

# Metal Stable Isotopes in Paleoceanography

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Annu. Rev. Earth Planet. Sci. 2007. 35:717–46

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

This article's doi:  
10.1146/annurev.earth.34.031405.125029

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0084-6597/07/0530-0717\$20.00

## Key Words

iron, molybdenum, copper, zinc, thallium, paleoredox

## Abstract

Considered esoteric only a few years ago, research into the stable isotope geochemistry of transition metals is moving into the geoscience mainstream. Although initial attention focused on the potential use of some of these nontraditional isotope systems as biosignatures, they are now emerging as powerful paleoceanographic proxies. In particular, the Fe and Mo isotope systems are providing information about changes in oxygenation and metal cycling in ancient oceans. Zn, Cu, Tl, and a number of other metals and metalloids also show promise. Here we review the basis of stable isotope fractionation as it applies to these elements, analytical considerations, and the current status and future prospects of this rapidly developing research area.

**Stable isotope geochemistry:** the study of variations in isotope composition that result from isotopic differences in chemical equilibrium constants and reaction rates

## INTRODUCTION

In the past ten years we have seen explosive growth in nontraditional stable isotope geochemistry, particularly of transition metals, largely as a result of analytical innovations in mass spectrometry. Researchers are now studying mass-dependent variations in the isotopic compositions of approximately 20 elements in addition to the traditional H, C, N, O, and S (**Figure 1**), giving rise to a new geochemical subdiscipline.

Questions in paleoceanography strongly motivate research into these new isotope systems. For decades, paleoceanographers have used isotope variations in ancient sediments as proxies to track changes through time in processes that cannot be measured directly. This work has centered on traditional stable isotopes and radiogenic isotope systems such as Rb/Sr, Sm/Nd, and U/Th/Pb as proxies for ocean temperature, carbon cycling, ocean circulation, hydrothermal activity, weathering, and other parameters and processes. The new stable isotope systems are particularly attractive to paleoceanographers because they can provide information about changes in seawater chemistry that is unattainable with other proxies.

Of the many nontraditional isotope systems, transition metals are of special interest to paleoceanographers for two primary reasons. The first reason is the potential of these systems to provide information about the biogeochemical cycling of bioessential metals. Bioessential metals have become a focus in paleoceanography because ocean primary productivity in some places and times may be controlled by the availability of metal micronutrients or the presence of toxic metals. The importance of metals as micronutrients received wide attention with the development of the iron hypothesis (Martin & Fitzwater 1988), which postulated that primary production in so-called

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	Uuq		Uuh			
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

**Figure 1**

Stable isotope systems for which variations have been reported as of 2006. Traditional (*green*) and nontraditional (*blue*) systems are indicated.

high nutrient–low chlorophyll oceanic regions, notably the Southern Ocean, was limited by Fe scarcity, <1 nM in the surface ocean (e.g., Boyle et al. 2005, Wu et al. 2001). Subsequent ocean-going experiments confirmed that changes in Fe supply to the upper ocean may lead to climate change by affecting biological productivity and altering the rates of carbon sequestration (e.g., Boyd et al. 2000, Coale et al. 1996, Martin et al. 1990), generating intense interest in the sources, sinks, and species of Fe in the oceans and in the mechanisms of Fe uptake and utilization by marine microorganisms (especially phytoplankton). Beyond Fe, this hypothesis highlighted the importance of metal micronutrients more generally, stimulating analogous interest in the marine biogeochemistries of Cd, Co, Cu, Mn, and Zn (e.g., Franck et al. 2003, Lane et al. 2005, Saito et al. 2002, Shaked et al. 2006, Sunda & Huntsman 1998). The toxicity of metals such as Cd, Cr, Cu, and Hg, particularly in coastal settings proximal to anthropogenic sources, also received increased attention through the 1990s (e.g., Mann et al. 2002, Sunda & Huntsman 1996). For these reasons, there is a need for new techniques to provide insights into the biogeochemical cycles of this class of elements and how these cycles may have been different in the past.

The second major reason that paleoceanographers are drawn to transition-metal stable isotopes is the emerging connection between metal isotope variations and ocean oxygenation, a consequence of redox-related changes in global ocean isotope budgets of some metals. Large-scale changes in seafloor oxygenation have occurred repeatedly in Earth's history, on various timescales, but are poorly understood (Arthur & Sageman 1994, Bekker et al. 2004, Canfield 1998, Holland 1984, Wignall & Twitchett 1996). Because O<sub>2</sub> consumption in the deep sea is a function of carbon export from the photic zone and O<sub>2</sub> resupply from ocean mixing, the history of ocean oxygenation is intertwined with the history of carbon cycling and global climate. Ocean oxygenation history is also intertwined with the evolution of biological sulfate reduction, oxygenic photosynthesis, nitrogen fixation, and other metabolisms (Canfield 2005, Canfield et al. 2000, Fennel et al. 2005). In fact, evolutionary questions bring together paleoceanographic interests in bioessential metals and ocean redox because changes in ocean oxygenation alter the availabilities of Fe, Mo, Mn, Cu, and other bioessential elements (Anbar & Knoll 2002, Falkowski et al. 2004, Kirschvink et al. 2000, Quigg et al. 2003, Saito et al. 2003, Zerkle et al. 2005). As a result, there is increasing interest in deep-time paleoredox proxies, particularly proxies that can provide information on global rather than local redox.

As we discuss below, metal stable isotopes have great potential to shed light on temporal and spatial changes in both metal cycling and ocean oxygenation through time. This chapter provides an introduction to this new area of research, including an orientation to key conceptual and analytical topics. Reflecting the early evolution of the field, we emphasize the stable isotope systematics of Fe and Mo and their emerging applications in paleoceanography, particularly as paleoredox proxies.

## FRACTIONATION FUNDAMENTALS

Researchers have studied the stable isotopes of H, C, O, N, and S in oceanographic settings for over a half-century. During most of this time, metal isotopes received little

**Isotope fractionation:** the unequal distribution of two or more isotopes of an element between two reservoirs

**Mass dependence:** the variations in isotope composition of an element that result from isotope fractionation typically scale systematically with isotopic mass, and so are said to be mass dependent

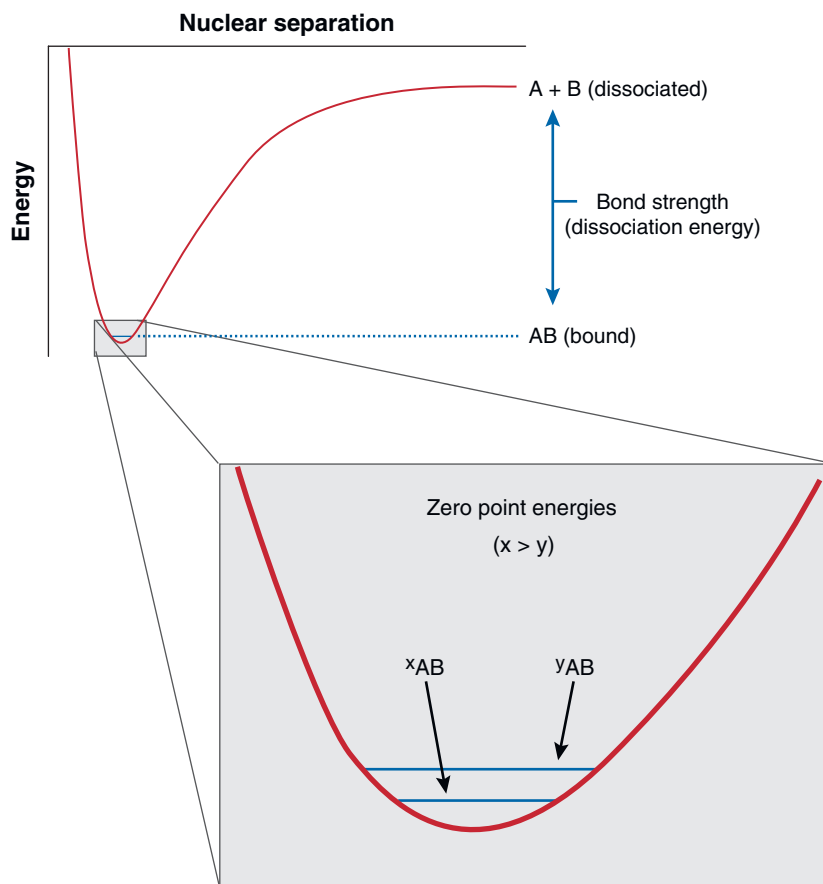
attention because conventional wisdom argued they were too heavy to fractionate. As is often the case, this conventional wisdom was distilled from a more complex reality. Below we briefly review the basis of stable isotope fractionation as a phenomenon, and the analytical challenges associated with measuring fractionation effects, to place metal isotope systems in the context of stable isotope geochemistry generally.

