

Extraterrestrial dust, the marine lithologic record, and global biogeochemical cycles

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ABSTRACT

Delivery of bioavailable iron and other bioessential metals to the sea surface influences the ocean-climate system through stimulation of marine primary productivity and organic carbon export in areas where eolian iron input is low, such as the Southern Ocean. In these regions, extraterrestrial dust may provide a significant fraction of bioavailable iron, due to the high reactivity of re-condensed material following ablation. If so, past episodes of increased extraterrestrial dust flux should be evident in lithologic, and potentially climatic, records. Here we show that the well-documented increase in extraterrestrial flux associated with the Ordovician L-chondrite parent-body breakup is close in time to proliferation of ooidal ironstones on continental shelves. We hypothesize that benthic iron flux from shelf sediments was increased by expanded oxygen minimum zones driven by broader regions of increased primary productivity. A later Mesozoic interval of global proliferation of ooidal ironstones and black shales also occurs at a peak in asteroid family ages formed by major main-belt collisions. Although internal forcings and feedbacks, such as global tectonic and magmatic processes, play the dominant control on long-term changes in biogeochemical cycles and related marine lithologic records, we suggest that extraterrestrial dust flux may play a role as an external forcing on Earth's climate system.

EXTRATERRESTRIAL DUST AND OCEAN BIOGEOCHEMISTRY

Concentrations of dissolved iron are extremely low (<0.2 nM) in most regions of the surface ocean, as are concentrations of other bioessential metals, due to planktonic uptake and export to sub-photoc zone depths (e.g., Morel and Price, 2003). In high-nitrogen, low-chlorophyll (HNLC) regions, iron and trace metals limit marine primary productivity in much of the surface ocean (e.g., Boyd and Ellwood, 2010; Olgun et al., 2011). Recycling from the deep ocean and other sources supplies significant bioavailable iron and other metals in some regions, but models and experiments show that enhanced flux of bioavailable iron and metals to the ocean surface can strongly increase marine primary productivity, particularly in the Southern Ocean and other HNLC regions (Coale et al., 2004; Boyd et al., 2010; Smetacek et al., 2012; Tagliabue et al., 2017; Pabortsava et al., 2017). The extent to which this, in turn, leads to long-term organic carbon export to the deep

ocean, and whether variations in iron and metal flux could significantly affect global seawater chemistry and climate, and be reflected in the lithologic record, however, remain unclear.

The most important external source of iron and other bioessential metals to the surface of the open ocean today is eolian dust, but the proportion that is soluble and thus bioavailable (typically defined as the fraction smaller than 0.2 μm) is not well known. Globally averaged, the bioavailable eolian flux is estimated at $\sim 50\text{--}100 \mu\text{mol/m}^2/\text{a}$, $\sim 10\text{--}100\times$ higher than other sources to the open ocean (Fig. 1). However, this flux is highly spatially heterogeneous, and is particularly low in the Southern Ocean ($\sim 0.2\text{--}5 \mu\text{mol/m}^2/\text{a}$).

As suggested by Johnson (2001) for iron, in some regions the modern flux of extraterrestrial dust may be a significant source of bioessential metals. Modern extraterrestrial iron flux has been estimated from atmospheric, ice core, sediment, direct sampling, and zodiacal cloud observations as between 2×10^6 and 1×10^8 kg/a (Plane, 2012), but the most direct lines of

