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# A model for late Archean chemical weathering and world average river water

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A B S T R A C T

Interpretations of the geologic record of late Archean near-surface environments depend very strongly on an understanding of weathering and resultant riverine transport to the oceans. The late Archean atmosphere is widely recognized to be anoxic ($pO_{2,g} = 10^{-5}$ to $10^{-13}$ bars; $pH_{2,g} = 10^{-3}$ to $10^{-5}$ bars). Detrital siderite ($FeCO_3$), pyrite ($FeS_2$), and uraninite ($UO_2$) in late Archean sedimentary rocks also suggest anoxic conditions. However, whether the observed detrital minerals could have been thermodynamically stable during weathering and riverine transport under such an atmosphere remains untested. Similarly, interpretations of fluctuations recorded by trace metals and isotopes are hampered by a lack of knowledge of the chemical linkages between the atmosphere, weathering, riverine transport, and the mineralogical record.

In this study, we used theoretical reaction path models to simulate the chemistry involved in rainwater and weathering processes under present-day and hypothetical Archean atmospheric boundary conditions. We included new estimates of the thermodynamic properties of Fe(II)-smectites as well as smectite and calcite solid solutions. Simulation of present-day weathering of basalt + calcite by world-average rainwater produced hematite, kaolinite, Na–Mg-saponite, and chalcedony after $10^{-4}$ moles of reactant minerals $kg^{-1}$ $H_2O$ were destroyed. Combination of the resultant water chemistry with results for granitic weathering produced a water composition comparable to present-day world average river water (WARW). In contrast, under late Archean atmospheric conditions ($pCO_{2,g} = 10^{-1.5}$ and $pH_{2,g} = 10^{-5.0}$ bars), weathering of olivine basalt + calcite to the same degree of reaction produced kaolinite, chalcedony, and Na–Fe(II)-rich-saponite. Late Archean weathering of tonalite–trondhjemite–granodiorite (TTG) formed Fe(II)-rich beidellite and chalcedony. Combining the waters from olivine basalt and TTG weathering resulted in a model for late Archean WARW with the composition $Na^+–Ca^{2+}–Fe^{2+}–Mg^{2+}–Cl^-–HCO_3^-–SiO_{2,aq}$. The pH of the water was 6.3 and it is much richer in $HCO_3^-$, and in Mg + Fe relative to Ca + Na, compared to present-day WARW. At higher $pH_{2,g}$ (e.g. $10^{-4.0}$ bars) organic acid anions could be metastable. Our results are consistent with the thermodynamic stability of Fe(II)-clays, pyrite, uraninite, and, under some conditions, siderite during weathering and riverine transport. Overall, our results provide a basis for assessing the formation of organic hazes and the mobility of trace elements and nutrients due to fluctuations of the late Archean atmosphere.

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## 1. Introduction

Numerous studies have been carried out to attempt to unravel the nature of different parts of the near-surface early Earth system. Sulfur isotopic studies have established that the atmosphere was anoxic prior to 2.33 Ga (Farquhar et al., 2000; Luo et al., 2016). Based on non-equilibrium atmospheric models, the Archean atmosphere has been described as anoxic with high $pCO_{2,g}$

(Catling and Claire, 2005; Kasting, 2014), although considerable controversy surrounds the $CO_{2,g}$ content of the Archean atmosphere (Haqq-Misra et al., 2008; Hessler et al., 2004; Kasting, 2014; Ohmoto et al., 2004; Rosing et al., 2010; Rye et al., 1995; Sheldon, 2006; von Paris et al., 2008). Combined sulfur and carbon isotopic studies, and atmospheric models, have documented the likely importance of global organic-rich hazy atmospheres alternating with periods of no haze in the Neoarchean from 2.7–2.5 Ga (Izon et al., 2015; Zerkle et al., 2012).

It is also expected that many important aspects of surficial water chemistry in the late Archean were very different from the

present-day. For example, it has been suggested that the oceans were probably rich in dissolved silica (Siever, 1992), low in sulfate (Crowe et al., 2014), and contained redox-sensitive elements in their reduced forms, for example $H_2S(aq)$, $Fe^{2+}$ and $NH_4^+$ (Catling and Claire, 2005; Holland, 1984; Lyons et al., 2014). On the late Archean continents, paleosol studies imply the mobility of aqueous $Fe^{2+}$-species in the near-surface weathering environment, detrital mineral records suggest preservation of uraninite, siderite, pyrite, and ferrous clay minerals (Frimmel, 2005; Hessler and Lowe, 2006; Johnson et al., 2014; Rasmussen and Buick, 1999), and mineral evolution studies are consistent with major changes in the near-surface environment (Hazen et al., 2014). Furthermore, numerous studies of the sedimentary marine record (e.g. banded iron formations and shales) have suggested that trace metals were mobilized during oxidative weathering processes on the late Archean continents (Anbar et al., 2007; Frei et al., 2009; Gregory et al., 2015; Konhauser et al., 2015; Large et al., 2014; Stüeken et al., 2015). Whether or not these processes involved molecular $O_{2,g}$ is unclear. Finally, oscillation between hazy and non-hazy atmospheres proposed for the Neoarchean has been attributed to fluctuations in the production of trace nutrients (organic species or trace metals) in the weathering environment on the continents or in the oceanic hydrothermal environment (Izon et al., 2015). However, little is really known about the potential linkages between the atmosphere, the water chemistry during weathering and riverine transport, and the mineralogic record, which makes it difficult to interpret the causes of fluctuations in trace metal or nutrient availability during late Archean weathering.