### Why Mass Matters

Isotope fractionation during chemical reactions is fundamentally a quantum chemical phenomenon that arises from differences in the zero point energies (ZPEs) between chemical bonds that are identical except for isotopic substitution (Bigeleisen 1965, Urey 1947). In the simple case of a diatomic molecule, AB,  $ZPE = 1/2b\nu$ , where  $\nu$  is the vibrational frequency of the bond, and  $b$  is Planck's constant. Approximating the bond as a harmonic oscillator,  $\nu = 1/(2\pi)\sqrt{(k/\mu)}$ , where  $k$  is the force constant, and  $\mu$  is the reduced mass of the bond [ $\mu = m_A m_B / (m_A + m_B)$ ]. Hence, bond strengths are mass dependent because  $\nu$  and ZPE are functions of the masses of A and B. Because a lower ZPE results in a greater energy difference between the bound and dissociated atoms, bond strength increases when heavier isotopes are substituted for lighter ones. If we consider two isotopes of A,  $^x\text{A}$  and  $^y\text{A}$ , where  $x > y$ , bond  $^x\text{AB}$  is stronger than  $^y\text{AB}$  (Figure 2).

This mass dependence of bond strengths leads to differences in reaction rate constants;  $^x\text{AB}$  will react more slowly than  $^y\text{AB}$ . This is the origin of kinetic isotope effects when reactions are unidirectional or incomplete. The mass dependence of bond strengths also leads to the mass dependence of equilibrium constants; e.g., the equilibrium constant for the reaction  $^x\text{AB} + \text{C} \rightarrow ^x\text{AC} + \text{B}$  is different from that of  $^y\text{AB} + \text{C} \rightarrow ^y\text{AC} + \text{B}$ . This is the origin of equilibrium isotope effects. Importantly, even when complete equilibrium is not achieved, as is often the case in nature, such free energy differences can drive isotope fractionation (for a recent overview of fractionation fundamentals, see Criss 1999).

Rigorous and detailed treatments of isotope effects can be found elsewhere (for a recent overview applied to nontraditional systems, see Schauble 2004). However, we can roughly compare the relative potential for fractionation of different isotope systems by looking at possible AB bonds and their isotopically substituted versions. For example, let us consider two isotopes of Fe,  $^{54}\text{Fe}$  and  $^{56}\text{Fe}$ , each bound to an atom of  $^{16}\text{O}$ . If  $\mu_1$  and  $\mu_2$  are the reduced masses of  $^{54}\text{Fe}-^{16}\text{O}$  and  $^{56}\text{Fe}-^{16}\text{O}$ , respectively, it is straightforward to show that substitution of  $^{56}\text{Fe}$  for  $^{54}\text{Fe}$  changes the ZPE of the Fe- $^{16}\text{O}$  bond by a fractional amount  $[\sqrt{(1/\mu_2)} - \sqrt{(1/\mu_1)}] / \sqrt{(1/\mu_1)} \sim 4\%$ . By comparison, substitution of  $^{13}\text{C}$  for  $^{12}\text{C}$  in the C- $^{16}\text{O}$  bond changes the ZPE by  $\sim 22\%$ . **Supplemental Table 1** tabulates the results of such calculations for a range of elements (follow the Supplemental Material link from the Annual Reviews home page at <http://www.annualreviews.org>). It is immediately apparent that the values for transition metals are generally smaller than for the lighter elements, indicating that isotope fractionation should indeed generally be smaller for these heavier elements. However, it is equally apparent that the values for all isotope systems are generally within an order of magnitude. Therefore, a priori metal isotopes clearly will undergo



**Figure 2**

Schematic illustration of how isotope substitution affects zero point energies (ZPEs) and bond strengths. (*Inset*) Detail of the potential energy well that describes the diatomic bond between two atoms, A and B. If there are two isotopes of A,  $^x\text{A}$  and  $^y\text{A}$ , they will have different ZPEs and hence different bond strengths.

fractionation, and the magnitude of fractionation should not be vanishingly small relative to traditionally studied systems; ‰-scale effects are plausible. Isotope effects for transition metals can only be said to have been too heavy with respect to the precision of available analytical methods.

### Analytical Advances

The development of the geochemistry of transition-metal stable isotopes lagged behind that of lighter elements primarily for analytical reasons. Two critical, related issues had to be tackled. First, researchers needed methods to efficiently convert analyte elements to ions suitable for analysis by a mass spectrometer. Second, it was critical to develop a routine way to monitor or compensate for the fact that ionization and other steps in mass spectrometric analysis can themselves induce an isotope fractionation that is an order of magnitude larger than the natural variations being measured.

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**$\delta$  values:** stable isotope compositions are expressed as parts-per-thousand (‰) deviations in isotope abundance ratios between samples and a reference standard, where  $\delta > 0$  is said to be “heavy” and  $\delta < 0$  “light;” see examples below

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These analytical issues were solved with the development of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Walder & Freedman 1992). ICP instruments generate ions efficiently by aspirating analyte solutions into a high-temperature Ar plasma (Colodner et al. 1994, Falkner et al. 1995, and references therein), allowing most of the periodic table to be analyzed rapidly and with high sensitivity. Instrumental mass fractionation by ICP-MS, although large, is relatively stable with time, facilitating accurate and precise comparison of the isotopic compositions of samples with standards (Albarède & Beard 2004). MC-ICP-MS capitalizes on these features by combining an ICP ion source with a magnetic sector mass analyzer, making it possible to determine isotope ratios by simultaneously measuring two or more ion beams using multiple detectors (collectors). Multiple collector measurements compensate for time-dependent variations in ion-beam intensities that would otherwise degrade determinations of isotope ratios (i.e.,  $\delta$  values).

Although stable isotope analysis by MC-ICP-MS also presents a unique set of challenges (e.g., Albarède & Beard 2004, Anbar et al. 2001, Maréchal et al. 1999, Weyer & Schwieters 2003), this method has come to dominate metal stable isotope research as such challenges have been addressed. Even Fe isotopes (analytically challenging because of interferences from  $^{40}\text{Ar}^{14}\text{N}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^+$ , and  $^{40}\text{Ar}^{16}\text{OH}^+$  at masses 54, 56, and 57, respectively) are now measured routinely to a precision of  $\pm 0.05\%$ , using conventional sample introduction methods on chemically purified samples containing  $\sim 1$   $\mu\text{g}$  of Fe (e.g., Arnold et al. 2004b, Schoenberg & von Blanckenburg 2005). Researchers can analyze samples one-tenth as large with alternative introduction systems (e.g., Beard et al. 2003a, Schoenberg & von Blanckenburg 2005).

## Mastering Mechanisms

As discussed above and reviewed below, theory predicts and observations demonstrate extensive metal isotope fractionation in nature. What are the oceanographically relevant processes that can cause these isotopes to fractionate? We summarize a number of simple but important generalizations here and discuss specific processes for particular elements later in this chapter.

First, isotope effects between dissolved aqueous species in solution, particularly at different redox states, are important drivers of fractionation. This is no surprise in view of the rich speciation chemistry of metals in solution; most metals can coordinate with a range of ligands in seawater, and many occur in more than one redox state across the range of typical oceanographic conditions. Metal-ligand bond energies vary among these species, resulting in unequal isotope partitioning among species at equilibrium. Such effects can be theoretically predicted with good confidence (Anbar et al. 2005, Schauble 2004). Redox differences are particularly important because the change in bond energy on the gain or loss of an electron from a metal center is typically larger than that resulting from ligand substitution. Such effects are best studied in the case of Fe (Anbar et al. 2005, Welch et al. 2003) but probably exist for other elements as well (Schauble 2004).

Second, isotope effects observed in seemingly simple systems are often complicated. For example, the isotope fractionation between ferrihydrite formed during

oxidative precipitation and dissolved  $\text{Fe}^{2+}$ ,  $\sim 1\%$  (Bullen et al. 2001), is 30% as large as the fractionation arising from equilibrium isotope exchange between dissolved  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  aquo complexes (Anbar et al. 2005, Welch et al. 2003). Most likely, the exchange effect is overprinted by a kinetic effect during ferric iron precipitation (Skulan et al. 2002, Welch et al. 2003).

Third, fractionation between dissolved species and inorganic particulate phases, including metals adsorbed on particle surfaces, is critically important in governing the isotope variations seen in the oceans. Such fractionation can impart unique isotopic signatures, allows for the separation of isotopically distinct reservoirs, and provides a major pathway for the preservation of isotope signatures in the geologic record. Clear examples exist for Fe (Bullen et al. 2001, Icopini et al. 2004), Mo (Barling & Anbar 2004, Barling et al. 2001, Siebert et al. 2003), and probably also Tl (Rehkämper et al. 2002).

