of 600 km to the source, total bremsstrahlung production efficiency of 13% (27), 30 photons detected for an average TGF, and an instrumental effective area of 250 cm², we require ~3 x 10¹⁵ 35-MeV electrons, for a total energy of ~20 kJ or a power of ~40 MW over 0.5 ms. Beamming would make these numbers lower, even as it made the inferred number of TGFs higher. Although thin-target bremsstrahlung gives a better fit, the electron content in the thin-target case is unconstrained and could be much higher. For upward-beamed electrons, ignoring Earth’s magnetic field, the transition between thin and thick target would take place at ~30 km.

TGFs near geomagnetic latitude 45° have been considered as a source of ~1 MeV electrons in Earth’s inner radiation belt by Lehtinen et al. (17). Inner-belt electrons above 10 MeV are more relevant to our results and were detected by Mariya-2 on the Mir station (28). The RHESSI TGFs, however, have an average geomagnetic latitude of 14°, and for these the electrons would be tied to magnetic field lines that skim the atmosphere and could not become trapped. As we analyze the whole RHESSI data set—almost 3 years and counting—we will either measure or place limits on high-latitude TGFs that may contribute to the inner-belt electrons above 10 MeV.

We are searching with a number of groups for coincidences between RHESSI TGFs and different kinds of lightning and TLEs. With TGFs for the whole RHESSI mission, we will compare these populations statistically as well.

References and Notes
20. Materials and methods are available as supporting material on Science Online.
23. R. Roussel-Dupré, personal communication.
29. The v1.0 gridded satellite lightning data were produced by the NASA Lightning Imaging Sensor/ Optical Transient Detector Science Team (Principal Investigator, H. J. Christian, NASA/ Marshall Space Flight Center) and are available from the Global Hydrology Resource Center (http://ghrc.msfc.nasa.gov).
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Iron Isotope Constraints on the Archean and Paleoproterozoic Ocean Redox State

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The response of the ocean redox state to the rise of atmospheric oxygen about 2.3 billion years ago (Ga) is a matter of controversy. Here we provide iron isotope evidence that the change in the ocean iron cycle occurred at the same time as the change in the atmospheric redox state. Variable and negative iron isotope values in pyrites older than about 2.3 Ga suggest that an iron-rich global ocean was strongly affected by the deposition of iron oxides. Between 2.3 and 1.8 Ga, positive iron isotope values of pyrite likely reflect an increase in the precipitation of iron sulfides relative to iron oxides in a redox stratified ocean.

The rise of atmospheric oxygen, which began by about 2.3 Ga (1–3), was one of the most important changes in Earth’s history. Because Fe, along with C and S, are linked to and maintain the redox state of the surface environment, the concentration and isotopic composition of Fe in seawater were likely affected by the change in the redox state of the atmosphere. The rise of atmospheric oxygen should have also led to dramatic changes in the ocean Fe cycle because of the high reactivity of Fe with oxygen. However, deposition of banded iron formations (BIFs) during the Paleoproterozoic era suggests that the deep ocean remained anoxic, at least episodically, until about 1.8 Ga, which allowed high concentrations of Fe(II) to accumulate in the deep waters (4).

Here we use Fe isotope systematics (5) to provide constraints on the redox state of the Archean and Paleoproterozoic oceans and to identify direct links between the oxidation of the atmosphere and the Fe ocean cycle.

Laboratory and field studies suggest that Fe isotope variations are associated mainly with redox changes (6, 7). Lithogenic sources of Fe on the modern oxygenated Earth, such as weathering products, continental sediments, river loads, and marine sediments, have isotopic compositions similar to those of igneous rocks (8, 9). In contrast, seafloor hydrothermal sulfides and secondary Fe-bearing minerals from the altered oceanic crust span nearly the entire measured range of δ⁵⁶Fe values (5) on Earth, from −2.1 to 1.3 per mil (‰) (10, 11). Large variations of δ⁵⁶Fe (from −2.5 to 1.0‰) in Late Archean to Early Paleoproterozoic BIFs have been also reported (12), which highlight the roles of ferrous Fe oxidation, fluid-mineral isotope fractionation, and potentially microbial processes in the fractionation of Fe isotopes.

