” the geochemistry of which is reminiscent of boninites (15) and, hence, ties Isua supracrustals to an island arc environment. Serpentinites are also abundant in the metaba
salt series (16–18). Modern serpentinites from three representative geological settings also were investigated to provide a context for the Archean data. These are from (i) the magma-starved Gakkel Ridge (Arctic Ocean), which supplies well-serpentinitized samples from a midocean ridge setting; (ii) Baja California and the Alps, which typify ophiolites obducted onto continents; and (iii) Mariana forearc serpentinite mud volcanoes (19), which represent a subduction zone setting far from continental influence.
shifted toward negative values by 0.2 to 0.5‰ relative to igneous samples, with an average δ⁶⁸/Zn value of −0.01‰, similar to that of Isua serpentinites within the reported analytical uncertainty. Pentlandite samples separated from the S c, 940094, and M1 serpentinites and metallic iron separated from sample M1 have Zn isotope compositions that are only slightly different from the corresponding whole-rock values. Sulfide and metal therefore seem to have formed or reequilibrated during serpentinization. In contrast, Isua sphalerite veins, t alc schists, and hydrothermal (metasomatic) carbonates give igneous-like δ⁶⁸/Zn values (approximately 0.33, 0.24, and 0.35‰, respectively). Zn from Isua banded iron formations also fall within the general range of igneous and clastic rocks, whereas turbidites, with values ranging from −0.08 to + 0.28‰, can be interpreted as representing mixtures of igneous rock debris. Comparison of Zn serpentinite concentrations measured in this work with literature data (22) on peridotites suggests that about 30−60% Zn may be leached from the parent peridotite during serpentinization. Such an extent of Zn extraction requires that the nonigneous δ⁶⁸/Zn values of serpentinite reflect a strong partitioning of the light isotopes into the solid, whether Zn was present in the peridotite initially or was added later by fluid.

**The Kinetic Isotope Effect.** In a number of cases, isotope fractionation is not the result of equilibrium processes, but rather the outcome of isotope-dependent reaction rates (known as the kinetic isotope effect or KIE). The role of KIE is well documented for hydrogen, carbon, and sulfur, especially in biologically mediated reactions (23). It has, in particular, been invoked to account for δ⁶⁸/Zn values down to −0.17‰ in sphalerite from the Irish Midlands ore field (21), but the negative correlation between δ⁶⁸/Zn and δ⁴⁴/S also observed at this locality would require an inverse rate isotopic effect on sulfur (23), which has not so far been documented. Furthermore, the lack of fractionation of sulfur isotopes in Isua hydrothermal sulfides (24, 25) with respect to planetary abundances argues against a strong kinetic effect for Zn, which is much heavier than S.

**Fractionation at Equilibrium.** Recent theoretical work combining ab initio structure calculations and statistical mechanics (12, 13) is now allowing the role played by different species in solution in the fractionation of Zn isotopes to be determined over a broad range of temperatures. The ratio β of the partition functions for the ⁶⁶Zn and ⁶⁴Zn chl oro, aqua ions, and sulfide isotopomers is very similar (Fig. 2), which discounts these species as being responsible for major isotope fractionation within the fluid. At temperatures of 100−350 °C and for solutions with carbonate and sulfate concentrations similar to that of seawater and other near-surface fluids, Zn²⁺ and Zn chloride and sulfide complexes are the dominant Zn species in low-pH solutions (26) reacting with peridotites. Solutions are dominated by Zn²⁺ at pH < 3, and, with increasing pH, by Zn(HS)₂, Zn(HS)₃, and finally ZnS/HS⁻. None of these species are expected to induce significant Zn isotope fractionation (Fig. 2), and this is exactly what is observed in solutions and sulfide ores from the hot low-pH environments of black-smoker vent fields (27). Progressive, Rayleigh-type leaching of sulfide can certainly account for the Zn depletion upon serpentinization but demands large and therefore unsupported isotope fractionation among S-rich species, typically >1‰ for 50% Zn removal.

**The Role of Sulfate.** Because Zn sulfate complexes (12) stand out as particularly enriched in heavy isotopes, the effect of Zn complexation by sulfate in hydrothermal fluids must be considered. At ambient temperature and for sulfate concentration typical of modern seawater (28.6 mmol kg⁻¹), Zn-sulfate complexes are subordinate, making up less than a few percent of the metallic ion and chloride complexes (12, 28). Seawater-like abundances are too low to induce a substantial isotopic shift of the sulfide species, and therefore of the sulfide minerals precipitated from the solutions, toward negative δ⁶⁸/Zn values. Sulfate usually is absent from black-smoker vent solutions but may be present at low concentration levels in white smoker fluids such as at the TAG (290 °C) (27) and Lost City (40−70 °C) (29) vent fields on the Mid-Atlantic ridge. However, correlated Mg excesses strongly suggest that the white smoker sulfate originates from subsurface mixing of seawater and hydrothermal fluids. Regardless, the limited data on white smoker fluids do not indicate anomalous Zn isotope compositions (27). More generally, the range of variations of δ⁶⁸/Zn in sulfide ores from a wide variety of depositional environments (20, 21, 27, 30, 31) and, as shown in this study, also in Alpine ophiolites and Gakkel serpentinites, is quite narrow: The striking lack of negative δ⁶⁸/Zn values indicates that if Zn sulfate complexes were present in the parent hydrothermal fluid, they were not abundant enough to create major Zn isotope