Finally, many metal isotopes are fractionated by oceanographically important biological processes. This is particularly true of Fe, which has been studied most intensely (see review by Johnson et al. 2004). However, it is not clear for any transition metals that biological effects dominate the isotope variability seen in the paleoceanographic record (unlike the C, N, and S isotope systems). This is an area of active research.

## EXEMPLAR ELEMENTS: IRON AND MOLYBDENUM

To date, Fe and Mo have drawn more attention than other metal stable isotopes in paleoceanography. This attention derives from the critical importance of both elements in biology—particularly in key enzymes in the nitrogen cycle—and the sharp changes in the geochemical behavior of both elements with changes in environmental oxygenation.

Additionally, these elements are a complementary pair because they are geochemical opposites. In Earth's crust (Taylor & McLennan 1985), Fe is the fourth most abundant element ( $\sim 5\%$ ), whereas Mo is a trace element ( $\sim 1$  ppm). This situation is reversed in the oceans in which Fe concentrations rarely exceed  $\sim 2$  nM (Gordon et al. 1982, Bruland et al. 1979, Wu et al. 2001), whereas the concentration of Mo is a uniform  $\sim 105$  nM (Collier 1985). This reversal is a consequence of the elements' contrasting solution chemistries. In oxygenated waters, Fe oxidizes and hydrolyzes to make insoluble ferric oxyhydroxides, whereas Mo speciation is dominated by the soluble, highly unreactive  $\text{MoO}_4^{2-}$  ion. Hence, whereas Fe is highly immobile during weathering and has a short ocean residence time, Mo is readily transferred to the oceans in which its residence time is  $\sim 800,000$  years (Morford & Emerson 1999). As reviewed below, the isotopes of both elements are fractionated during key steps in their geochemical cycling in ways that allow us to use their isotope variations in sediments to probe changes in ocean chemistry through time.

### Iron

In this section we summarize the oceanographically relevant processes known to fractionate Fe isotopes, review the emerging understanding of the Fe isotope

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**Isotope exchange reaction:** a chemical reaction in which isotopes repartition among reacting species until the equilibrium distribution among the species is attained

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**Fractionation factor:**

defined by  $\alpha = (^xA/{}^yA)_p / (^xA/{}^yA)_q$ , where  $p$  and  $q$  denote the reservoirs being compared, or colloquially by  $\Delta^xA_{p-q} = \delta^xA_p - \delta^xA_q$  [ $\sim 1000 \ln(\alpha)$ ]

budget of modern oceans, and discuss the initial application of Fe isotopes as a paleo-oceanographic proxy. More comprehensive reviews of Fe isotope geochemistry can be found elsewhere (e.g., Anbar 2004a, Beard & Johnson 2004, Dauphas & Rouxel 2006, Johnson et al. 2004).

**Isotope systematics.** Fe has four naturally occurring stable isotopes:  ${}^{54}\text{Fe}$  (5.84%),  ${}^{56}\text{Fe}$  (91.76%),  ${}^{57}\text{Fe}$  (2.12%), and  ${}^{58}\text{Fe}$  (0.28%). Natural mass-dependent Fe isotope variations span a range of up to 5‰ in  ${}^{56}\text{Fe}/{}^{54}\text{Fe}$  ratios, commonly expressed as  $\delta^{56}\text{Fe}$  relative to the international standard IRMM-14 (Belshaw et al. 2000). Some earlier literature reported  $\delta^{56}\text{Fe}$  values relative to the average bulk silicate Earth (e.g., Beard et al. 2003a).

$$\delta^{56}\text{Fe} = \left[ \frac{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}}{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-14}}} - 1 \right] \times 1000$$

**Fractionating processes.** Fe isotopes are emerging as particularly useful tracers of biogeochemical redox cycling of Fe in modern and ancient marine environments because biotic and abiotic redox processes are among the principal factors that fractionate Fe isotopes (see **Supplemental Table 2** for a summary of experimentally determined isotopic fractionation factors). These redox processes include dissimilatory Fe(III) reduction (Beard et al. 1999, 2003a; Icopini et al. 2004), anaerobic photosynthetic Fe(II) oxidation (Croal et al. 2004), abiotic Fe(II) oxidation and precipitation of ferric hydroxides (Balci et al. 2006, Bullen et al. 2001), and sorption of aqueous Fe(II) onto ferric hydroxides (Icopini et al. 2004, Teutsch et al. 2005). Investigators have observed and theoretically calculated equilibrium isotope fractionations as large as 3‰ between coexisting Fe(III) and Fe(II) aqueous species (Anbar et al. 2005, Welch et al. 2003).

Significant kinetic and/or equilibrium Fe isotope fractionation (up to  $\sim 1\%$ ) can also result from nonredox processes such as inorganic mineral precipitation of Fe oxides (Skulan et al. 2002), carbonates (Wiesli et al. 2004), and sulfides (Butler et al. 2005). Significant Fe isotopic fractionation (up to  $-0.8\%$ ) also occurs during the dissolution of silicates and ferric oxides in the presence of simple organic ligands such as oxalate (Brantley et al. 2001, 2004; Wiederhold et al. 2006) and during the dissolution of silicates by siderophores produced by soil bacteria (Brantley et al. 2001, 2004). Fractionation may even occur during ligand exchange reactions (Anbar et al. 2000, Roe et al. 2003, Schauble 2004).

In view of the variety of fractionating processes, it is not surprising that researchers have observed marked variations in Fe isotope composition in organic-rich sediments and associated sulfides (Matthews et al. 2004, Rouxel et al. 2005, Severmann et al. 2006, Yamaguchi et al. 2004), banded iron formations (Dauphas et al. 2004, Johnson et al. 2003, Rouxel et al. 2005), and hydrothermal fluids and precipitates (Beard et al. 2003b; Rouxel et al. 2003a, 2004b; Severmann et al. 2004; Sharma et al. 2001).

**The modern ocean isotope budget.** Fe precipitates rapidly and quantitatively from oxic seawater. Hence, the Fe isotope budget of bulk sediments deposited under oxic



conditions is dominated by the isotopic composition of Fe sources rather than fractionation during removal from seawater. For this reason, much research focuses on Fe isotope variability in the sources of Fe to seawater and associated fractionation processes.

The integration of source studies into a quantitative model of the Fe isotope oceanic budget remains difficult because of the lack of data on the Fe isotope composition of seawater. Nevertheless, we can present an emerging picture of the modern biogeochemical cycle for Fe isotopes (Figure 3). Hydrogenous accumulations in the form of ferromanganese (Fe-Mn) oxides display variable, but negative  $\delta^{56}\text{Fe}$  values that may provide a record of marine Fe isotope composition. Among the potential sources of negative  $\delta^{56}\text{Fe}$  components in seawater, continental runoff and oceanic crust alteration may provide significant dissolved and particle Fe in coastal oceans and deep sea, respectively (Beard et al. 2003b, Bergquist & Boyle 2006, Fantle & De Paolo 2004). Another source of low- $\delta^{56}\text{Fe}$  iron to the oceans, especially in coastal areas, is diagenetic pore fluids from shelf sediments (Severmann et al. 2006, Staubwasser et al. 2006). In addition, the dissolution of aerosols in the water column, which represent probably the major source of Fe in the open surface ocean,

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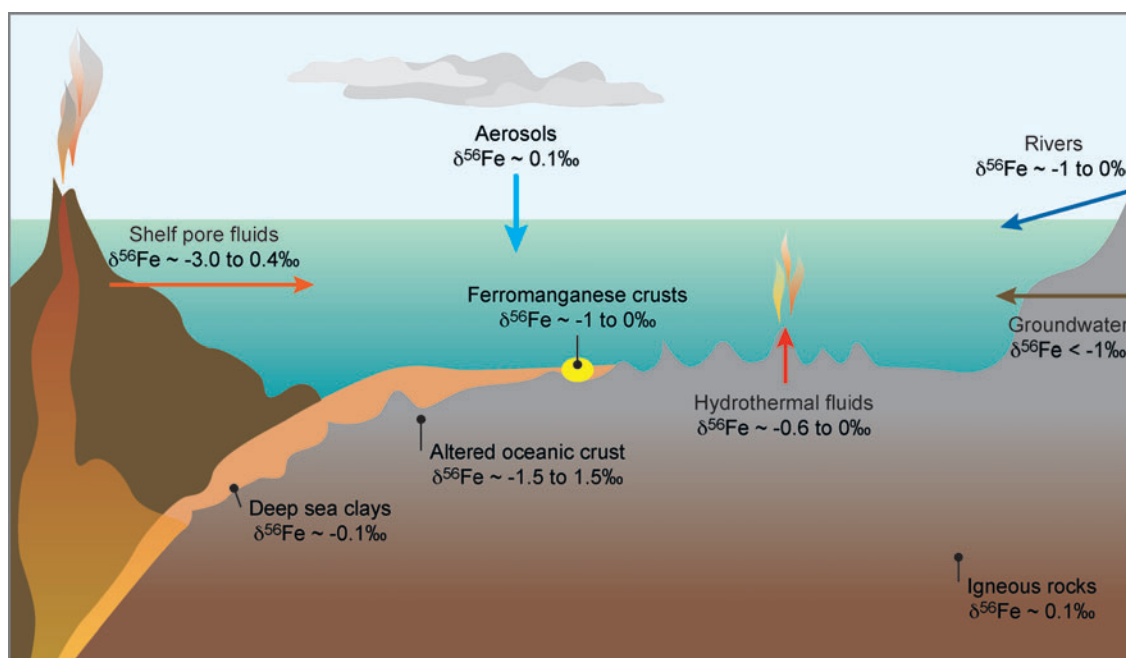
**Oxic:** in common usage, water containing  $>5$  micromolar  $\text{O}_2$

