Chemical Archeoceanography

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Plain language summary. We here evaluate the constraints on seawater chemistry before free oxygen was introduced into the atmosphere some 2.4 billion years ago. We suggest a simple conceptual framework which we validated on modern seawater and which is based on two so-far largely overlooked observations, namely that the phosphorus concentration and strontium isotopic records in ancient sediments require that emerged continental land masses were covering only ~7% of Earth's surface at the time of the Great Oxidation Event instead of 30% today. Atmospheric and seawater chemistry critically depend on this proportion as well as on the chlorinity of the ocean. The oxygen-free atmosphere allowed iron to remain in solution and to reduce atmospheric carbon dioxide to methane. The pH of the ancient oceans must have been lower because less river water was available to neutralize the acidic submarine high-temperature hydrothermal fluids emitted at mid-ocean ridges. Limited continental surface starved the sedimentary column for clays. The low pH and scant phosphorus drainage led to rare carbonate deposition. We conclude by proposing a new scheme for Archean marine chemistry and geochemical cycles that can explain the chemical and geological observations from the Archean and early Proterozoic rock record.

Abstract. Elemental fluxes to the ocean are expected to increase with the surface area of continental exposure to weathering and atmospheric P_{CO_2} . The record of phosphorus in sediments, which has no notable source within the ocean, and the radiogenic strontium isotopes in Archean carbonates indicate that, prior to the Great Oxidation Event (GOE), subaerial expanses represented only about 20% of the modern continental surface area, i.e. 7% of the surface of the Earth. Because these simple first-order observations, in contrast to the low oxygen content of the pre-GOE atmosphere, have so far received only little attention in the appraisal of the marine chemistry of the early Earth, a reassessment of the chemistry of the pre-GOE ocean is warranted. Here we discuss some of the geochemical cycles of the Archean world, including protons, alkalinity, electrons, and other electrolytes, and attempt to build a first conceptual framework for Chemical Archeoceanography. The smaller subaerial exposures characterizing the Archean and the low abundance of Archean carbonates and mudstones imply that the flux of alkalinity to the ocean was much weaker than today and therefore that the capacity of the runoff to neutralize the high-temperature hydrothermal fluids was less important. Such a reduced flux in turn entails lower seawater pH and higher chlorinity. The lack of atmospheric O_2 allowed iron to be in its soluble Fe(II) form and to reduce HCO_3^- to CH_4 while liberating large amounts of protons. The low pH of the pre-GOE

ocean and the reduced alkalinity input, reinforced by scant P supply, account for reduced carbonate precipitation. Ocean chemistry evolved under the control of two changing factors: (i) the balance between chemical weathering and hydrothermal fluxes and (ii) the oxygen pressure in the ocean and the atmosphere. Seawater iron concentration was controlled by high $[Fe^{2+}]/[H^+]^2$ ratios. The temperature of hydrothermal fluids at mid-ocean ridges and in other active volcanic edifices being determined by the expansion properties of seawater, the chemistry of hydrothermal fluids is controlled by the chlorinity of the ocean. Of all the major element cycles in seawater, those of Na, Mg and P seem to be unbalanced when runoff falls below the modern value. The very low P content of banded iron formations is inconsistent with a major role of biological activity in the oxidation of Fe^{2+} dissolved in the Archean ocean. Prior to the GOE, banded iron formations were the major sedimentary sink of seawater cations, a role now played by carbonates. The controls of seawater alkalinity, which today are exerted by the Ca^{2+} - $CaCO_3$ couple, was exerted by dissolved Fe^{2+} -magnetite or Fe^{2+} -ferrihydrite.

Keywords: Archean ocean chemistry; methane; geochemical cycles; continental surface; runoff; hydrothermal fluids

1. Introduction

The ocean prior to the Great Oxidation Event (GOE) some 2.4 Gy ago differed from its modern counterpart in many compositional, physiographic, and dynamic aspects. The most dramatic difference in the physics of the Archean ocean was the smaller extent of subaerial continental expanses (Arndt, 1999; Kump and Barley, 2007). Although it is firmly established that continents have grown over time (Hurley and Rand, 1969; Reymer and Schubert, 1984), it is still not clear how much of the crust stood above sea level at any given time, in particular

because the assumption of constant freeboard can be evaluated only for post-Precambrian
times (Wise, 1973).

