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Trace Metals

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Synonyms

Transition metals

Definition

Trace metals are metallic elements on the periodic table that are found in low concentrations in both aqueous environments (seawater, freshwater, mine waters) and geologic samples (minerals, rocks, and mine tailings). In aqueous environments, trace metals include any metal element present at concentrations between 10^{-15} mol/L (1 fM) and 10^{-5} mol/L (10 μM). In geological samples, trace metals are present in abundances of <0.1% by weight and typically quantified in either ppm (mg/kg) or ppb (μg/kg). With regard to trace metals in astrobiology and geobiology, there is an increased focus on transition metals in columns 3–12 of the periodic table.

Overview

Trace metals are ubiquitous components of aqueous environments, geological samples, and biological processes. In biological systems, trace metals play critical roles as reaction centers and structural components in metalloenzymes or can even be used as terminal electron acceptors in redox-driven metabolisms such as manganese reduction. Within metalloenzymes, trace metals act either as reaction centers or as a structural component that enhances the integrity of enzymes. This is especially true of the first-row transition metals (V, Mn, Fe, Co, Ni, Cu, and Zn) as well as Mo. While essential for life at low concentrations, at elevated concentrations many trace metals (Fe, Cu, Zn, etc.) prove toxic. Thus, trace metals offer the potential to trace biological processes in modern and ancient environments and from an astrobiological perspective may be useful as a paleoenvironmental or biotic tracer.

Trace Metals in Seawater
In aqueous environments, such as seawater, trace metals tend to display one of the four profile types: (i) conservative, (ii) nutrient-like, (iii) particle-scavenged, or (iv) a hybrid distribution (Bruland et al. 2014). Trace metals with conservative profiles (e.g., Mo, W, Re) are those that

have high concentrations relative to the efficiency of their sinks, and they tend to display little variation in concentration. In nutrient-like profiles, trace metals (e.g., Zn, Cd, Ag) are heavily depleted in the shallow surface water because of incorporation by phytoplankton communities through either surface adsorption or assimilation. Both processes are a function of microbial surface reactivity and microbial metal binding. These trace metals are then replenished at depth, as cellular biomass decays, and eventually return to the photic zone via upwelling. Conversely, particle-scavenged trace metals (e.g., Co) exhibit peak concentrations in the ocean's surface and become depleted at depth. This may be due to settling following their adsorption onto reactive particles or biological surfaces or through their incorporation into authigenic marine precipitates (i.e., chemical sediments formed in marine systems). Ultimately, this results in the export of trace metals to seafloor sediments. Certain elements may be defined by a hybrid distribution, a notable example being Fe (Bruland et al. 2014). Elements that display a hybrid distribution are dependent on the geographical location and basin characteristics, which ultimately dictate whether they display nutrient-like or particle-scavenged features. Notably, the profile type of a given trace metal can be dependent on the prevalent biological and redox conditions in the oceans and can change on geological timescales.

In modern oceans, trace metals are strongly bound by microbial ligands, in some cases exceeding 97% of their total concentration. Chelation by microbial ligands is especially prevalent for Fe, Zn, Ni, Co, Cd, and Cu (Vraspir and Butler 2009; Bruland et al. 2014). Perhaps the best-known examples are the Fe-specific ▸ ligands, siderophores, which act to keep insoluble Fe(III) in solution, thereby increasing Fe bioavailability for planktonic microbial species. Conversely, other ligands may act to decrease the free concentrations of trace metals, such as Cu, keeping them below toxic levels for microbial communities (Bruland et al. 2014). Today, Fe is a co-limiting nutrient over large areas of the oceans, depressing nitrogen fixation and primary productivity (e.g., Falkowski et al. 1998; Mills et al.

2004). Yet, despite the potential for Fe co-limitation in the modern ocean, on geological timescales, phosphorous is considered to be the ultimate limiting nutrient (Tyrrell 1999).