**Euxinic:** containing measurable  $\text{H}_2\text{S}$  (typically  $>1 \mu\text{M}$ )

**Suboxic:** commonly containing  $<5 \mu\text{M}$   $\text{O}_2$

**Anoxic:** without  $\text{O}_2$  (but also without  $\text{H}_2\text{S}$ )

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**Figure 3**

A schematic of the Fe ocean isotope budget. The main sources of dissolved Fe into the ocean are wet and dry deposition from the atmosphere, input from rivers, resuspended sediment, and pore water along continental shelves and hydrothermal vents (e.g., de Barr & La Roche 2003, Elderfield & Schultz 1996, Elrod et al. 2004, Johnson et al. 1999a, Wells et al. 1995). The Supplemental Appendix summarizes the isotope systematics of these sources.

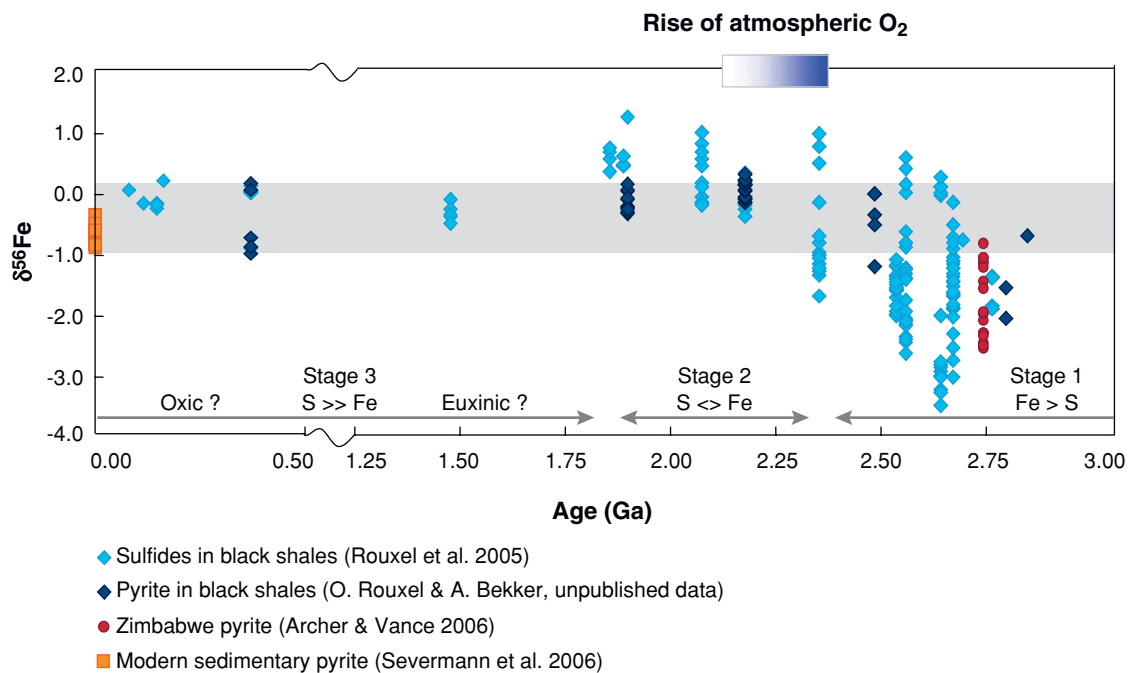
may lead to Fe isotope variability that is dependent on the biological productivity, either through dissolution by biogenic organic ligands (Brantley et al. 2001, 2004; Wiederhold et al. 2006) or biological assimilation (Zhu et al. 2002a). However, despite its importance, the control of Fe isotope composition of particulate Fe in seawater remains largely unexplored. Because the cycling of Fe in the water column involves complex transformations between lithogenic (e.g., clays), biogenic (i.e., organically bound Fe), and hydrogeneous (e.g., Fe oxides) phases, the potential exists for the use of Fe isotopes as tracers of Fe biogeochemical cycling in the water column.

**Paleoceanographic records.** Researchers have explored three types of Fe isotope paleorecords. Temporal variations in seawater could be mirrored in Fe-Mn crusts, providing a paleorecord of oceanic Fe isotope composition through the Cenozoic. An alternative record extending much further in time may exist in black shales, providing a paleorecord of redox-related changes in Fe cycle. Finally, Fe isotope compositions in banded iron formations also may be useful in probing changes in Fe biogeochemical cycling on the early Earth (Dauphas et al. 2004, Johnson et al. 2003).

**Cenozoic Fe-Mn crusts.** In the past, researchers have used the variations of Hf, Nd, Pb, and Os isotopic composition in hydrogenous Fe-Mn crusts to provide information on changes in ocean circulation patterns, and their relations to tectonic and climatic events through time (Frank et al. 1999, Klemm et al. 2005, Ling et al. 2005). If there is no significant Fe isotope fractionation during crust growth, then Fe isotopes in such sediments should provide a new proxy for such studies and powerful insights into historical changes in the fluxes of Fe to the marine system such as continental weathering and ocean floor hydrothermal activity. Documented temporal variations of  $\delta^{56}\text{Fe}$  in Fe-Mn crusts suggest this tantalizing possibility (Chu et al. 2006, Levasseur et al. 2004, Yang et al. 2006, Zhu et al. 2000b).

The factors controlling these variations are still under investigation (Beard et al. 2003b, Levasseur et al. 2004, Zhu et al. 2000b). Beard et al. (2003b) suggested that  $\delta^{56}\text{Fe}$  variations reflect changes in the relative fluxes of Fe from aerosol particles ( $\sim 0\%$ ) and mid-oceanic ridge hydrothermal vents ( $\sim -0.5\%$ ). Hydrothermal Fe clearly contributed significantly to some Fe-Mn crusts in the west Pacific, at which low  $\delta^{56}\text{Fe}$  values correlate with increases in the concentration of elements enriched in hydrothermal fluids (Chu et al. 2006). However,  $\delta^{56}\text{Fe}$  at approximately  $-0.7\%$ , as observed in northeast Atlantic Fe-Mn crusts (Zhu et al. 2000b), would require an unrealistically high contribution of hydrothermally derived Fe. Instead, other marine Fe sources with  $\delta^{56}\text{Fe}$  values less than 0, such as continental runoff or shelf sediments, may contribute to these paleoceanographic records (Severmann et al. 2006, Staubwasser et al. 2006).

**Black shales.** The rise of atmospheric oxygen that started by  $\sim 2.3$  Ga (Bekker et al. 2004, Farquhar et al. 2000, Holland 1984) was one of the most important changes in Earth's history. Because Fe, along with C and S, is coupled with (and maintains) the redox state of the surface environment, concentrations and isotopic compositions of Fe in seawater were likely affected by the rise of atmospheric oxygen.



**Figure 4**

Plot of  $\delta^{56}\text{Fe}$  values versus sample age for pyrite in organic-rich marine sediments. On the basis of the  $\delta^{56}\text{Fe}$  values, the Fe ocean cycle can be roughly divided into three stages, which likely reflect redox-related changes in the global Fe and S cycle. Note the scale change between 0.5 to 1.25 Ga. The gray area corresponds to  $\delta^{56}\text{Fe}$  values of Fe derived from igneous rocks (at 0.1‰) and modern marine sedimentary pyrite (down to  $-1.0\text{‰}$ ). The rise of atmospheric oxygen is defined by multiple sulfur isotope analyses of pyrite in the same samples as analyzed for Fe isotopes (Bekker et al. 2004).