An Archean world with reduced continental surface would have been very different from the familiar Cenozoic ‘conveyor belt’ (Broecker and Peng, 1982), in which oceanic circulation is shaped by a particular plate configuration and deep-water formation reflects the distribution and latitude of continents. In the modern ocean, most of the runoff ends up in the Atlantic Ocean with its load of nutrients and alkalinity, whereas the receiving end of mechanical transport is in the Indian and the Pacific Oceans. By contrast, a world with little land mass would be more akin to aquaplanets, such as in the models of Smith et al. (2006) and Marshall et al. (2007). Ocean circulation would be dominated by zonal jets with a transport pattern resembling that of the Circum-Antarctic Current. A water world has no equivalent of the Gulf Stream and deep-water masses are difficult to form by processes similar to those operating in the modern Norwegian and Weddell seas. Gyres would not exist and ocean circulation would be reduced to broad eastward jets at mid-latitude separated by an intertropical westward jet. Winds and deep tides, not buoyancy, would force oceanic circulation and vertical mixing (Ferrari and Wunsch, 2009; Wunsch and Ferrari, 2004). Maintaining a stratified ocean (Beukes et al., 1990; Klein and Beukes, 1989; Lowe, 1980) therefore would require special circumstances. Understanding the chemistry of a mostly submerged Archean and pre-GOE world is an important challenge.

The issue of the extent of exposed surface is particularly important because weathering, both today and during the Precambrian, is by far the most important sink of atmospheric CO₂, thereby rendering continents the main source of alkalinity which is eventually stored in carbonates. It took the re-examination of Sr isotopes in marine carbonates through time (Flament et al., 2008) to promote the idea that the divergence of marine ⁸⁷Sr/⁸⁶Sr from the mantle evo-

lution curve at 2.7-2.4 Ga is not so much a marker of crustal growth as of onset of massive continental weathering. Calcium carbonates were much less abundant in the Archean than today (Cameron and Baumann, 1972; Engel et al., 1974; Grotzinger, 1989; Lowe, 1980; Ronov, 1968), and whatever carbonate did form as stromatolites and other microbialites was restricted to continental shelves (Buick et al., 1998; Grotzinger, 1989; Lowe, 1980) and lakes (Flannery et al., 2016). Precipitation of carbonates in lakes and on continental shelves is controlled by the input of alkalinity and phosphorus. It is unlikely that ancient carbonates have been lost as compelling reasons for why they would have been selectively removed from the sedimentary record are missing.

The chemistry of ancient oceans is a topic that has been addressed repeatedly in the literature (Coogan et al., 2019; Grotzinger and Kasting, 1993; Holland, 1984; Lyons et al., 2014; Morse and Mackenzie, 1998; Walker et al., 1983) with rather diverging conclusions. Seawater composition is controlled by elemental sources and sinks, while the pace of elemental throughput is via adsorption on particles and biological activity. The main sources are continental runoff and hydrothermal vents, while the main sinks are sediments. Other sources and sinks are submarine volcanic exhalations and hydrothermal alteration of the oceanic crust by percolating seawater, the latter of which acts as both a source and a sink while the former is solely a source.

In principle, because runoff intensity and water-rock interaction at the bottom of the ocean may have varied through time, the $\delta^{18}\text{O}$ record of marine carbonates and silica should help us interpret changes in the water cycle associated with evolving chemical fluxes. This record shows both scatter and trends and has been receiving conflicting interpretations in the literature. To some authors, the signal is significant and is used to trace the history of land emergence and hydrothermal water fluxes (Bindeman et al., 2018; Jaffrés et al., 2007; Johnson

and Wing, 2020). To others, carbonate diagenesis is ubiquitous, both at the bottom of the sea and on land, with severe effects on both conventional and clumped isotopes (Derry, 2010; Edgar et al., 2015; Leutert et al., 2019). Unless the minimum assumption of no correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is verified, ancient carbonates should always be considered diagenetically altered at best and metamorphic in most cases. In addition, most Archean carbonates are platform sediments (Grotzinger, 1989; Kamber and Webb, 2001; Klein and Beukes, 1989) and enrichment of surface water in ^{18}O due to evaporation (Craig et al., 1963; Kim and Lee, 2011) is another serious limitation to robust interpretations.

