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

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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 serpentines, 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/δ⁶⁴Zn 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 = −0.48 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

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 concentrations of carbon, sulfur, and nitrogen.

The complex lithology of the Isua Supracrustal Belt, Greenland (3.81–3.70 Ga old), includes metabasalts, which can be divided into an ophiolite-like unit and a second unit known as “Garbenschierf,” 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 metabasalt series (16–18). Modern serpentinite samples 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-serpentinized 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.


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shifted toward negative values by 0.2 to 0.5 ‰ relative to igneous samples, with an average δ66Zn value of -0.01 ‰, similar to that of Isua serpentinites within the reported analytical uncertainty. Pentlandite samples separated from the 8 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, talc schists, and hydrothermal (metasomatic) carbonates give igneous-like δ66Zn 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 δ66Zn 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 δ66Zn values down to -0.17 ‰ in sphalerite from the Irish Midlands ore field (21), but the negative correlation between δ66Zn and δ34S also observed at this locality would require an inverse isotope 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-chloride, 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 δ66Zn 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 δ66Zn 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 δ66Zn values indicates that if Zn sulfate complexes were present in the parent hydrothermal fluid, they were not abundant enough to create major Zn isotope...
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, complexion 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$_3$, CO$_2$, and CO$_3^{−2}$ is not significantly dissociated. High carbonate concentrations can, however, be achieved at depths typical of arc environments, where subduction of carbonate 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$^6$ 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 serpentinite 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 underneather 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 serpentinite mud volcanoes. The presence of extremophilic *Archaea* 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 (Bf) Baja California sample M1 were purified by sieving and heavy-liquid separation. Analysis of Isua serpentinites by secondary electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) did not reveal the presence of sphalerite (Fig. 3). Instead, the dominant sulfide mineral in Isua serpentinites is cobalt-rich pentlandite, a common mineral in Archean mafic and ultramafic rocks (44). Pentlandite is also the sulfide mineral present in the M1 serpentinite. A metal phase was 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 PE-tails. 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 free-aspiration using a glass microconcentric nebulizer (uptake rate: 80 μL/min) and a glass cyclonic spray chamber. Peak intensities (M = 64, 66, 67, and 68) were measured in Faraday detectors in static 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 δ66Zn based on repeated measurements of the Zn standard is 0.05‰.

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