Recent studies of the Fe isotope composition of marine sediments over geological time have provided new insights into the ancient Fe cycle (Rouxel et al. 2005, Yamaguchi et al. 2004). In particular, Rouxel et al. (2005) investigated the record of Fe isotope composition in sedimentary pyrite in organic-rich marine sediments (black shales) (**Figure 4**). The general pattern of this record divides Earth's history into three stages, which are strikingly similar to those defined by other indicators of atmosphere-ocean redox evolution (Bekker et al. 2004, Kasting 1993). Stage 1 (>2.8 to ca. 2.32 Ga) is characterized by highly variable and negative  $\delta^{56}\text{Fe}$  values of pyrite, as low as  $-3.5\text{‰}$ . Stage 2 (ca. 2.32 to ca. 1.6 Ga) is characterized by unusually high  $\delta^{56}\text{Fe}$  values ranging from  $-0.3$  to  $1.2\text{‰}$ . Stage 3 (from 1.6 Ga throughout the Phanerozoic) is characterized by sedimentary pyrite having limited range of  $\delta^{56}\text{Fe}$  values from  $\sim 0\text{‰}$  to  $-1\text{‰}$ .

These temporal shifts likely reflect redox-related changes in the global Fe cycle. Interpretations are being investigated, but it is likely that the shift from high

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**Reservoir effect:** the concept that preferential transfer of light isotopes from reservoir  $p$  to  $q$  makes reservoir  $p$  isotopically heavier, and  $q$  isotopically lighter

**Rayleigh distillation:** a type of reservoir effect in which reaction products are irreversibly separated from the reactant reservoir, potentially driving the reservoir to extreme fractionation

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$\delta^{56}\text{Fe}$  variability in Stage I to little variability in Stage III reflects secular change in the ocean abundance of Fe. During Stage III, the formation of sedimentary pyrite typically results in the near-complete scavenging of dissolved Fe by the reaction with biogenic  $\text{H}_2\text{S}$  to form Fe sulfide minerals (Rouxel et al. 2005, Severmann et al. 2006). Hence, mass balance limits the extent of Fe isotope variability in Stage III pyrites. In contrast, Canfield et al. (2000) hypothesized that Stage I oceans were characterized by high concentrations of Fe(II) in anoxic or suboxic oceans, as well as low concentrations of sulfate. Under such conditions, large and variable Fe isotope fractionations may be expressed owing to partial Fe(II) oxidation, Fe(III) reduction, and Rayleigh distillation processes during Fe-mineral precipitation. For example, the highly variable and negative  $\delta^{56}\text{Fe}$  values of pyrite during Stage I may reflect reservoir effects in ocean Fe resulting from the removal of isotopically heavy Fe during oxidative precipitation to form banded iron formations or disseminated in marine sediments on continental shelves (Rouxel et al. 2005). Similarly, the positive  $\delta^{56}\text{Fe}$  values in the intermediate Stage II might be related to the increased effect of sulfide precipitation in a redox-stratified ocean (Rouxel et al. 2006a). Such interpretations indicate that Fe isotope variations in sedimentary pyrite are particularly sensitive to the dissolved Fe(II) concentration in seawater, and hence they can be used to place important constraints on the oxygenation of ancient oceans. Additional work in modern oxygen-deficient oceanic systems, such as in euxinic basins (Malinovsky et al. 2005b, Severmann et al. 2006) and redox-stratified lakes, is required to better constrain the origin of highly fractionated Fe in Archean and Paleoproterozoic sediments.

## Molybdenum

In this section we summarize the oceanographically relevant processes known to fractionate Mo isotopes, review the emerging understanding of the Mo isotope budget of the modern oceans, and discuss the initial application of Mo isotopes as a paleoceanographic proxy. We refer readers interested in a more comprehensive review of Mo isotope geochemistry to Anbar (2004b).

**Isotope systematics.** Mo has seven naturally occurring stable isotopes:  $^{92}\text{Mo}$  (14.84%),  $^{94}\text{Mo}$  (9.25%),  $^{95}\text{Mo}$  (15.92%),  $^{96}\text{Mo}$  (16.68%),  $^{97}\text{Mo}$  (9.55%),  $^{98}\text{Mo}$  (24.13%), and  $^{100}\text{Mo}$  (9.63%). Natural mass-dependent Mo-isotope variations span a range of  $\sim 1\text{‰}$   $\text{amu}^{-1}$  mass difference, usually reported as  $\delta^{97/95}\text{Mo}$  or  $\delta^{98/95}\text{Mo}$ . There is presently no international Mo reference standard. Data are typically reported relative to in-house laboratory standards calibrated against the apparently homogeneous seawater Mo-isotope composition (Barling et al. 2001, Siebert et al. 2003). The laboratory standards are close to the apparent average  $\delta^{97/95}\text{Mo}$  of the continental crust.

$$\delta^{97/95}\text{Mo} = \left[ \frac{(^{97}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{97}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right] \times 1000$$

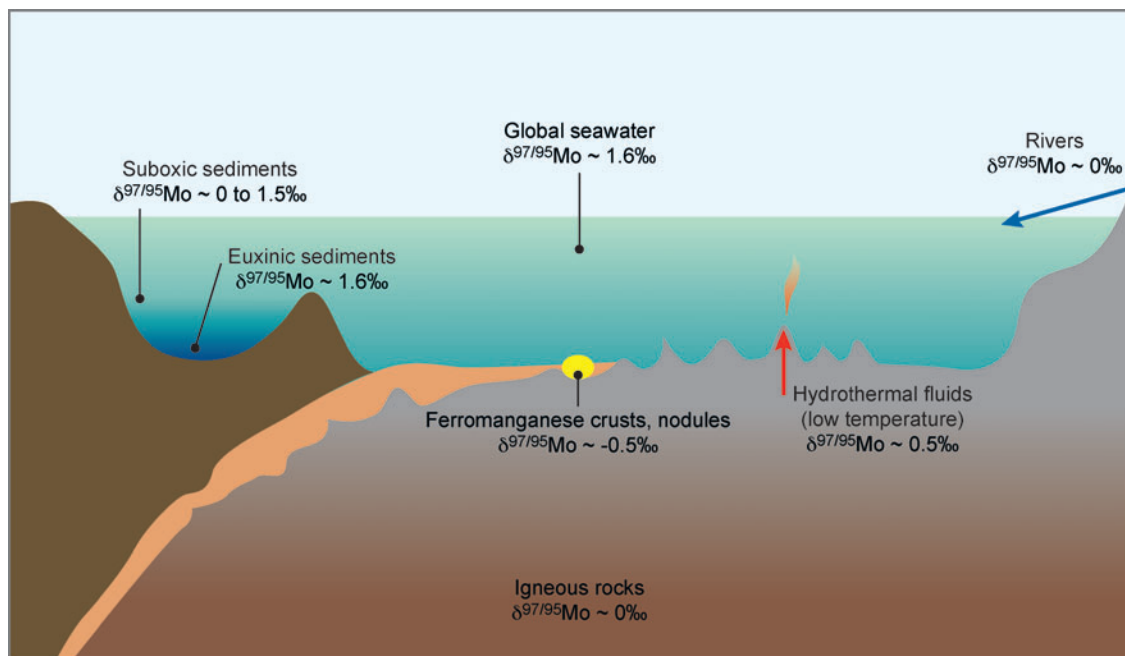
**Fractionating processes.** The largest known Mo-isotope effect occurs during adsorption of dissolved Mo to Mn-oxide particles. Light isotopes are preferentially removed from solution, so dissolved Mo is  $\sim 1\%$   $\text{amu}^{-1}$  heavier than particle-bound Mo. First inferred from natural observations in oxic seawater and sediments (Barling et al. 2001), this fractionation has been reproduced in the laboratory (Barling & Anbar 2004, Wasylenki et al. 2006). The fractionation factor is relatively unaffected by pH or temperature. Ironically, despite the rich redox chemistry of Mo (reviewed in Anbar 2004b), this fractionation may not involve a change in Mo-oxidation state. It may result from the fractionation between  $\text{MoO}_4^{2-}$ , which dominates Mo speciation in seawater, and one or more scarce, dissolved Mo species, such as  $\text{Mo}(\text{OH})_6$  or  $\text{MoO}_3$ , that adsorb more readily (Siebert et al. 2003, Tossell 2005). Alternatively, fractionation may result from isotope exchange between  $\text{MoO}_4^{2-}$  and a surface-bound Mo species (Barling & Anbar 2004).