evidence have led to a widely accepted flux of $4 \pm 2 \times 10^7$ kg/a (Peucker-Ehrenbrink et al., 2016). Assuming an iron concentration in extraterrestrial material of 25%, typical of >70% of incoming extraterrestrial material today (see the GSA Data Repository¹), yields a globally averaged iron flux of $0.35 \mu\text{mol/m}^2/\text{a}$. The vast majority of this is likely soluble, because most incoming material (except for the finest $\sim 1\%$ of incoming dust) vaporizes during atmospheric entry and re-condenses into nanometer-scale particles whose high surface-area and negligible settling rates lead to high reactivity and bioavailability in the surface ocean (Hunten et al., 1980; Flynn, 2001; Saunders and Plane, 2006; Plane, 2012). Atmospheric circulation also focuses most of this deposition to latitudes of $\sim 50\text{--}70^\circ$ (Vondrak et al., 2008; Plane, 2012; Dhomse et al., 2013), so that in the Southern Ocean, the modern flux of extraterrestrial iron (and other bioessential metals) is comparable to, and potentially larger than, that of bioavailable eolian iron (Fig. 1).

Multiple lines of evidence suggest that the flux of extraterrestrial dust has been several times higher than modern in several intervals in the past. Increased flux of highly soluble iron and other bioessential metals could be manifest in the marine lithologic record in several ways. If the soluble metals fertilize marine primary productivity in HNLC regions, this could lead to increased organic carbon export and burial, expansion of oxygen minimum zones, and decreased oxygen bottom-water and/or water-column stratification. If sub-oxic conditions extended to continental shelf environments, where most of the preserved lithologic record originally formed, this could potentially increase the flux of reduced iron from within shelf sediments to the sediment-water interface (Severmann et al., 2010; Homoky et al., 2012). The extent and magnitude of such effects would

¹GSA Data Repository item 2018318, Figure 1 references and details, oolitic ironstones, iron fluxes, and asteroid family ages, is available online at <http://www.geosociety.org/datarepository/2018/> or on request from editing@geosociety.org.

CITATION: Reiners, P.W., and Turchyn, A.V., 2018, Extraterrestrial dust, the marine lithologic record, and global biogeochemical cycles: *Geology*, v. 46, p. 863–866, <https://doi.org/10.1130/G45040.1>