The present work addresses the dynamic regime of the pre-GOE ocean and its associated geochemical cycles. Emphasis will be placed on the effect that continent rise above sea level has on oceanic circulation, seawater and atmosphere chemistry, nutrient availability, and sediment composition. The role of methane and carbon dioxide in defining the composition of the ocean and the atmosphere further will be re-evaluated, leading to a revised representation of the Archean ocean-atmosphere system and a new understanding of the GOE.

2. The controls on ocean chemistry

For the sake of illustrating the discussion, a simplified model of the pre-GOE ocean electrolyte chemistry is depicted in Figure 1.

Figure 1. A simple box-model representation of the pre-GOE ocean. Runoff is a first-order input (left), chemical sediments (carbonates and oxyhydroxides) a first-order output (right). Interaction between seawater and the oceanic crust at high (mid-ocean ridge crests) and low (mid-ocean ridge flanks and marine volcanoes) temperature combines outputs of seawater and inputs of hydrothermal fluids. This model can be evaluated for the modern ocean using the numbers in

Table 1.

Seawater chemistry is controlled by (i) the runoff and, therefore, the atmospheric P_{CO_2} and the extent of subaerial continental expanses; (ii) hydrothermal activity associated with mid-ocean ridges, which today produce about $3.0\text{--}3.5 \text{ km}^2 \text{ a}^{-1}$ of new oceanic crust (Becker et al., 2009; Sclater et al., 1981) and account for 95% of volcanic activity; (iii) off-axis, low-temperature alteration; and (iv) chemical sedimentation (carbonates, and before the GOE, banded iron formations, or BIF). Item (i) is an input to the ocean, (iv) an output, while (ii)

and (iii) combine the output of unfractionated seawater into the oceanic crust with the input of hydrothermal solutions. The mass balance equation for element i in seawater reads

$$M_{SW} \frac{dC_{sw}^i}{dt} = \Phi_{riv} C_{riv}^i - \Phi_{ch} C_{ch}^i + \Phi_{HT} (C_{HT}^i - C_{sw}^i) + \Phi_{LT} (C_{LT}^i - C_{sw}^i) \quad (1)$$

where C^i stands for the concentration of element i in seawater (sw), rivers (riv), chemical sediments (ch), high-temperature vents (HT), and low-temperature fluids (LT). Φ stands for mass fluxes. Time is noted t and M_{sw} is the mass of the ocean. The residence time τ_i of element i is given by

$$\tau_i = \frac{M_{SW}}{\Phi_H + \Phi_{ch} D_{ch}^i} \quad (2)$$

where $\Phi_H = \Phi_{HT} + \Phi_{LT}$ and D_{ch}^i is the fractionation coefficient of element i between chemical sediments and seawater. At steady state:

$$C_{sw}^i = C_{HT}^i + f_{LT} (C_{LT}^i - C_{HT}^i) + \frac{\Phi_{riv}}{\Phi_H} C_{riv}^i - \frac{\Phi_{ch}}{\Phi_H} C_{ch}^i \quad (3)$$

in which f_{LT} is the fraction of hydrothermal solutions emitted at low temperature. From a long-term geological perspective, we will focus on the main parameters controlling the steady-state concentrations. We recognize in this equation the riverine and hydrothermal inputs on the one hand and the outputs on the other hand (seawater feeding the hydrothermal systems and chemical sediments).

This simple model can to some extent be tested on modern seawater. Estimates exist for the fluxes of some major elements (Table 1). However, given the modern climatic fluctuations, it is difficult to assess whether these values are representative of long-term fluxes for time scales in excess of the major element residence times, (~ 10 Ma). We therefore allowed for uncertainty by introducing correction factors to some of the fluxes.

	f_{LT}	Φ_H	Φ_{riv}	Φ_{ch}		
	0.4	$1.00 \cdot 10^{14}$	$3.73 \cdot 10^{16}$	$4.0 \cdot 10^{12}$		
factor	1	1	1.094	0.3945		
gat/kg	C_{HT}^i	C_{LT}^i	C_{riv}^i	C_{ch}^i	C_{sw}^i calc	C_{sw}^i meas
Alk	0	0	0.001	25.7	0.0023	0.0024
Ca ²⁺	0.0156	0.0102	0.00038	10	0.01	0.01
Mg ²⁺	0	0	0.00014	2.9	0.01	0.01
Na ⁺	0.432	0.336	0.00026	0	0.5	0.48
Sr ²⁺	$8.10 \cdot 10^{-5}$	$9.70 \cdot 10^{-5}$	$8.90 \cdot 10^{-7}$	$2.29 \cdot 10^{-2}$	$9.0 \cdot 10^{-5}$	$8.60 \cdot 10^{-5}$
K ⁺	0.0232	0.00625	$3.25 \cdot 10^{-5}$	0	0.0297	0.0104
Rb ⁺	$2.80 \cdot 10^{-5}$	$1.07 \cdot 10^{-6}$	0	0	$1.72 \cdot 10^{-5}$	$1.30 \cdot 10^{-6}$
Li ⁺	$8.91 \cdot 10^{-4}$	$7.30 \cdot 10^{-5}$	0	0	$5.64 \cdot 10^{-4}$	$2.60 \cdot 10^{-5}$