Study of S isotope composition of sedimentary pyrite over geological time has placed important constraints on the S cycle and the evolution of ocean chemistry (13). Here we apply a similar time-record approach in order to explore potential changes in Fe isotope compositions. Pyrite formation in modern organic-rich marine sediments is mediated by sulfate-reducing bacteria and proceeds essentially through the dissolution and reduction of lithogenic Fe oxides and Fe silicates to Fe(II), either below the sediment-water interface or in stratified euxinic bottom waters (14–16). During reduction of Fe oxides, diagenetic fluids with isotopically light Fe(II) may be produced (17, 18). However, the Fe

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isotope composition of sedimentary pyrite from Phanerozoic organic-rich sediments studied so far (Fig. 1 and table S2) (19) suggests that such processes are unlikely to produce sedimentary pyrite with δ56Fe < -0.5‰. It is presumed that most of reactive Fe is scavenged to form pyrite, minimizing Fe isotope fractionation regardless of the isotope effect during Fe reduction (17) and precipitation (20). In contrast, when high concentrations of Fe(II) accumulate under anoxic conditions and low sulfide concentrations, large δ56Fe variations (10–12) may occur because of partial Fe(II) oxidation, Fe(III) reduction, and distillation processes during mineral precipitation. We thus hypothesize that Fe isotope variations in sedimentary pyrite are particularly sensitive to the concentration of dissolved Fe(II) and can be used to place important constraints on the sources and sinks of the Fe(II) reservoir.

We analyzed Fe isotope composition of sulfides in black shales ranging in age from Precambrian to Late Cretaceous, specifically focusing on Late Archean to early Paleoproterozoic time (Fig. 1) (21). The emerged general pattern of Fe isotope variations suggests that Earth’s history may be divided into three stages, which are strikingly similar to the stages defined by multiple sulfur isotope and carbon isotope records, as well as other indicators of the redox state of the atmosphere and ocean (2, 3, 13, 22).

Stage I extends from before 2.8 Ga to about 2.3 Ga and is characterized by highly variable and negative δ56Fe values. The range of δ56Fe values between 0.5 and −3.5‰ is often observed within a single section of black shales, but individual pyrite nodules from the same stratigraphic level have similar δ56Fe values (Fig. 2). Because dissimilatory Fe(III) reduction has been suggested to be important on early Earth (23) and is known to produce large Fe isotope fractionations (6, 24), it can be hypothesized that these extreme Fe isotope fractionations were produced by this metabolic activity. However, three independent observations argue against this hypothesis. First, Fe isotope fractionation during single-step bacterial reduction of Fe oxides (with an initial δ56Fe value of 0‰) is unlikely to produce Fe(II) with δ56Fe less than −1.3‰ (17). Second, if a δ56Fe value as low as −3.5‰ can be generated through multiple steps of Fe oxidation and reduction, then the evidence for these processes should be evident in younger sediments, but they are not documented (Fig. 1). In addition, bacterial Fe(III) reduction is expected to produce pyrite with locally highly variable negative δ56Fe values, depending on the extent of Fe(III) reduction and Fe(II) reoxidation. Our samples (Fig. 2 and table S2) do not show great variability between individual sulfide nodules and suggest a common source of Fe(II). Third, the amount of biogenically produced Fe(II) would need to be unrealistically high during the Archean to swamp the global influence of hydrothermally derived Fe(II) with δ56Fe values between 0 and −0.5‰ (8) delivered to the deep ocean.

Values of δ56Fe as low as −2.3‰ have been observed in Fe-rich groundwater springs that precipitate isotopically heavy ferrihydrite along a fluid-flow path (25) and yield low δ56Fe values in a residual Fe(II) pool. Adsorption of Fe(II) onto Fe oxide particles may also provide an additional means to produce an isotopically negative Fe(II) pool through the preferential sorption of 56Fe onto Fe oxide surfaces (24). In a similar manner, low δ56Fe values for Archean oceans may reflect preferential sequestration of 56Fe on Fe oxides (26, 27). Indeed, magnetite and hematite in BIFs are often characterized by positive δ56Fe values (12), for example, δ56Fe values up to 1.6‰ in iron formations of the ~2.7 Ga
Belingwe Belt, Zimbabwe (Fig. 1). Large stratigraphic variations in δ56Fe of sedimentary pyrites in ~2.7- to ~2.5-Ga black shales, up to 3% over tens to hundreds meters of section (Fig. 2), suggest changes in Fe isotope composition of seawater over short periods of time on the order of a few million years. This implies a nonsteady state of the Archean Fe cycle with variable Fe concentrations caused by the competitive effect of Fe oxide precipitation and Fe supply from hydrothermal sources. These rapid changes of Fe concentrations are consistent with the idea that Fe oxide deposition in BIFs resulted from the episodic upwelling of Fe-rich deep waters accompanied by partial biological and/or abiological oxidation (26) in shallow waters (28). Alternatively, Fe oxide deposition within marine sediments on continental shelves or in the deep ocean may have also provided an important sink for Fe between periods of large BIF deposition.

