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Mobility of nutrients and trace metals during weathering in the late Archean

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ABSTRACT

The evolution of the geosphere and biosphere depends on the availability of bio-essential nutrients and trace metals. Consequently, the chemical and isotopic variability of trace elements in the sedimentary record have been widely used to infer the existence of early life and fluctuations in the near-surface environment on the early Earth, particularly fluctuations in the redox state of the atmosphere. In this study, we applied late Archean weathering models (Hao et al., 2017), developed to estimate the behavior of major elements and the composition of late Archean world average river water, to explore the behavior of nutrient and trace metals and their potential for riverine transport. We focused on P, Mn, Cr, and Cu during the weathering of olivine basalt.

In our standard late Archean weathering model ($p\text{CO}_{2,g} = 10^{-1.5}$ bars, $p\text{H}_{2,g} = 10^{-5.0}$ bars), crustal apatite was totally dissolved by the acidic rainwater during weathering. Our model quantitatively links the $p\text{CO}_{2,g}$ of the atmosphere to phosphate levels transported by rivers. The development of late Archean river water (pH = 6.4) resulted in riverine phosphate of at least 1.7 μmolar , much higher than at the present-day. At the end of the early Proterozoic snowball Earth event when $p\text{CO}_{2,g}$ could be 0.01–0.10 bars, river water may have transported up to 70 μmolar phosphate, depending on the availability of apatite, thereby stimulating high levels of oxygenic photosynthesis in the marine environment.

Crustal levels of Mn in olivine dissolved completely during weathering, except at large extents of weathering where Mn was stored as a component of a secondary carbonate mineral. The corresponding Mn content of river water, about 1.2 μmolar , is higher than in modern river water. Whiffs of 10^{-5} mole O_2 gas or HNO_3 kg^{-1} H_2O resulted in the formation of pyrolusite (MnO_2) and abundant hematite and simultaneous dramatic decreases in the concentration of Mn(II) in the river water.

Chromite dissolution resulted in negligible dissolved Cr in Archean river water. However, amorphous $\text{Cr}(\text{OH})_3$ representing easily-weatherable Cr-bearing minerals dissolved totally during the weathering simulations, resulting in concentrations of Cr(III) in the river water of up to 0.14 μmolar , higher than at the present-day.

Late Archean weathering of accessory chalcopyrite produced chalcocite and bornite, and extremely low concentrations of Cu ($<10^{-15}$ molar) because of the low solubilities of the copper sulfides. However, pulses of either $\text{O}_{2,g}$ or HNO_3 produced native copper, chalcocite, and bornite, much more hematite, and river water containing levels of dissolved Cu comparable to the present-day. Copper mineralogy predicted by weathering models might provide a new correlation with evidence from studies of copper mineral evolution.

Overall, our results implied that the redox state of the atmosphere, the pH of surface waters, and the availability of easily-weatherable minerals are all important factors controlling the dissolution of trace elements in river water. Interpretation of the sedimentary signatures of trace elements should consider not only the redox state but also the pH and availability of accessory minerals.

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1. Introduction

The availability of bio-essential nutrients and trace metals in the surface environment was a critical factor for the origin and

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evolution of life throughout Earth history (Anbar, 2008; Williams and Da Silva, 2003; Zerkle et al., 2005). However, large uncertainties exist in estimation of the levels of nutrients and trace elements in the surface waters of early Earth. For example, in the case of phosphate, Archean productivity was first thought to be limited by low dissolved phosphate in the seawater due to adsorption onto iron oxides deposited as banded iron formations (Bjerrum and Canfield, 2002), but subsequent studies pointed out that the high concentration of dissolved silica and cations expected in Archean seawater would affect phosphate adsorption sites on iron oxides and therefore complicated the simple interpretation of phosphate in iron-formation as indicator of dissolved phosphate levels (Jones et al., 2015; Konhauser et al., 2007). Recent compilations of phosphate in iron formation and shales suggested that phosphate concentrations in the surface seawater might be comparable to or lower than modern (Planavsky et al., 2010; Reinhard et al., 2017). Such disputes mainly focused on the removal of phosphate from seawater and did not address the important role of weathering and riverine transport, which was the dominant influx of phosphate to the early oceans. The importance of this role has been emphasized for the Phanerozoic (Guidry and Mackenzie, 2000). Here we apply recent developments in the modeling of late Archean weathering and river water chemistry (Hao et al., 2017) to simulate the dissolution of phosphate minerals and riverine transport of dissolved phosphate under late Archean atmospheric conditions.

In the case of trace metals, the redox-sensitive trace metals, such as Cr, Cu, U, Mo, and Re, and their isotopic fractionations recorded in various sedimentary rocks are now widely used to infer fluctuations in the redox history of Earth's surface environment (Anbar and Rouxel, 2007; Farquhar et al., 2014; Tribouillard et al., 2006). The atmosphere before the Great Oxidation Event (GOE) is widely accepted to be anoxic with relatively high $p\text{H}_{2,\text{g}}$. Consequently, during normal weathering processes in the late Archean, elements such as Cr, Cu, U, Mo, and Re would have been immobile, but the solubilities of Fe and Mn would have been much higher than in present-day surface waters. However, recent studies reported enrichments of several trace metals (e.g. Mo, Re, Cr) and the variability of isotopic fractionations in some sedimentary records that have been interpreted as evidence of "whiffs of molecular oxygen" in the Archean atmosphere (Anbar et al., 2007; Frei et al., 2009).