Table 1. Upper panel: fraction f_{LT} of the low-temperature hydrothermal fraction of off-axis hydrothermal fluids and mass fluxes Φ . The value $f_{LT} = 0.4$ is consistent with Hasenclever et al.'s (2014) estimate. The modern runoff value of $3.73 \cdot 10^{16} \text{ kg a}^{-1}$ was taken from (Wu et al., 2016). The flux of Ca carbonates of $4.0 \cdot 10^{12} \text{ kg a}^{-1}$ was taken from (Mackenzie and Morse, 1992) and the adopted calcite/dolomite molar ratio of 3.5 is consistent with Milliman's (1993) estimates. A Φ_H value of $1.0 \cdot 10^{14} \text{ kg a}^{-1}$ (total hydrothermal water flux) is consistent with Hasenclever et al.'s (2014) estimate for 40,000 km of fast-spreading ridges similar to the East Pacific Rise and with Palmer and Edmond's (1989) estimate from Sr isotopes. Lower panel, inputs (first three columns): concentrations of high- and low-temperature hydrothermal solutions. The 21°N site on the East Pacific Rise (Von Damm, 1990b) is representative of the high-temperature component because its Cl content indicates little liquid-vapor separation. Likewise, fluids from hole 504B, ODP leg 137 extrapolated at Mg=0 (Magenheim et al., 1995) can be chosen as the low-temperature end-member. Lower panel, outputs: runoff values from Berner and Berner (2012) and sedimentary carbonate composi-

tion (ch) from Mackenzie and Morse (1992). The last two columns compare the calculated and measured seawater compositions.

The conservative, non-redox Na, Ca, Mg, and Sr concentrations calculated for seawater are consistent with the observed values to within a few percent on the condition that the carbonate flux is reduced by a factor of ~ 3 (see Table 1). This solution is not unique and a range of alternative solutions can be obtained by changing the values of Φ_{riv} and Φ_{ch} . Modelled seawater K, Rb, and Li concentrations are significantly too high, which signals that these elements are lost via their adsorption on clay minerals, a process not captured by the model. The overall agreement between predictions and observations, however, suggests that this simple model also provides an acceptable framework for the Archean ocean and shows that the modern seawater composition can be accounted for by a simple combination of realistic inputs and outputs. Of course, the solution is still underdetermined because fluxes, and the interval over which they apply, are not constrained with a high degree of certainty.

2.1. The rise of continents and the changing runoff

Arndt (1999) first pointed out that many Archean and Proterozoic greenstone belts contain volcanic rocks that erupted subaqueously. Subaerial stretches of land are known from Pilbara, Australia (Buick et al., 1995), 3.4 Gy ago and from Kaapvaal, South Africa (Eriksson et al., 2006), 3.25 Gy ago, while eolianites (Simpson et al., 2012) make a strong case for a continental environment. Very low sedimentation rates observed for mudstones around Archean greenstone belts (Kamber and Tomlinson, 2019; Thurston et al., 2008) confirm that only a small fraction of volcanic edifices was standing above sea level and prone to weathering. Additional evidence in favor of reduced continental expanses in the Archean was discussed

by Flament et al. (2008), who argued that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the carbonate record tracks the surface area of emerged land submitted to chemical erosion. The $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater and of carbonates precipitated from the ocean reflects the balance between hydrothermal and riverine inputs. $^{87}\text{Sr}/^{86}\text{Sr}$ of the high-temperature hydrothermal fluids is $\sim 0.703\text{--}0.704$ (Albarède et al., 1981), unambiguously reflecting interaction of the fluids with the low-Rb/Sr upper mantle. The modern riverine input has $^{87}\text{Sr}/^{86}\text{Sr}$ of ~ 0.711 (Palmer and Edmond, 1989), which equally unambiguously reflects the high Rb/Sr ratio and the old mean age of the crust. Veizer and Compston (1976) observed that the $^{87}\text{Sr}/^{86}\text{Sr}$ record of marine carbonates began diverging from mantle values in the early Proterozoic, while Kamber and Webb (2001) argued that the divergence took place at about 2.5 Ga. Flament et al. (2008) used geophysical modeling to predict that the pre-GOE world had less than 10% of its surface exposed to subaerial erosion.