![Fig. 1. Zinc isotope compositions of Isua supracrustal rocks and serpentinites from the Mariana forearc, Gakkel Ridge, and Alpine ophiolites, compared with δ⁶⁸/Zn data in marine shales (this study and data from ref. 48), deep-sea carbonates (data from refs. 47 and 48), and FeMn nodules (data from ref. 31). The gray field represents the worldwide igneous average (20).](image-url)
fractionation in hydrothermal solutions and sulfide deposits. Moreover, sulfate is widely thought to be missing from the Archean ocean (32), and the dominant sulfur species in Isua serpentinites is sulfide, not sulfate.

**The Role of Carbonate.** For want of a strong isotopic effect induced by sulfates, complexation by carbonate ions is a potential alternative. In seawater and in other hydrous fluids equilibrated under surface conditions, carbonate complexes are not abundant (13, 28). High carbonate concentrations are unlikely along midocean ridges because there is no other source of CO$_2$ than mantle outgassing and even that CO$_2$ is largely reduced to methane by hydrogen. In addition, the pH of hydrothermal fluids is usually very low (<5) and under such conditions, H$_2$CO$_3$ is not significantly dissociated. High carbonate concentrations can, however, be achieved at depths typical of arc environments, where subduction of carbonated basalts and calcareous sediments provides a potential source of CO$_2$. Fuji et al. (13) considered the case for a CO$_2$ pressure of 5 × 10$^8$ Pa, which may be equated with a depth of 1 km below the seafloor and 15% CO$_2$ in the fluid. They concluded that, under these conditions and at temperatures <150°C, ZnCO$_3$ dominates Zn species for pH > 8. Thus, Zn in high-pH, medium-temperature fluids is largely in the form of carbonate complexes. Carbonate concentrations in hydrothermal fluids can be estimated from pH and alkalinity, with the caveat that precipitation of hydrothermal carbonates, for which there is plenty of observational support (33), reduces alkalinity. In addition to the low $^{66}$Zn observed, the widespread occurrence of carbonates at Isua (10) and in Mariana mud volcanoes away from the trench by >70 km (33, 34), is a feature common to both sites and indicates that fluids in these localities were rich in carbonates. The presence of aragonite, a mineral species unstable under the conditions prevalent at the local seafloor and in Mariana serpentinite mud volcanoes (34), strongly supports decarbonation as a CO$_2$ source. The associated fluids have high alkalinity and H$_2$S contents, and their carbon isotope compositions confirm that CO$_2$ does not derive from the atmosphere but from the breakdown of subducted carbonates (33, 35, 36).

**Isua Serpentine Mud Volcanoes and the Origin of Life.** The association of Isua serpentinites with carbonates and negative $^{66}$Zn suggests that these rocks formed in conditions similar to those of the Mariana forearc, which is in line with previous conclusions about the Isua environment (15, 37). Of all the parameters that this comparison with mud volcanoes (33, 37) entails, the temperature range of 100–300°C (19) and the high pH of fluids (9–12.6) are the most noticeable. Metamorphic transformation of ultramafic rocks requires massive CO$_2$ uptake (10), while boiling of CO$_2$-rich fluids causes a sharp increase of the pH of hydrothermal solutions and promotes crystallization of calcite, ankerite, and dolomite (38). Because, at depth, ZnCO$_3$ accounts for most of the Zn dissolved in hydrothermal fluids (13), its $^{66}$Zn is essentially unfractuated with respect to the bulk of the fluid. The igneous-like $^{66}$Zn of Isua carbonate veins, therefore, are explained by precipitation from high-pH fluids percolating through serpentinites. In contrast, any sulfide precipitating from the same fluid must show markedly negative $^{66}$Zn, which is what Isua and Mariana serpentinites do. In contrast, Isua talc schists and sphalerite veins contain Zn processed by hydrothermal transformation of peridotites at metamorphic temperatures around 500°C (10), causing their $^{66}$Zn to be essentially unfractuated with respect to the igneous range and, hence, reflect $^{66}$Zn of the fluid.