Smaller but significant Mo-isotope effects are inferred to exist during the reduction of Mo in suboxic and euxinic environments based on observations in reducing sedimentary basins (McManus et al. 2002, 2006; Nagler et al. 2005; Poulson et al. 2006; Siebert et al. 2003, 2006). However, these effects, seen in complex sedimentary settings, have not been studied experimentally, and therefore the governing factors are not understood. Mo is highly reactive in reduced settings, particularly when dissolved  $[\text{H}_2\text{S}] > 11 \mu\text{mol kg}^{-1}$  and  $\text{MoO}_4^{2-}$  is transformed to particle-reactive oxythiomolybdates,  $\text{MoO}_{4-x}\text{S}_x^{2-}$  (Erickson & Helz 2000, Helz et al. 1996, Zheng et al. 2000). Mo-isotope fractionation likely occurs during the ligand-exchange steps or during Mo reduction.

Mo isotope variations of parts-per-thousand magnitude are also seen in continental molybdenites (Anbar et al. 2001, Malinovsky et al. 2005a, Pietruszka et al. 2006, Wieser & DeLaeter 2003). Biological isotope effects appear to be minor, although there are reports of preferential uptake of light isotopes (by  $\sim 0.25\%$   $\text{amu}^{-1}$ ) by N-fixing bacteria (Liermann et al. 2005, Nagler et al. 2004).

**Modern ocean budget.** It follows from the long residence time of Mo in oxic seawater that, in contrast to Fe, the Mo-isotope composition of bulk oxic sediments is controlled by fractionation during Mo removal to such sediments, if such fractionation occurs, as well as by the isotopic composition of Mo sources to the oceans. Similar considerations apply to suboxic sediments, which are turning out to be important to the Mo ocean budget (McManus et al. 2006). Hence, Mo-isotope oceanographic research has focused at least as much on understanding isotope effects during Mo removal to sediments as on Mo sources to the oceans.

Early data pointed to a first-order model in which Mo entering the oceans primarily from continental sources with average  $\delta^{97/95}\text{Mo} \sim 0\%$  undergoes fractionation during removal to Mn oxides, resulting in an isotopically heavy reservoir of Mo dissolved in seawater (Figure 5). The removal of Mo to euxinic sediments imparts little isotope effect. From a paleoceanographic perspective, this model implies that  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  should vary with the extent of oxic deposition; if there were no Mn-oxide deposition,  $\delta^{97/95}\text{Mo}_{\text{seawater}} \sim 0\%$  (Barling et al. 2001, Siebert et al. 2003). This schematic concept underlies the use of Mo isotopes as paleoredox proxies.



**Figure 5**

A schematic Mo ocean isotope budget. Mo enters the ocean primarily via rivers, probably with  $\delta^{97/95}\text{Mo} \sim 0\text{‰}$ . Light isotopes are preferentially removed from seawater into Fe-Mn oxides and suboxic sediments, making  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  heavy. There is relatively little fractionation during removal to euxinic sediments. Hence, paleo- $\delta^{97/95}\text{Mo}_{\text{seawater}}$  may be recorded in black shales. See Supplemental Appendix.

This model has three major uncertainties. First, continental rocks being weathered may not be isotopically uniform, so changes in weathering regimes could lead to changes in  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  independent of ocean redox. Second, the extent of Mo-isotope fractionation during weathering and transport to the oceans is not known. Leaching experiments with igneous rocks suggest that weathering effects are minimal (Siebert et al. 2003), but isotopic research in rivers and estuaries is needed. Third, and most important, suboxic sedimentary environments, once thought to be of negligible importance to the Mo elemental and isotope budgets (Barling et al. 2001, Morford & Emerson 1999), may account for as much as 60% of Mo removal (McManus et al. 2006). If so, an effect on the ocean isotope budget is likely because Mo isotopes are significantly fractionated in pore waters and sediments from such settings (McManus et al. 2002, Poulson et al. 2006). Relative to seawater Mo, the direction of this effect is the same as fractionation by removal to Mn-oxide sediments, so in paleoceanographic reconstructions changes in  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  owing to the contraction of oxic deposition could be partially countered by the expansion of suboxic deposition, and vice versa.

**Paleoceanographic records.** Researchers are exploring three types of Mo-isotope paleorecords. Temporal variations of  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  could be mirrored in Fe-Mn crusts, providing a paleorecord through the Cenozoic (Siebert et al. 2003). An alternative record extending much further in time may exist in black shales (Barling et al. 2001). Finally, Mo isotopes may also be useful in probing local, rather than global, redox conditions.

**Cenozoic Fe-Mn crusts.** Siebert et al. (2003) examined Mo isotopes in well-dated Fe-Mn crusts from the Pacific, Atlantic, and Indian Oceans. These sediments span  $\sim 60$  million years and were sampled at a resolution of  $\sim 1\text{--}3$  million years. The Mo-isotope composition of all these samples is remarkably uniform. Overall, Mo in these sediments varies within a range of  $< \pm 0.25\%$ . The data overlap with measurements of Atlantic and Pacific Fe-Mn nodules (Barling et al. 2001), despite greatly different accumulation rates of these sediment types. The only significant  $\delta^{97/95}\text{Mo}$  variation in these samples is a small offset of  $\sim 0.15\%$  seen between Pacific and Atlantic crusts, just outside the  $\pm 2\sigma$  uncertainties of Siebert et al. (2003). Systematic differences in sediment composition may play a role (Barling & Anbar 2004).

The isotopic uniformity of this record is taken to reflect the invariance of  $\delta^{97/95}\text{Mo}_{\text{seawater}}$  at the sampled resolution through the Cenozoic and may indicate that ocean oxygenation has varied less than 10% from modern values over this time (Siebert et al. 2003). This conclusion is not unreasonable. Although larger ocean redox perturbations are possible during this time in association with glacial  $p\text{CO}_2$  drawdown, their duration does not approach the  $\sim 10^6$ -year timescale of crust sampling and the mean ocean residence time of Mo.

Several caveats to this interpretation point to areas for further work. Mo in Mn oxides is strongly fractionated from seawater. It is assumed that the offset in isotope composition between dissolved and Mn-bound Mo is relatively insensitive to temperature, pH, or the details of Mn-oxide mineralogy. Theoretical modeling suggests a strong temperature dependence (Tossell 2005), but the predicted effect is not seen experimentally (Wasylenki et al. 2006). It is also assumed that there was no isotope exchange with Mo in seawater subsequent to deposition and early diagenesis. This assumption requires further study, particularly in view of the rapid isotope exchange reported by Barling & Anbar (2004).

**Black shales.** Black shales are promising recorders of the Mo-isotope composition of ancient seawater. The basis of this paleorecord is the observation of little or no Mo-isotope fractionation between seawater and euxinic sediments in the Black Sea and Cariaco basin (**Figure 4**). Although Mo isotopes likely fractionate during chemical transformations in sulfide-rich waters, Mo transfer from water column to sediment is quantitative, or nearly so, if  $\text{H}_2\text{S}$  is high and Mo resupply is limited on the timescale of removal processes (Algeo & Lyons 2006). Hence, mass balance dictates that  $\delta^{97/95}\text{Mo}$  in such sediments will be similar to that of overlying seawater.

Despite the simplicity of the concept, the Mo-isotope paleorecord in black shales must be developed with care. First, it is important to demonstrate that sampled shales represent a persistently euxinic water column to minimize the possibility of

Mo-isotope artifacts arising from nonquantitative scavenging. Recent studies have documented that nominal black shales identified in the field were not necessarily deposited under euxinic water columns analogous to the modern Black Sea (Werne et al. 2002) and that  $\delta^{97/95}\text{Mo}$  is systematically offset in settings that were not persistently euxinic (Williams et al. 2004). The measurement of local redox proxies, especially the degree of pyritization, is critical (Arnold et al. 2004a, Williams et al. 2004). Second, some hydrographic constraints are required. To record  $\delta^{97/95}\text{Mo}_{\text{seawater}}$ , the depositional basin must have been in contact with the open ocean on a timescale shorter than the Mo ocean residence. At the same time, recent studies indicate that Mo scavenging in euxinic basins may not be quantitative if recharge from the open ocean is vigorous, even when  $[\text{H}_2\text{S}] > 100 \mu\text{M}$  (Algeo & Lyons 2006). Rapid recharge likely explains the small but measurable  $\delta^{97/95}\text{Mo}$  offsets between seawater and sediments from the Cariaco Basin and Unit II of the Black Sea (Arnold et al. 2004a).