Trace Metals as Drivers of Ecosystem Change

Changes in the bioavailability of these trace elements have long been recognized to have the potential to drive biological evolution or control ecosystem structure over geological time (e.g., Frausto da Silva and Williams 2001). It has been suggested that the timing of the proliferation of specific metalloenzymes should broadly track changes in the environmental availability of the requisite trace metals (Dupont et al. 2010). Further, it has been debated if environmental trace metal availability limited the size and scope of the biosphere for much of Earth's early history (e.g., Anbar and Knoll 2002). For example, methanogens have a high requirement for Ni, due to its incorporation into enzymes needed to carry out methanogenesis (Ragsdale and Kumar 1996). It follows that methanogens would be sensitive to environmental fluctuations in Ni availability (see discussion below).

Sedimentary Trace Metal Archives

Trace metal concentrations in the oceans in deep time, and by extension first-order trends in their bioavailability, are primarily unlocked by examining trace metal abundances in marine chemical sediments. These archives include black shales (e.g., Scott et al. 2008, 2013; Chi Fru et al. 2016), banded iron formations (e.g., Konhauser et al. 2009, 2011; Robbins et al. 2013), sedimentary to early diagenetic pyrite (e.g., Large et al. 2014; Mukherjee et al. 2018), and carbonates (Liu et al. 2016). Reconstructions of trace metal inventories of these records have been variously related to the ▸ oxygenation of Earth's atmosphere (Mo, V, Zn), the marginalization of methanogens (Ni), the onset of aerobic oxidation of terrestrial minerals (Cr), and the role that intrinsic biological processes may play in the evolution of complex life (Zn, Cu). Additional trace metal compilations produced temporal records for V (Sahoo et al. 2012), U (Partin et al. 2013a, b), Co (Swanner et al. 2014), and Re (Sheen et al. 2018).

While these records are variably susceptible to overprinting during ▶ diagenesis and metamorphism, it is telling that many of the temporal trends are reproducible across multiple chemical sedimentary records, suggesting that these sedimentary archives are tracking first-order trends in global trace metal concentrations in seawater.

Basic Methodology

Today, the most common methods for measuring trace metal concentrations involve the use of inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectroscopy (ICP-OES). These methodologies can be used to directly analyze aqueous samples and, via laser ablation, geological samples. Additionally, both anodic and cathodic voltammetric stripping have been used in measurements of shipborne seawater samples and have proven critical in assessing the degree of organic ligand complexation of trace metals such as Fe, Zn, Cu, and Cd (Bruland et al. 2014).

Aqueous Samples
Generally speaking, for aqueous samples including seawater and freshwater, a sample is collected and then filtered and acidified prior to analysis. Filter size is generally in the range of 0.22 μm such that microbial, particulate, and colloidal material is removed and the dissolved concentration of trace metals is measured; although, ultrafiltration is common and provides a true dissolved concentration. Following collection, samples may be diluted in a weak acid and introduced into an ICP-OES or ICP-MS or measured directly depending on instrument sensitivity and initial metal concentration. Analyses are generally calibrated against internal matrix-matched standards prepared with certified, commercial standards.

Geological Samples
Geological samples (e.g., banded iron formations, black shales, carbonates, pyrite) may be completely digested using various concentrated acids (such as a combined HNO_3-HCl-HF attack). This involves several steps of acid addition,

heating the sample, and evaporating the sample to a residue. The residue is then dissolved into a dilute acid matrix, typically 1–2% HNO_3, and analyzed by ICP-MS. Alternatively, samples may be subjected to a series of sequential extractions designed to leach the authigenic and typically more reactive phases. Analyses are typically calibrated against internal standards and compared to well-characterized geological standards. Alternatively, trace metals may be measured by coupled laser ablation ICP-MS. In LA-ICP-MS analysis, a geological sample (thin section, small rock or mineral) is ablated in an airtight chamber with a laser, and the liberated fine particles are then carried to the ICP-MS by an inert gas line. Similar to solution analyses, LA-ICP-MS measurements are calibrated against well-known geological standards. Stable isotope measurements of trace metals are becoming commonplace by multi-collector ICP-MS (MC-ICP-MS), which often require additional sample processing and purification.