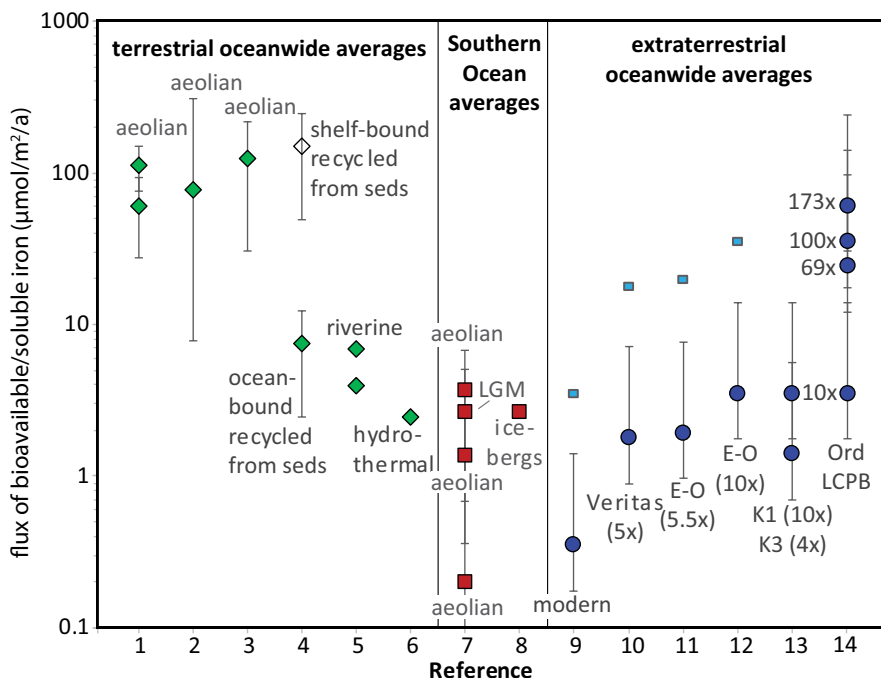


Figure 1. Fluxes of bioavailable iron to the open ocean from terrestrial sources on a global ocean-wide average basis (green), in the Southern Ocean (red), and from extraterrestrial dust (blue). Full explanation and sources are provided in the Data Repository (see footnote 1). Points and error bars represent either (1) mean of range provided in references with minima and maxima, or (2) assumptions of 1%, 10%, or 40% bioavailability, as noted for each reference in the Data Repository. Three estimates of modern, and one for Last Glacial Maximum (LGM), of Southern Ocean eolian flux are shown. Extraterrestrial fluxes (as factors of modern) are shown for the late Miocene Veritas event, end-Oligocene (E-O), two late Cretaceous events (K1, K3), and the Ordovician L-chondrite parent-body breakup (LCPB). Small blue squares for E-O, Veritas, and modern represent approximate 10x effect of atmospheric focusing in Southern Ocean.

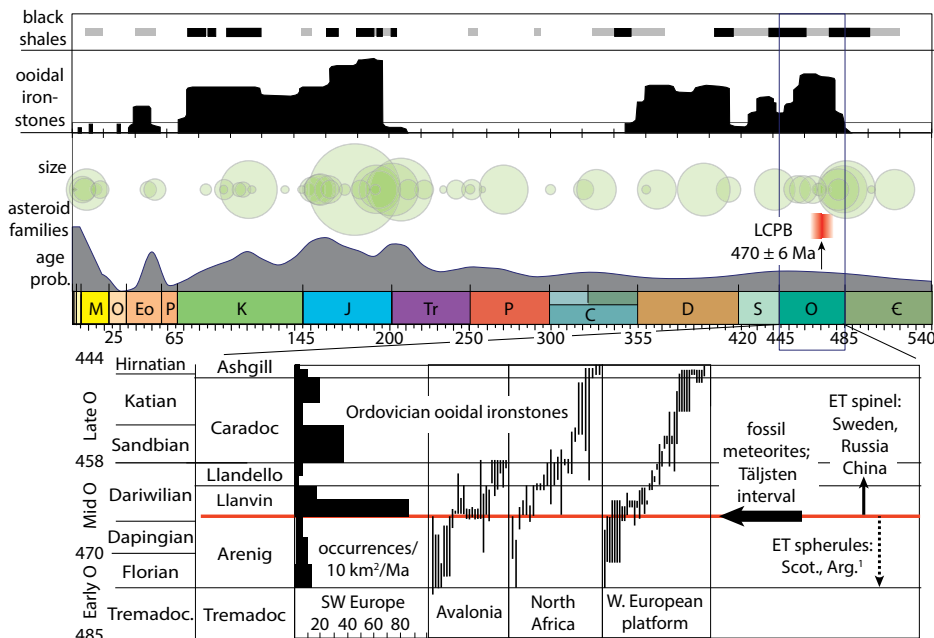


Figure 2. Upper: Phanerozoic intervals of abundant black shales (black [most widespread] and gray bars), ooidal ironstone occurrences (Van Houten and Arthur, 1989), and relative asteroid family sizes (green circles) and age-probability density (gray field) (see Table DR1 [see footnote 1]). Lower: Ordovician Gondwanan ooidal ironstone occurrences (Young, 1992), showing proliferation at increased extraterrestrial flux and higher productivity interpreted from Täljsten and coeval intervals. Studies in note 1 (see the Data Repository) suggest increased extraterrestrial flux slightly earlier than the spinel and fossil meteorite interval, near the earliest ironstone appearances. LCPB—L-chondrite parent-body breakup; €—Cambrian; O—Ordovician; ET—extraterrestrial; Scot.—Scotland; Arg.—Argentina.

likely depend on continent-ocean configurations and circulation patterns. Large regions of high-latitude open ocean might create large HNLC zones sensitive to changes in external bioavailable metal flux.