With these concerns in mind, Arnold et al. (2004a) analyzed  $\delta^{97/95}\text{Mo}$  in black shales from the MacArthur Basin, Australia, of age 1.6–1.4 Ga, to assess the possibility of expanded ocean euxinia during this time (Anbar & Knoll 2002, Canfield 1998). They found that values were distinctly lighter than modern equivalent sediments and modern seawater (**Figure 4**), consistent with the euxinic hypothesis. Siebert et al. (2006) measured  $\delta^{97/95}\text{Mo}$  in black shales from several locations in South Africa and Zimbabwe that ranged in age from 3.25 to 2.2 Ga. They observed generally increasing  $\delta^{97/95}\text{Mo}$  through time, hovering at approximately 0‰ before 3 Ga. These data are consistent with an increase in ocean oxygenation during this time, as expected from proxies of atmospheric  $\text{O}_2$ . Despite these exciting results, the use of Mo isotopes to quantify the degree of ocean oxygenation remains a challenge because of the uncertainties of the Mo ocean element budget described above. Further work is required on modern systems and on younger (Paleozoic and Cenozoic) sediments in which depositional context is better understood.

**Local redox.** The recent data open new possibilities for the use of Mo as proxy of local redox conditions, in addition to its use as a global redox indicator. Data from reducing sediment cores and ancient black shales available to date indicate that Mo isotopes show distinct isotope signatures with various depositional (and early diagenetic) environments (e.g., suboxic to anoxic to euxinic). Therefore, when the Mo-isotope composition of seawater is constant,  $\delta^{97/95}\text{Mo}$  may monitor the extent of local redox conditions at the time of deposition (Poulson et al. 2006). Mo isotopes might therefore become a powerful tool for understanding redox on a local or regional scale, the depositional conditions of sediments, and therefore the geochemical cycles of C or S.

## EMERGING ELEMENTS: ZINC, COPPER, AND THALLIUM

### Zinc

Zn has five naturally occurring stable isotopes:  $^{64}\text{Zn}$  (48.63%),  $^{66}\text{Zn}$  (27.90%),  $^{67}\text{Zn}$  (4.10%),  $^{68}\text{Zn}$  (18.75%), and  $^{70}\text{Zn}$  (0.62%). Natural mass-dependent Zn-isotope



variations span a range of  $\sim 1\%$   $\text{amu}^{-1}$ , usually expressed as  $\delta^{66}\text{Zn}$  relative to the NIST 683 standard (Albarède 2004, Maréchal et al. 1999, Dolgoplova et al. 2006). (**Supplemental Figure 3** presents a summary of natural variations of Zn isotopes.) Researchers have reported many results with respect to a laboratory standard offset by 0.06‰ relative to NIST 683 (Albarède 2004).

$$\delta^{66}\text{Zn} = \left[ \frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{NIST683}}} - 1 \right] \times 1000$$

Over the past three decades, there has been increasing evidence that Zn is correlated with silica in seawater and occurs at very low concentrations in surface waters (e.g., Bruland 1980, Franck et al. 2003). More recently, Zn has been recognized as an essential element involved in a variety of enzymatic reactions [e.g., carbonic anhydrase (Morel et al. 2004)]. In addition, Zn is incorporated and preserved into foraminifera shells and diatoms, leading to the use of Zn/Ca and Zn/Si ratios as paleoceanography proxies (Ellwood & Hunter 1999, Marchitto et al. 2005). Hence, Zn isotopes have great potential for paleoceanography research and may have applications similar to those of N and Si isotopes for tracing nutrient cycling in seawater (De La Rocha et al. 1998, Sigman et al. 1999).

An early study reported that Fe-Mn crusts are isotopically heavier (average  $\delta^{66}\text{Zn} = 0.90 \pm 0.28\%$ ) relative to the average continental crust ( $\delta^{66}\text{Zn} = 0.30\%$ ), suggesting that seawater has a heavy Zn-isotope composition (Maréchal et al. 2000). In contrast, marine particles from sediment traps have generally lighter Zn-isotope composition relative to Fe-Mn nodules, which may reflect the preferential uptake of light Zn isotopes by plankton. More recently, an investigation of the record of Zn isotopes in deep-sea carbonates over the past 175 thousand years in the equatorial Pacific found downcore variations of  $\delta^{66}\text{Zn}$  values from 0.6 to 1.2‰ (Pichat et al. 2003). The researchers attributed these variations to secular changes of the Zn-isotope composition of surface waters owing to the competitive effect of biological activity, presumed to deplete seawater of lighter Zn isotopes, and the upwelling of deep water with lower  $\delta^{66}\text{Zn}$  values.

Importantly, such interpretations assume there is negligible isotope fractionation between Zn in seawater and sediments such as carbonates and Fe-Mn nodules. They also depend on hypothetical biological effects. With respect to sediments, the fractionation of Zn isotopes in carbonate is uncertain, but recent experimental studies have shown that the fractionation of Zn isotopes during Zn adsorption on Fe and Mn oxyhydroxides does not exceed 0.2‰ (Pokrovsky et al. 2005). These results indicate that inorganic adsorption processes should be of second-order importance compared to biological factors (Gelabert et al. 2006). However, the systematic enrichment in heavy Zn isotopes found in cultured diatoms cells—fractionation of  $0.3 \pm 0.1\%$  (Gelabert et al. 2006)—is at odds with the expectation of isotopically light Zn in plankton. Preliminary analyses of the Zn-isotope composition of northeast Pacific seawater have also shown that seawater may not be characterized by heavier Zn-isotope composition relative to the crust (Bermin et al. 2006). Hence, additional work on Zn-isotope composition in seawater and plankton is required to further the application of Zn isotopes as paleoceanographic proxies.

## Copper

Cu has two naturally occurring stable isotopes:  $^{63}\text{Cu}$  (69.17%) and  $^{65}\text{Cu}$  (30.83%). Natural mass-dependent variations in  $^{65}\text{Cu}/^{63}\text{Cu}$  span 10‰ (Larson et al. 2003, Maréchal et al. 1999, Mathur et al. 2005, Rouxel et al. 2004a, Shields et al. 1965, Zhu et al. 2000a), expressed relative to NIST 976 as  $\delta^{65}\text{Cu}$ . (**Supplemental Figure 4** presents a summary of natural variations of Cu isotopes.)

$$\delta^{65}\text{Cu} = \left[ \frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST976}}} - 1 \right] \times 1000$$

Recent studies of Cu isotopes have been mainly directed toward the understanding of fractionation processes in seafloor hydrothermal systems (Rouxel et al. 2004a, Zhu et al. 2000a); magmatic, hydrothermal, and supergene Cu deposits (Larson et al. 2003); and products of Cu-sulfide leaching experiments (Mathur et al. 2005). Greater isotopic fractionation is generally observed in hydrothermal sulfides that were altered, reworked by high-temperature hydrothermal fluids, or weathered/oxidized on the ocean floor (Larson et al. 2003, Rouxel et al. 2004a).

Cu is important in marine ecosystems because it is biologically essential and yet toxic above certain levels in the form of free  $\text{Cu}^{2+}$  species. Because Cu speciation in seawater is dominated by Cu(II) complexation with organic ligands (Coale & Bruland 1988, Moffett et al. 1990), changes of Cu speciation in seawater have important implications for its bioavailability and toxicity. Although little is known about the isotope composition of Cu in seawater and marine plankton, preliminary studies suggest that Cu isotopes may be useful tracers of Cu biogeochemical cycling. For example, Zhu et al. (2002a) reported significant Cu-isotope fractionation of up to  $-1.5\%$  during biological Cu uptake.  $\delta^{65}\text{Cu}$  values of the surface layers of Fe-Mn nodules show little deviation from basaltic values with a mean value of  $0.31 \pm 0.23\%$ , which may reflect little Cu-isotope variability in seawater (Albarède 2004).

Experimental studies, so far, have indicated that redox transformations between Cu(I) and Cu(II) species are the principal process that fractionate Cu isotopes in natural systems (Ehrlich et al. 2004, Zhu et al. 2002a). In particular, precipitated Cu(I) species are lighter by 3 to 5‰ relative to dissolved Cu(II) species during Cu(II) reduction. Although the relative effects of equilibrium versus kinetic isotope fractionation remain unclear, this demonstrates the great potential for using Cu isotopes as redox tracers in oxygen-deficient marine environments. In particular, the reduction of Cu(II) to Cu(I) in suboxic and anoxic pore waters may potentially explain the large variations of  $\delta^{65}\text{Cu}$  values between  $-0.94$  to  $-2.83\%$  in marine sediments (Albarède 2004). Despite these advances, our knowledge of Cu-isotope systematics in oceanic systems is extremely incomplete.