Key Research Findings

While the fact that >97% of certain trace metals are organically complexed in seawater is a profound observation in of itself (Vraspir and Butler 2009; Bruland et al. 2014), some of the most powerful inferences regarding trace element chemistry and their relation to Earth systems evolution have been garnered from the geological record. For instance, the enrichments of several transition metals in black shales, including Mo, V, Cr, U, and Re (Scott et al. 2008; Sahoo et al. 2012; Partin et al. 2013b; Reinhard et al. 2013; Sheen et al. 2018), are known to track the two-stage oxygenation of the ocean-atmosphere system (see Lyons et al. 2014 for a review).

A late-Archean secular decline in Ni/Fe ratios in banded iron formations indicates a decrease in Ni bioavailability (Konhauser et al. 2009, 2015) that is critical for methanogens (Ragsdale and Kumar 1996). This secular decline is the result of decreasing komatiite weathering and may have led to the marginalization of ancient methanogens, allowing for oxygenic

cyanobacteria to expand into previously occupied environmental niches. These events, in turn, led to the first permanent rise in atmospheric oxygen ~2.48–2.3 Ga, a period known as the Great Oxidation Event (GOE) (e.g., Konhauser et al. 2011).

While Mo, V, U, Cr, Re, and Ni show stark temporal trends that track the rise and fall of oxygen, several trace metals show records that are considerably more static in both banded iron formations and black shales. Static records for trace metals, such as Zn and Cu (Robbins et al. 2013; Scott et al. 2013; Chi Fru et al. 2016), hint at the possibility of pervasive microbial ligand complexation in deep time, which would have stabilized trace metal concentrations against changes in bulk ocean chemistry or atmospheric conditions. These static records stand in stark contrast to the assertion that evolving trace metal abundances should be trackable by the proliferation of corresponding trace metal complexes in biological systems (e.g., Dupont et al. 2010). For example, despite geological evidence that points toward an attenuated marine reservoir for Mo in the Archean to Proterozoic (Anbar and Knoll 2002; Scott et al. 2008), isotopic evidence points to an Archean appearance of Mo nitrogenase (Stüeken et al. 2015). This questions the idea that an organism's elemental stoichiometry always reflects the fundamental chemistry of the environments in which they evolved.

Future Directions

▶ Transition metals and their isotopes are increasingly measured in both modern and ancient settings. The advent of MC-ICP-MS has led to a rapid proliferation of trace and transition metal isotope data. Studies that utilize this new avenue of data collection are primed to explore the response of the ancient biosphere to changes in environmental conditions or shifts in community structure. For instance, recent examinations of zinc isotopes have shown shifts in their signature that coincide with the rise of eukaryotes to dominance at ~800 Ma (Isson et al. 2018) and may indicate the recovery of biosphere primary productivity or changes in zinc cycling following the

Cryogenian glaciations at ~635 Ma (Kunzmann et al. 2013; John et al. 2017). Copper isotopes measured in black shales (Chi Fru et al. 2016) show a distinct shift around the GOE and are attributed to changes in oxidative weathering and a decline in banded iron formations, whereas changes in Mo isotope ratios through the Paleoproterozoic point to major fluctuations in redox balance in the oceans (Asael et al. 2018). Studies such as these highlight the utility of non-traditional stable isotopes of trace metals in extracting information about changes in ancient environmental conditions and offer a clear avenue for future studies that can be focused on shifts recorded in a given basin or over geological time.

Cross-References

▶ Banded Iron Formations
▶ Chelation
▶ Copper Isotopes
▶ Diagenesis
▶ Manganese Reduction
▶ Methanogenesis
▶ Microbial Ligands
▶ Microbial Metal Binding
▶ Microbial Surface Reactivity
▶ Oxygenation of the Earth's Atmosphere
▶ Phytoplankton
▶ Siderophores
▶ Transition Metals and their Isotopes
▶ Zinc Isotopes

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