THE ORDOVICIAN L-CHONDRITE EVENT

The dominant source of Earth-bound extraterrestrial material is the main asteroid belt, where episodic collisions of large asteroids create clusters of fragments with similar orbital and spectral characteristics that compose asteroid families and dust (e.g., Kortenkamp et al., 2001). Major collisions eject micrometer- to millimeter-sized particles toward the terrestrial planets on 10^5 a time scales, but dust bands may persist much longer, and large (50–100 km) parent-body collisions increase fluxes over much longer intervals, on the order of 10–150 Ma (Durda and Dermott, 1997; Nesvorný et al., 2003; Bottke et al., 2007). Ages of parent-body collisions are constrained by backtracking of orbital configurations of asteroid families (e.g., Nesvorný et al., 2015). A compilation of available age estimates shows more than 70 Phanerozoic families (Fig. 2; see also the Data Repository). Several of these have been associated with intervals of high extraterrestrial dust flux as interpreted from He and Os isotopic signatures in sediments (see the Data Repository).

The best documented interval of enhanced extraterrestrial flux is associated with the mid-Ordovician L-chondrite parent-body breakup (LCPB). This event, documented in both meteorite geochronology and terrestrial stratigraphic records, likely resulted from the collision that created most, if not all, L-chondrite meteorites (Haack et al., 1996; Schmitz et al., 2001; Nesvorný et al., 2007), composing ~40% of all Earth-bound objects today. A long-recognized thermochronologic age peak of ca. 500 Ma in L-chondrites probably represents a single episode of intense shock metamorphism at 470 ± 6 Ma (Korochantseva et al., 2007; Swindle et al., 2014), possibly associated with formation of the Gefion asteroid family (Nesvorný et al., 2009).

The Ordovician L-chondrite event occurred within a few million years of a well-documented episode of extraterrestrial material influx 100–1000x higher than modern (for objects smaller than ~100 m) that lasted at least 2 Ma, and possibly much longer, based on observations from multiple stratigraphic sections including several in Sweden with abundant ~1–20 cm fossil meteorites (Schmitz, 2013; Schmitz et al., 1996; 1997; 2001; 2015; Alwmark et al., 2012). Extraterrestrial spinel grains at least 100x higher than background are found in this interval in Sweden, China, and Russia (Schmitz, 2013; Schmitz et al., 2008; Lindsog et al., 2012). The terrestrial cratering record also shows an anomalous

peak in large craters between 440 and 480 Ma (Schmitz et al., 2001).

In Baltoscandia, the sudden increase in extraterrestrial flux coincides with a widespread, lithologically distinct, glauconite-rich unit known as the Täljsten interval, with similar manifestations in Russian and China, which led Schmitz (2013) to suggest a widespread increase in marine productivity at this time. This is also close to the beginning of the first of two global ~100-Ma-long intervals of abundant ooidal ironstones (Van Houten and Bhattacharyya, 1982; Van Houten and Arthur, 1989) (Fig. 2). The formation and depositional significance of ooidal ironstones are controversial, but they are abundant over large regions only in certain time intervals, in which they cut across facies boundaries over large distances, and are generally associated with black shales and condensed sections (low sedimentation rates). In multiple regions, oolitic ironstones dramatically increase in abundance at the fossil-meteorite/extraterrestrial chromite/Täljsten interval (Fig. 2).