We used a simple Rayleigh distillation model to explore the influence of Fe oxide deposition on the Fe isotope composition of seawater (29). Fe is delivered to the ocean from rivers and from seafloor hydrothermal systems with δ56Fe values ranging from 0.0 to −0.5‰ (δ). Fe is then removed by precipitation of Fe oxides. δ56Fe values as low as −3.5‰ are only reached when more than 90% of the Fe from the initial Fe pool is precipitated as Fe oxides. δ56Fe values of −1.5 to −2.0‰, which are more typical of Late Archean sulfides, correspond to about 50% of the Fe precipitated as oxides. This value is similar to the estimates of Fe sink in BIFs based on P adsorption (30).

Stage II, which covers the time interval from about 2.3 to about 1.7 Ga, is characterized by the disappearance of negative δ56Fe values and the emergence of positive δ56Fe values up to 1.2‰. Major perturbations in biogeochemical and climatic record occurred during the beginning of stage II. These include the following: (i) negative and positive carbon isotope excursions in carbonates sandwiched between glacial diamictites, (ii) Earth’s earliest global glaciations, and (iii) oxidation of Earth’s atmosphere as suggested by increasing seawater sulfate content inferred from the δ34S record and appearance of sulfate evaporites; disappearance of nonmass-dependent S isotope fractionation; appearance of red beds, oxidized paleosols, hemaitic oolites, and pisolithes; Mn oxide deposits; and Ce anomalies in chemical sedimentary deposits (3, 13, 22, 31). The appearance of positive δ56Fe values, which persisted until about 1.7 Ga, together with the disappearance of strongly negative δ56Fe values, occurred during the period when the most sensitive indicators for the rise of atmospheric oxygen first appeared. All these observations suggest that the oxidation of the surface environment in the early Paleoproterozoic was relatively rapid and that it directly affected the Fe isotope composition of the ocean.

How the change in the Fe isotope record about 2.3 Ga corresponds with change of the oceanic Fe cycle and the redox state of the ocean is not straightforward. Large BIF deposits are almost entirely lacking between 2.3 and 2.1 Ga (32), which is consistent with the lack of negative δ56Fe values during this period. However, BIF deposition returned at about 2.1 Ga, and major BIFs were deposited in North America and Australia (32). If δ56Fe values of pyrites in black shales that were deposited between 2.1 and 1.8 Ga are representative of the whole ocean, then BIF deposition mechanisms were different from those prevailing during the Archean. We infer that late Paleoproterozoic BIFs were deposited in an oxygenated layer of the ocean, and complete precipitation of Fe from Fe-rich plumes upwelling from the deep ocean did not affect the Fe isotope composition of the deep ocean. Despite the limited number of analyses, the narrow range of δ56Fe values of hematite and magnetite from the 1.88-Ga Biwabik and Tyler formations compared with Archean BIFs (Fig. 1 and table S3) is consistent with this assumption.

An important consequence of the rise of atmospheric oxygen levels was the initiation of oxidative weathering and an increase in sulfate delivery to seawater (13). Consequently, the formation of Fe sulfides in the water column of pericratonic basins may have become the dominant part of the global ocean Fe cycle and may have prevented deposition of large BIFs, except during periods of intense submarine volcanic activity followed by high hydrothermal input of Fe. The effect of the increased role of sulfide production on the Fe isotope record is presently uncertain because reliable estimates of equilibrium Fe isotope fractionation during pyrite formation are lacking (20). One plausible hypothesis is that the positive δ56Fe values in 2.3 to 1.8 Ga sedimentary sulfides might be related to sulfide precipitation from an Fe-rich pool with δ56Fe composition around 0‰ and a pyrite-Fe(II) fractionation factor of up to 1‰ as suggested in previous studies (10, 33). This hypothesis indicates that sulfate produced by sulfate-reducing bacteria during this period has been completely titrated by dissolved Fe species in the Fe-rich and sulfide-poor ocean.