Overall, the rich record of clues about the nature of the near-surface environment on early Earth offers a tantalizing, if not confusing, picture that is marked by numerous uncertainties and outright disagreements. However, the consistency of all these lines of evidence has not been examined with the aid of geochemical theory. Quantitative geochemical models of rainwater, river water, the oceans, and water–rock interactions could, in principle, be applied to early Earth, but have rarely been used (Alfimova et al., 2014; Fabre et al., 2011; González-Álvarez and Kerrich, 2012; Lafon and Mackenzie, 1974; Schmitt, 1999; Sverjensky and Lee, 2010). Nor has there been any attempt to link such models to the long literature on models of the early Earth atmosphere (e.g. Claire et al., 2014; Kurzweil et al., 2013). With one exception (Alfimova et al., 2014) involving paleosols on basalts, the application of quantitative models of chemical weathering that include the chemical speciation of surface waters on the continents and the chemical speciation and state of saturation with respect to minerals in the shallow and deep oceans have not been addressed for the late Archean. The lack of quantitative chemistry prevents construction of an internally consistent, quantitative picture of the evolution of the near-surface environment of early Earth through deep time.

The present weathering study was designed to build a quantitative linkage between the results of atmospheric modeling of early Earth, the chemistry of surface waters on the continents, and the associated mineral weathering products that might be preserved in the geologic record. We focus here on water chemistry and the mineralogic record of change in the near-surface environment. In order to do this, we applied theoretical geochemical models of aqueous speciation, solubility, and chemical mass transfer to weathering on early Earth during the late Archean (3.0–2.5 Ga). This time period was chosen because of the reported occurrences of unusual detrital minerals in rocks interpreted to represent the sediments from riverine systems (Frimmel, 2005; Hessler and Lowe, 2006; Johnson et al., 2014; Rasmussen and Buick, 1999) and the formation of major continents and therefore weathering and riverine transport (Taylor and McLennan, 2009). Similar approaches have focused previously on chemical weathering processes on Mars (Catalano, 2013) and on perturbations of

early Earth's atmosphere that might affect weathering (Sverjensky and Lee, 2010), but these emphasized $pO_{2,g}$ in the early atmosphere. Here, we focus on the simulation of weathering processes with a steady-state atmosphere defined by atmospheric models in which the role of $H_{2,g}$ is emphasized. An overall goal in this project is to build a chemical model of the connection between weathering and late Archean world-average river water (WARW). This model will serve as a framework for examining the potential mobility of trace metals and nutrients during weathering processes and is also a first step towards developing a geochemical model for the late Archean oceans.

## 2. Theoretical modeling approach and assumptions

### 2.1. Modeling approach

Detailed studies of individual riverine, soil zone, aquifer, and weathering systems have documented the many factors that can influence weathering rates. These factors include the effects of temperature, $pCO_{2,g}$ in the soil, vegetation, precipitation, and runoff (Bluth and Kump, 1994; Dessert et al., 2003; Gíslason et al., 1996; Lasaga et al., 1994; Maher, 2010; West et al., 2005; White and Buss, 2014), as well as the kinetics of dissolution of primary minerals and the precipitation of secondary minerals (Bethke, 1996; Brantley and Olsen, 2014; Kump et al., 2000; Steinmann et al., 1994; Zhu, 2009). Complex weathering models that include chemistry, kinetics, hydrology, and climate change have addressed all these factors, but are still site-specific, primarily owing to the need to fit the thermodynamic properties of clay minerals or to test alternate kinetic models for mineral reactivity using measured weathering fluxes (Beaulieu et al., 2012; Dosseto et al., 2015; Dupré et al., 2003; Goddéris et al., 2006; Maher et al., 2009; Violette et al., 2010). For the Archean, this degree of constraint is clearly impossible. Consequently, a simpler approach is warranted.

Our focus is on the simulation of global late Archean weathering and its contribution to world average late Archean river water chemistry. One source of uncertainty in our simulations is the surficial temperature. Considering the wide range of previously proposed Archean surface temperatures from mild, e.g., $T < 35\,°C$ (Blake et al., 2010; Shields and Kasting, 2007) to hot e.g., $T \sim 80\,°C$ (Knauth, 2005; Robert and Chaussidon, 2006), we carried out weathering calculations over a range of temperature conditions. For the purposes of this paper, we only show the results under $25\,°C$ conditions. We further assumed that during the late Archean, biological effects on weathering would have been small compared to those of the present-day. Soil cover may have been thinner, permitting greater chemical interaction between the $CO_{2,g}$ in the atmosphere, water, and rock. However, many other factors important at the present day are not known. Consequently, we applied purely chemical irreversible mass transfer models (Helgeson, 1979) to simulate reactions between rainwater and representative minerals in major crustal rocks. All the calculations were carried out with the aqueous speciation, solubility, and chemical mass transfer codes EQ3 & EQ6 (Wolery, 1992) using thermodynamic data files prepared as described in Sec. 2.2 and Suppl. Info.

Recognizing the simplifications in the above approach, we applied the chemical mass transfer calculations to present day and late Archean rainwaters reacting with crustal rocks. The purely chemical model of present-day weathering was developed in order to calibrate the extent of silicate and carbonate weathering contributions to present-day world-average river water and provide a basis for taking a similar approach to predicting late Archean world-average river water. The irreversible reaction of the initial present-day and late Archean rainwaters with an excess of minerals approximating crustal rocks was computed. For