The Isua environment is best interpreted as an equivalent of the Mariana forearc (19) with the Isua serpentinites being the Archean analogue of modern mud volcanoes. Modern active serpentine mud volcanoes are an unusual geological feature restricted to the Mariana and Izu-Bonin arc because the appropriate conditions at nonaccretionary, intraoceanic subduction zones are simply infrequent. The seismic structure of the Izu-Bonin underthrust serpentinite mud volcanoes shows low-strength serpentinite diapirs rising from the topmost layer of the mantle wedge above the subduction zone (39). This mechanism is consistent with the field observations at Isua, where serpentinite bodies occur as tectonized podded structures within pillow basalt units of the ophiolite sequence. An interpretation as a sea floor mud volcano is thus consistent with the overall forearc geologic environment (15, 37), with the composition of the ultramafic protolith of serpentines (40), and with the occurrence of a few $^{66}$Zn values lower than the igneous average in Isua turbidites, for which a dacitic or andesitic protolith has been acknowledged (18). An intriguing implication is that carbonate-rich seafloor lithologies were being subducted by 3.8 Ga.

Our data favor the existence of warm, highly reducing hydrothermal fluids with high pH in early Archean serpentinite mud volcanoes. In a world endowed with plate tectonics but with smaller continental expanses than today, intraoceanic arcs such as the Mariana arc must have been common and, hence, also serpentine mud volcanoes. The presence of extremophilic *Archaeae* on a Mariana forearc serpentinite mud volcano and their role in oxidizing methane from the ascending fluid to carbonate ion and organic carbon has been previously noted (41). Forearcs have the added appeal that, in addition to serpentinitization being a major source of hydrogen, subaerial volcanoes provide a proximal source of phosphorus, an indispensable nutrient for all forms of life, in a world where continents had not yet reached their modern surface areas (42). Unlike midocean ridges, which are generally deepwater structures and not a source but a sink for phosphorus (43), weathering of nearby aerial volcanic edifices from the arc system provides forearc vent field oceanic environments with a sustainable supply of phosphorus. The onset of plate tectonics, which presumably took place sometime during the Hadean, in addition to the existence of a water ocean with...
carbonate sedimentation and the resulting ocean-continent dichotomy, may have fostered the emergence of life on our planet in mud volcanoes.

**Materials and Methods**

Samples analyzed from Isua are serpentinites, talc schists, veins of sphalerite (ZnS), metasomatic carbonates, and banded iron formations (BIF). Sulfides from two Isua serpentinites (samples Bc and 940094) and from Baja California (ZnS), metasomatic carbonates, and banded iron formations (BIF). Sulfides were extracted from sample M1 using a hand magnet. The analytical techniques used for the chemical separation of Zn and for the isotopic analyses have been described elsewhere (45, 46) and are only repeated briefly here. Zinc was separated on Dowex AG1-X8 anion-exchange resin using HBr. Because ion-exchange resins fractionate Zn isotopes, full yields are required. By analyzing all the recovered fractions, we were able to demonstrate that the yield was better than 99%. All reagents were distilled in pyrex stills. Zinc isotope ratios were measured by multiple-collection induction-coupled plasma mass spectrometry (MC-ICP-MS) at ENS-Lyon on a Nu Plasma 500 HR. The samples were taken up in 0.05 N HNO₃ and run in wet plasma mode with a spectral resolution of M/ΔM = 300. We used Cu NIST-SRM976 for doping the samples and an exponential mass fractionation law to correct for the instrumental mass bias. Samples were bracketed with standards, randomized, and the measurements duplicated. Sample solutions were diluted to match the concentration of the standard mixture (Zn 0.5 ppm–Cu 0.5 ppm). The total procedural blank including sample dissolution, chemical purification steps, and mass spectrometry measurements was 15 ng of Zn, which represents less than 0.5% of the total sample signal. The external reproducibility on δ⁶⁰Zn based on repeated measurements of the Zn standard is 0.05‰.

**ACKNOWLEDGMENTS.** We are grateful to Henry Dick, who provided the Gakkel Ridge samples with support from the National Science Foundation to the Woods Hole Oceanographic Institution collection; Bertrand Van de Moortele and the Centre Lyonnais de Microscopie for the SEM images; Philippe Télouk and Emmanuelle Albalat for maintaining an efficient and well-functioning work environment; Janne Blöchert-Toft for translating the English text; Mike Mottl for reviewing an earlier version of the manuscript; and anonymous reviewers for providing very helpful scientific and editorial comments. We thank the Institut des Sciences de l’Univers for steady support to F.A., in particular through the Origine des Planètes et de la Vie Program and the Agence Nationale pour la Recherche through the Begdy grant. Grants from the Carlsberg Foundation and the Danish National Research Foundation to M.R. supported field work in Greenland. Support of the Danish National Research Fund to NordøCE is gratefully acknowledged. The International Ocean Drilling Project provided samples from the Marianas. The Lyon ICP-MS facility is supported by Institut National des Sciences de l’Univers and the Ecole Normale Supérieure de Lyon.

---