Although the paleoenvironmental significance of ooidal ironstones is debated, most are thought to form at or near the sediment-water interface from iron derived from within underlying shelf sediment undergoing anoxic diagenesis; in anoxic sediments, reduced and soluble ferrous iron derived from detrital minerals or reduced from ferric iron (oxidized and insoluble) diffuses through the sediment into the overlying water (Cotter and Link, 1993; McLaughlin et al., 2012). In modern environments, the iron flux from anoxic sediment is strongly correlated with low oxygen levels near the sediment-water interface (Severmann et al., 2010; Homoky et al., 2012) and the amount of bacterial-iron-reduction-driven oxidation of organic carbon in the sediments (Elrod et al., 2004). We speculate that increased bioessential metals from extraterrestrial dust flux leads to higher marine primary productivity in HNLC regions, leading to lower-oxygen bottom water and enhanced preservation of organic carbon. If this, in turn, influences oxygen concentrations in waters bathing continental shelves, the benthic iron flux from shelf sediments would be enhanced, leading to precipitation of ooidal ironstones. This is consistent with increased glauconite (often interpreted as indicating low-oxygen conditions) and inferred high primary productivity at the L-chondrite/Täljsten interval, and more broadly with the temporal and spatial association of ooidal ironstones and black shales (from enhanced organic carbon burial) in the Phanerozoic (Fig. 2). Redox changes on continental shelves driven by extraterrestrial-flux-driven productivity changes could also be related to order-of-magnitude increases in trace metal concentrations in late Ordovician and Silurian seawater at stratigraphic intervals associated with ooidal ironstones, positive $\delta^{13}\text{C}$

excursions, and teratologic metal poisoning of plankton (Vandenbroucke et al., 2015).

The end-Ordovician mass extinction event, one of the largest in the Phanerozoic, is not associated with any major volcanic event, but is associated with glaciation (also preceded by malformed teratologic acritarchs; Delabroye et al., 2012). We speculate that if a lower, but still relatively high, extraterrestrial dust flux persisted significantly after the L-chondrite event (as predicted for large parent-body collisions), glaciation may have resulted from atmospheric CO_2 drawdown caused by organic carbon export associated with the high marine primary productivity fertilized by extraterrestrial metal flux. This organic carbon export may be reflected in the abundant contemporaneous black shales. Dalai et al. (2006) also suggested that end-Eocene glaciation may have been forced by increased export productivity driven by enhanced extraterrestrial dust flux. We also speculate that pulsed productivity, rather than atmospheric opacity changes (Montanari et al., 2017), may relate to enhanced extraterrestrial dust flux of the late Miocene Veritas event and oceanographic and climatic changes near that time (Diester-Haass et al., 2006; Herbert et al., 2016).

A second interval of globally abundant ooidal ironstones and black shales began in the early Jurassic and ended in the late Cretaceous. We note that this corresponds to a peak in probability density of asteroid family ages, including formation of some of the largest families (Fig. 2). In addition to oolitic ironstones and black shales, some early–middle Jurassic marine sections contain abundant “condensed sections” and hardgrounds with similarities to Ordovician fossil-meteorite sections (Schmitz, 2013), and in some cases preserved extraterrestrial material (see the Data Repository). Relating these to variations in extraterrestrial flux, however, is not straightforward because of the potential for concentration of extraterrestrial material in low-sedimentation-rate settings. In addition, evaluating such hypotheses for any time interval requires considering the possibility of post-collision size–based fractionation of extraterrestrial material over time. For example, dust finer than ~30 μm is required for a ^3He -in-sediment signal but would yield little bioavailable iron, whereas coarser fragments have the opposite manifestations. Nonetheless, if our hypothesized connection between asteroid family ages, extraterrestrial dust flux, marine productivity, and lithologic changes has any merit, extraterrestrial dust flux (at least in the >30 μm fraction that ablates and increases bioavailable iron) in the early Jurassic should have been anomalously high relative to most of the rest of the Phanerozoic.

In general, large-scale changes in marine biogeochemical cycles are undoubtedly forced by tectonic or magmatic processes. We suggest that an external forcing, in the form of variation

in the flux of extraterrestrial bioavailable metals, may in some cases also influence marine biogeochemical cycles, with lithologic and climatic consequences.

ACKNOWLEDGMENTS

We appreciate discussions with Tim Swindle, Vishnu Reddy, Birger Schmitz, Dan Schrag, Alec Hutchings, and Zvi Steiner, and constructive comments from an anonymous reviewer.

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