Figure 2. The evolution of phosphorus concentrations in ~ 8000 samples of marine sediments from the geological record (Reinhard et al., 2017). The red circles represent the average of the data binned by 100 My slices. The blue shaded area is the 1σ confidence interval. The white dotted line is an exponential fit to the average values. Phosphorus rises continuously

by, on average, 34% per Gy. The GOE (~2.4 Ga) does not seem to be associated with a sharp increase of phosphorus and therefore does not mark a sudden rise of continents above sea level.

The sedimentary phosphorus record also attests to reduced land surface in the Archean. Phosphorus is an essential bio-limiting element present in adenosine-triphosphate, phospholipids, and nucleic acids. The exogenous P cycle will be addressed in a subsequent section but it is well established that the only significant phosphorus input to the ocean is runoff, whereas both mid-ocean ridges, ridge flanks, and sediments, except when organic-rich, act as sinks (Baturin, 2003; Rittenberg, 1993; Wheat et al., 2003). Campbell and Allen (2008) suggested that periods of supercontinent formation coincided with enhanced flux of this element to the ocean. What is measured in sediments today entered the ocean in three forms: dissolved, clastic, and reactive (absorbed on FeMn-hydroxides). Prior to the GOE, the latter can be minimized because Fe(II) was soluble. Soluble P residence time (=oceanic load/output) in the modern ocean is short (20 to 100 kyr (Paytan and McLaughlin, 2007)). Biological recycling and diagenesis would affect P residence time in the pre-GOE ocean, but not the long-term P sedimentary output.

Phosphorus concentration in mudstones expresses the ratio between chemical and mechanical erosion. As such, the P abundance in mudstones can be used to infer continental surface area. The reliability of P contents of mudstones rests on two conservative assertions: (1) what goes around comes around, and hence, after a few residence times, sediments must reflect whatever is removed from continents, *regardless of the ocean composition*; and (2) subduction zones remove sediments in bulk, not selectively. Phosphorus abundance in mudstones is to some extent affected by local productivity. It should also vary with the ratio between coarse detrital sediments and mudstones, which probably accounts for some of the dispersion in Reinhard et

al.'s (2017) compilation. The sheer number of samples in this database ensures, however, that the mean values cannot be too far off. Phosphorites (apatite), which did not become a significant contributor to the P sedimentary budget before the Neo-Proterozoic (Cook et al., 2005), are not a major source of uncertainty. Likewise, aluminum phosphate interspersed in diagenetic or metamorphic quartzites is not known before the GOE (Morteani et al., 2007). Remarkably, the super-events of continental assembly (Campbell and Allen, 2008) do not show up as peaks in Reinhard et al.'s (2017) compilation (Figure 2), suggesting that the ratio of chemical to mechanical erosion during these events is not strongly influenced by plate tectonics.

Even though some authors have previously emphasized the contrast in P contents between Archean and modern sediments (Bjerrum and Canfield, 2002; Reinhard et al., 2017), re-evaluation of Reinhard et al.'s (2017) mudstone database including a log-normal distribution and its statistical dispersion (Figure 2) shows a steady, continuous rise through time of the P sedimentary output right through and unaffected by the GOE, an observation that is most simply interpreted to reflect a continuous increase of riverine fluxes with age T (Ga) following the relation

$$P(\text{wt}\%) = 0.0024 \times 10^{-0.3(\pm 0.1)T} \quad (4)$$

Since input must balance output there is no 'hidden source' of P in the ocean and, hence, low-P sediments in the past dictates that the surface area of emerged continents in the Archean and Paleoproterozoic be smaller than today. Given that continents represent 30% of Earth's surface today, it can be inferred that they were covering only ~ 7% of Earth's surface at the time of the GOE, which is consistent with the quantitative prediction by Flament et al. (2008).