The disappearance of major BIFs after about 1.8 Ga is thought to indicate that the deep ocean became either progressively oxic or euxinic (4). Because the solubility of Fe sulfides and Fe oxides was low, most of the hydrothermally derived Fe(II) was likely rapidly precipitated in the deep ocean, allowing few possibilities to produce Fe isotope fractionation. The lack of substantial δ56Fe value variations in sulfides from black shales younger than 1.5 Ga is thus consistent with the general picture that the whole ocean was Fe-poor after about 1.6 Ga. But the lack of variation does not place constraints on the oxic versus sulfidic nature of the deep ocean. More data that cover the Phanerozoic, Mesoproterozoic, and Neoproterozoic time intervals are required to understand fully the change in the ocean Fe cycle at about 1.8 Ga.

Our Fe isotope record provides new insights into the Archean and Paleoproterozoic ocean chemistry and redox state. Fe isotope compositions suggest that the Archean oceans were globally Fe rich and that their Fe isotope composition and Fe content were variable in response to the episodic establishment of an Fe-rich pool supplied by hydrothermal activity and the deposition of Fe oxides, either in BIFs or dispersed throughout sediments on continental shelves and in the deep sea. After the rise of atmospheric oxygen by about 2.3 Ga, the Paleoproterozoic ocean became stratified and characterized by an increase of sulfide precipitation relative to Fe oxide precipitation. During this period, BIFs were likely deposited by upwelling of Fe(II)-rich plumes and rapid oxidation in the oxygenated layer of the ocean. Conducting Fe isotope analyses of sedimentary sulfides in conjunction with S isotope analyses should enable a more refined understanding of the origin of the positive Fe isotope excursion and the biogeochemical cycles of Fe and S during the Paleoproterozoic era.

References and Notes
4. The disappearance of BIFs after about 1.8 Ga had been initially thought to indicate the transition to the oxygenated ocean (1), but a growing body of evidence suggests that sulfide, rather than oxygen, could have been responsible for removing Fe from deep ocean waters (13, 34–36).
5. Data are reported using the delta notation relative to the Institute for Reference Materials and Measurements (IRMM)–14 Fe isotope reference standard defined as δ56Fe = 1000 × [(56Fe/54Fe)sample/(56Fe/54Fe)IRMM–14] − 1. External precision of δ56Fe values are estimated at 0.1‰ (2σ level). Analytical procedures, sample descriptions, and Fe isotope composition of various georeferenced materials, black shales, and BIF are available as supporting materials on Science Online.
9. The range of Fe isotope composition of hydrogenic ferromanganese deposits near oxygenic oceans may be large [between −0.8 and −0.1‰ (37)], but it is unclear whether the variability is caused by changes of Fe isotope composition in the water column or by secondary effects.
17. Experimental studies suggest that Fe isotope fractionations during bacterial reduction of Fe oxides is
dependent on reduction rates [6]. At high reduction rates, rapid formation and sorption of Fe(II) to ferric oxide substrate produced fractionations as large as \(-2.3\%_\text{o}\), but this value corresponds to an extreme case and fractionation of \(-1.3\%_\text{o}\) between biogenic Fe(II) and ferric oxide is more representative [6].


20. Theoretical calculations predict that pyrite (FeS\(_2\)) is an isotopically heavy phase relative to Fe(II) with a fractionation factor similar to magnetite (23). However, experimental precipitation of magnetite (FeS\(_2\)) produces a kinetic isotope fractionation of 0.3\% (38), suggesting that the fractionation of pyrite is poorly constrained from 0.3 to 1.0% relative to dissolved Fe(II).

21. Samples from different black shale units of similar ages were selected to distinguish between local and global effects on Fe isotope composition of seawater. We extracted between 10 and 20 sulfide grains to obtain a best estimate for the average \(\delta^{68}\text{Fe}\) value for each sample. For comparison and to evaluate heterogeneity, we also analyzed several individual sulfide nodules from the same samples (table S2).