The "whiffs" interpretation currently contradicts the overall picture of an anoxic Archean atmosphere suggested by the mass independent fractionation of S isotopes (Farquhar et al., 2000; Luo et al., 2016), the Fe-loss from paleosols (Rye and Holland, 1998), and the preservation of detrital minerals unstable in the presence of molecular oxygen (Hessler and Lowe, 2006; Johnson et al., 2014; Rasmussen and Buick, 1999). However, the exact conditions under which trace metals and their isotopes might have been mobilized have not been examined in a comprehensive framework of weathering simulations that link trace metals and their potential sources, major elements and rock-forming minerals, and perturbations of an anoxic late Archean environment. Here we address how trace nutrients and metals might have behaved by using a framework of thermodynamic weathering models (Hao et al., 2017). After the GOE, the atmosphere became oxic with $p\text{O}_{2,\text{g}}$ around 1%–10% PAL (Kump, 2008; Lyons et al., 2014), resulting in oxidizing weathering and riverine transport of trace elements, similar to the present-day.

Although researchers have relied largely on sedimentary records to probe paleoredox and paleoproductivity processes, the interpretation of sedimentary profiles depends strongly on a clear understanding of weathering, riverine transport, sedimentation, and preservation history. Trace elements are commonly hosted in accessory minerals and solid solutions in silicates, carbonates, or oxides in the crust. Dissolution of these host minerals during

weathering is controlled by several factors including the mineral abundance and reactivity, the redox state, the pH of the water, and precipitation of secondary minerals (Aiuppa et al., 2000; Middelburg et al., 1988). After weathering, dissolved trace elements are transported by rivers to the ocean where they may be sequestered into sediments and preserved. Oxidation of several trace elements, e.g. Mn, Cr, Cu, Mo, and Re, can greatly enhance their solubility in surface waters, along with isotopic fractionation. Therefore, changes in the chemical profiles of these trace elements and their isotopic fractionation can be used as indicators of paleoredox. However, apart from the redox reactions, change of environmental pH, variation of weathering rates and the availability of easily-weatherable accessory minerals, and/or complexation with possible ligands may also lead to fluctuations in the mobility of trace elements and their isotopic fractionation. Moreover, sedimentary records, especially Archean ones, are usually the result of low- to medium-grade metamorphism and/or metasomatism. These post-depositional changes involving elevated temperature and pressure fluid-rock interactions can be expected to affect the original sedimentary records, confounding the interpretation of fluctuations in trace elements.

The present study was designed to simulate the dissolution of minerals that are hosting the nutrient P and the trace metals Mn, Cr, Cu during weathering of olivine basalt and the mobility of these trace elements in late Archean (3.0–2.5 Ga) surface waters. This time period is selected because life had already appeared by then (Arndt and Nisbet, 2012) and a supply of nutrients and trace metals is vitally important for the habitability and evolution of life in the late Archean which might cause the irreversible oxidation of the atmosphere. Geochemical reaction-path modeling, an overall irreversible, non-equilibrium modeling tool, considers many environmental factors simultaneously and offers a quantitative approach to predicting water-rock interactions (Bethke, 1996; Helgeson, 1979; Zhu and Anderson, 2002). With simplified assumptions regarding the kinetics of primary mineral dissolution and secondary mineral precipitation, reaction-path modeling can approximate the major chemical reactions involved in weathering contributions to present-day world average river water (Hao et al., 2017). The goal of this project is to apply this modeling approach to study the behavior of P, Mn, Cr, and Cu during Archean weathering and riverine transport. Additionally, the influence of whiffs of oxidants, e.g. $\text{O}_{2,\text{g}}$ or HNO_3 , on the behavior of the trace elements were investigated.

2. Factors affecting the dissolution of trace elements during weathering

2.1. Redox level of the atmosphere

The chemical weathering of redox-sensitive minerals is greatly affected by the redox level of the surface environment (Aiuppa et al., 2000). Among the elements covered in this study, phosphorus only has one stable valence in the ambient environment. However, under modern reducing, diagenetic environments where Fe^{2+} occurs, PO_4^{3-} can precipitate as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) which controls the availability of phosphate (Ruttenberg, 2003). This scenario might also be true in the late Archean environment where high concentrations of Fe(II) could have occurred in surface waters (Hao et al., 2017). Consequently, the possible formation of vivianite in the near-surface Archean environment needs to be addressed. The stability of Fe(II) in the Archean surface waters could also lead to an extremely low solubility for chromite and therefore limit the dissolution of Cr(III) during the weathering of chromite. Other elements, namely Mn and Cu, have variable valences depending on the redox state of the environment and therefore their weathering is redox-sensitive.

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