## Thallium

Tl has two naturally occurring isotopes:  $^{203}\text{Tl}$  (29.5%) and  $^{205}\text{Tl}$  (70.5%). Researchers have observed mass-dependent variations in  $^{205}\text{Tl}/^{203}\text{Tl}$  of approximately 2‰ in seawater and sedimentary rocks. Continental crust and upper mantle are characterized

by relatively constant Tl-isotope ratios of  $\delta^{205}\text{Tl} = -0.2 \pm 0.05\text{‰}$  relative to NIST 997. (Tl-isotope compositions are also reported as  $\epsilon^{205}\text{Tl}$ , the deviation of  $^{205}\text{Tl}/^{203}\text{Tl}$  in parts per 10,000.)

A survey of published data estimated that rivers and marine aerosols are important sources of Tl to seawater, contributing to  $\sim 25\%$  and  $\sim 10\%$  of the total Tl flux to the oceans, respectively (Rehkämper & Nielsen 2004). The remaining flux is largely dominated by volcanic-gas emission and hydrothermal circulation at the seafloor. The Tl-isotope composition of loess, water samples, and suspended riverine detritus from various rivers and estuaries is relatively uniform with a mean of  $\delta^{205}\text{Tl} = -0.2$  to  $-0.25\text{‰}$  and is similar to the average continental crust (Nielsen et al. 2005). Preliminary Tl-isotope compositions of high-temperature hydrothermal fluids from ridge axes display  $\delta^{205}\text{Tl} = -0.2\text{‰}$ , indistinguishable from unaltered mantle rocks. In contrast, the low-temperature alteration of the upper volcanic zone generates Tl-rich rocks that have  $\delta^{205}\text{Tl}$  as low as  $-1.6\text{‰}$  (Rehkämper et al. 2004b). These results indicate that the flux of Tl to the oceans is characterized by Tl-isotope composition close to the average silicate earth with  $\delta^{205}\text{Tl}$  values  $\sim -0.2\text{‰}$ .

In an initial study of Tl-isotope composition of marine sediments, Rehkämper et al. (2002) found that modern Fe-Mn crusts have a global signature of  $\delta^{205}\text{Tl} = 1.28 \pm 0.12\text{‰}$ , whereas seawater is characterized by  $\delta^{205}\text{Tl}$  values as low as  $-0.8\text{‰}$ . This  $\sim 2\text{‰}$  difference in isotope composition is thought to result from the equilibrium isotope fractionation during Tl adsorption onto Fe-Mn particles and subsequent oxidation. A further investigation examined the time-resolved Tl-isotope composition in Fe-Mn crusts over the past 25 Ma and found a systematic increase of  $\delta^{205}\text{Tl}$  with decreasing age, from  $\sim 0.6\text{‰}$  at 60–50 Ma to  $\sim 1.2\text{‰}$  at 25 Ma (Rehkämper et al. 2004a). At present, there is no unique explanation for these trends, but they likely reflect changes in the Tl-isotope composition in seawater. Because the flux of Tl to the oceans is probably characterized by  $\delta^{205}\text{Tl} \sim -0.2\text{‰}$ , the secular variation of Tl isotopes in seawater possibly was generated by variations in the oceanic input fluxes of Tl, such as benthic and riverine fluxes (Rehkämper et al. 2004a). Future studies need to test these hypotheses and better constrain the mechanisms of Tl-isotope fractionation between fluid and minerals. By analogy with Mo-isotope systematics, Tl isotopes may possibly find applications in the study of redox evolution in the oceans.

## Other Elements

High-precision isotopic measurements of other metals and metalloids in geological and biological materials have revealed small, but significant, mass-dependent variations resulting from a wide range of natural processes. For example, the Sb-isotope composition of seawater, mantle-derived rocks, marine sediments, and hydrothermal deposits has an overall variation of up to  $2\text{‰}$  in  $^{123}\text{Sb}/^{121}\text{Sb}$  (Rouxel et al. 2003b). In contrast to the relatively homogenous composition of Sb isotopes in the crust and seawater (defined at  $\delta^{123}\text{Sb} = 0.2 \pm 0.1\text{‰}$  and  $0.37 \pm 0.04\text{‰}$ , respectively), hydrothermal deposits display the largest variability of up to  $1.8\text{‰}$ . The reduction of Sb(V) to Sb(III) aqueous species produces an isotope fractionation of  $\sim 0.9\text{‰}$ ;

therefore, Sb isotopes may be useful tracers of redox transformations in oceanic systems.

Recent studies have also reported natural isotope variations of Hg and Cr, two metals of major environmental importance (Ellis et al. 2002, Smith et al. 2005). Because the toxicity of these metals is highly dependent on their speciation—i.e. Cr(III) versus Cr(VI), Hg<sup>0</sup> versus CH<sub>3</sub>Hg—there is an interest in analyzing their stable isotope compositions to trace sources and species transformations in natural environments. For example, the measurement of the Cr-isotope composition of contaminated aquifers has been particularly useful for indicating the extent of the reduction of toxic Cr(VI) to less mobile and toxic Cr(III) (Ellis et al. 2002). Despite the major health issues regarding Hg bioaccumulation in the marine food web, the variability of Hg isotopes in oceanic systems is still unknown.

Given the wealth of information conveyed by Cd as an indicator of primary productivity in ancient oceans (Boyle 1981, 1986; Elderfield & Rickaby 2000), Cd isotopes may also carry paleoceanographic importance. However, analyses of the Cd-isotope composition of marine sediments reported so far have shown limited variation of Cd-isotope ratios of less than 0.1‰ amu<sup>-1</sup> (Cloquet et al. 2005). Hence, using Cd isotopes as paleoceanographic tracers requires additional work, especially regarding the precision of measurement.

In recent years, researchers have also explored the natural variations of Ti (Zhu et al. 2002b), Sn (Clayton et al. 2005), Ag (Woodland et al. 2005), and Te (Fehr et al. 2004) isotopes, and although the variations are generally smaller than 0.1‰ amu<sup>-1</sup>, these metal isotopes may find future applications in paleoceanography. Larger variations of stable isotope compositions of metalloids such as Se and Ge have been also reported. Researchers have observed an overall Se-isotope variation of up to 2‰ amu<sup>-1</sup> in marine sediments and hydrothermal deposits (Johnson & Bullen 2004, Rouxel et al. 2002), suggesting that Se isotopes fractionate readily and are useful tracers of Se redox cycling in aqueous systems (Johnson et al. 1999b). An initial study reported a total range of <sup>74</sup>Ge/<sup>70</sup>Ge ratios in marine sediments and biogenic opal of up to 2.5‰ (i.e., 0.6‰ amu<sup>-1</sup>) (Rouxel et al. 2006b). The results indicate that seawater may be enriched in heavy Ge-isotopes with respect to igneous rocks. Although further work is required to determine Ge-isotope fractionation by siliceous organisms and to investigate the effect of diagenetic processes, Ge-isotope composition in marine opal may provide paleoceanographic information on past oceanic Ge cycles.

## FUTURE DIRECTIONS

Few investigators in 1997 foresaw the trajectory that transition-metal stable isotope research would take in the following ten years. Even in 2001, looking at the technology of that time, it was hard to imagine that such analyses would become routine enough to emerge from the isotope boutique. The opportunities and challenges of the next 10 years are a bit less obscure. A handful of oceanographically interesting elements not yet explored—most notably, Ni, Re, and U—are sure to be examined. For these and other elements, reconnaissance of natural materials and environments must continue. As made clear above, important gaps remain, even in the cases of Fe and Mo isotopes,

which are most mature. Further advances in analytical capabilities will no doubt aid such reconnaissance and will open new avenues for exploration analogous to the multiple isotope studies at the forefront of O- and S-isotope geochemistry (e.g., Farquhar et al. 2000, Luz & Barkan 2005). However, the primary challenge to this field is no longer analytical. Indeed, the technology has advanced so rapidly that our ability to measure isotopic variations in complex natural systems has outrun our understanding of fractionation processes. Reconnaissance must increasingly give way to systematic research that involves a balanced combination of field, laboratory, and theoretical investigations.

## ACKNOWLEDGMENTS

Anbar's research on Fe and Mo isotopes would not have been possible without support from the National Science Foundation, the NASA Astrobiology Institute, Arizona State University, and the University of Rochester. Critical help and inspiration were provided by coworkers, notably Gail Arnold, Jane Barling, Gwyneth (Williams) Gordon, Jo Roe, Chris Siebert, and Laura Wasylenki, and by many collaborators and colleagues, especially Francis Albarède, Susan Brantley, Andy Knoll, Tim Lyons, Ken Nealson, and Greg Ravizza. Rouxel thanks the Woods Hole Oceanographic Institution, the National Science Foundation, University of Cambridge, CNRS, and IFREMER for their support over the years. He also acknowledges his collaborators, including Andrey Bekker, Harry Elderfield, Yves Fouquet, Albert Galy, Katrina Edwards, John Ludden, and Ed Sholkovitz.

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