26. Because the atmosphere was still reducing during this period, the mechanisms by which oxidation of ferrous Fe sources occurred are extensively debated. Biogeochemical evidence for oxygenic photosynthesis exists in sediments as old as 2.7 Ga (39) and may have contributed to ferrous iron oxidation with \(O_2\). Alternatively, a direct mechanism for Fe oxidation by anoxygenic phototrophic bacteria has been suggested (40), and abiotic photochemical oxidation may have also contributed to Fe oxidation in the Archean (41).

27. A magnetite-Fe(II) fractionation factor of about 2.4\% has been inferred from BIF data [12], which is slightly less than the equilibrium Fe(III)-Fe(II) fractionation factor of 2.9\% at 22°C [42]. The fractionation between ferricyanide and Fe(II) of 1.5% measured during anaerobic photosynthetic Fe(II) oxidation by bacteria [43] is slightly larger than the 0.9% fractionation measured during abiotic oxidation of Fe(II) to ferricyanide [25].


29. In our model, we assumed that an initial pool of Fe(II) supplied by hydrothermal activity was depleted through Fe oxidation and precipitation of Fe oxides. The isotope composition of residual Fe(II) is linked to \(\epsilon\), the ratio of remaining to initial Fe(II), following the distillation equation

\[
\delta^{68}\text{Fe} = \left(1000 + \delta^{68}\text{Fe}_\text{ residual}ight) \times e^{(\epsilon/0.2)} - 1000
\]

where \(\delta^{68}\text{Fe}_\text{ residual}\) is the initial value of hydrothermally derived Fe(II) at \(-0.5\%_\text{o}\) and \(\epsilon\) is the fractionation factor during Fe oxidation and Fe oxide precipitation, ranging between 1.0015 and 1.0023 [6].


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Materials and Methods

Fig. S1

Tables S1 to S3

References

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Stem Lagomorpha and the Antiquity of Glires

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We describe several fossils referable to Gomphos elkeana from deposits close to the Paleocene-Eocene boundary at Tsagan Khusu, Mongolia. Gomphos shares a suite of cranioskeletal characters with extant rabbits, hares, and pikas but retains a primitive dentition and jaw compared to its modern relatives. Phylogenetic analysis supports the position of Gomphos as a stem lagomorph and excludes Cretaceous taxa from the crown radiation of placental mammals. Our results support the hypothesis that rodents and lagomorphs radiated during the Cenozoic and diverged from other placental mammals close to the Cretaceous-Tertiary boundary.

Rodents and lagomorphs, collectively known as Glires, represent much of the modern diversity of mammals and have played an important role in understanding the timing of placental mammal diversification. On paleontological grounds, the origin of Glires is hypothesized to have taken place close to the Cretaceous-Tertiary boundary (1–3), a result compatible with some recent estimates from molecular studies (4,5). In contrast, other molecular estimates of Glires divergence have suggested a much older date, extending to 80 (6) or even more than 110 (7) million years ago (Ma). Paleontological support for an older date for Glires divergence has been proposed by studies supporting a close relationship between fossil zalambdalestids and Glires (8–10). Zalambdalestids are an extinct central Asian group of eutherian mammals (11, 12); their first appearance 85 to 90 Ma (10), coupled with a sister-taxon relationship with lagomorphs and/or rodents, would imply the presence of a Glires stem lineage more than 20 million years before the first appearance of any undisputed placental mammal. Until recently, stem lagomorphs (13, 14) were known from fragmentary craniodental remains (15), with few specimens associated with postcrania (16). Here we describe fossils of Gomphos elkeana, including a specimen with an articulated skull and skeleton (Fig. 1), from the Nemegt Basin, Mongolia, and re-evaluate the origin of Glires.

G. elkeana was first described as a paromysid-like rodent on the basis of lower-cheek teeth from deposits overlying Paleocene rocks at Gashato, Mongolia (17–19). The specimens discussed here are older and were recovered from a number of localities near Tsagan Khusu, Mongolia (19, 20), from the base of the Bumber Member of the Naran Bulak Formation, dating to the Paleocene-Eocene boundary (21). Gomphos has enlarged, gliriform

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