2.2. Chemical sedimentation

A first output channel is the sedimentation of CaMg-carbonates, which regulates the alkalinity of the modern ocean. The striking scarcity of marine carbonates in the Archean geological record with respect to its Proterozoic and Phanerozoic counterparts, first identified decades ago (Pettijohn, 1943), was reviewed 40 years ago (e.g., (Lowe, 1980) and references therein). Until rather recently, the consensus held that carbonates, notably calcium carbonates, were inconspicuous in the Archean rock record and, consequently, were considered a trace component found largely at major breaks within volcanic sequences (Lowe, 1980). Even the most spectacular carbonate sections in the Archean sedimentary record remain relatively thin, e.g. the Wittenoom dolomites (Jahn and Simonson, 1995), the Dresser ankerite and the Strelley Pool Chert dolomite from Pilbara, Australia (Van Kranendonk et al., 2003), and calcite from the Campbellrand-Malmani sequence of the 2.5 Ga old Kaapvaal Craton, South Africa (Kamber and Webb, 2001; Sumner, 1997). The assumption that carbonates were less well preserved than other rock types as a result of their deposition as supracrustal rocks is immaterial to this conclusion, simply because whatever carbonate was dissolved must have been quickly re-precipitated at sea. Alkalinity is conservative and Archean Ca fluxes to the ocean, therefore, must have been smaller than at later times.

A second output channel is represented by Fe- and Mn-oxides and oxihydroxides, which form a complex family of minerals (Lemire et al., 2013; Majzlan et al., 2004). Two distinct types of reactions affect Fe compounds: hydrolysis and redox transformations. In the modern ocean, typical chemical sediments are FeMn-nodules and encrustations, in which Fe is in the Fe(III) form. In the pre-GOE world, magnetite (Fe_3O_4), which dominates BIF sediments, is often considered diagenetic, and ferrihydrite ($\text{FeO}(\text{OH})$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is a probable precursor (Konhauser et al., 2017). Regardless of magnetite's status with respect to diagenesis, au-

thors have stressed both the prevalence of this mineral in Archaean BIF and the delicacy of the microstructures it preserves (Li et al., 2017).

2.3. The mid-ocean ridge hydrothermal systems

The temperature range of hydrothermal venting along mid-ocean ridges and back-arcs, at typically 360-420°C, is a result of water thermal expansion and compressibility rising sharply near the critical point (Bischoff and Rosenbauer, 1985; Coogan et al., 2019) and, hence, the effect of water depth should be secondary. The same argument applies to most submarine volcanic activity, such as greenstone belts. Above this temperature range, hydrothermal fluids separate into a low-chlorinity solution and a brine (Von Damm et al., 2003). At a given temperature, the element concentrations and the pH of hydrothermal solutions at mid-ocean ridges are tightly controlled by a series of buffer reactions, typically those of the greenschist facies, informally reading as $[M^{n+}]/[H^+]^n = \text{Const.}$ (where M stands for any metal). For basaltic lithologies, the dominant minerals are albite, epidote, chlorite, and actinolite $\pm$ paragonite (Bowers and Taylor, 1985). Examples of such reactions are (with the buffered element in parenthesis):

2.4. Low-temperature marine sources and sinks

This issue has been addressed repeatedly for the modern oceanic crust but only with moderate success. Low-temperature processes (subaerial weathering and alteration of the oceanic crust at temperatures $\leq 100^\circ\text{C}$) cannot be handled within the same simplified framework for a number of reasons. In this environment, the primary control of boiling temperature is water

depth (Bischoff and Rosenbauer, 1985). Many phases, notably paragonite (Stroncik and Schmincke, 2002) are composite of different alteration products. Typically, clay minerals and zeolites formed by off-axis, low-temperature alteration of the oceanic crust should react with each other, but the clay minerals are rarely pure enough to act as buffers and form mixed-layer phases and complex solid solutions. Equilibrium is also hindered by the low temperature, and thermodynamic properties are difficult to validate (e.g., (Blanc et al., 2015; Ransom and Helgeson, 1994). Evidence of alkali element uptake by the upper basaltic section is not consistent with the expected proton uptake at low temperature. Data on drill holes such as at the ODP 504B site shows, instead, that their abundance in the upper crust results from the overprint of alteration phases over a wide range of temperatures (Alt et al., 1996) giving rise to an ambiguous metamorphic rock record. For Mg and Ca, even the direction of change is problematic (Paul et al., 2006)}. One observation stands out: alteration of the oceanic crust at low temperatures is a significant sink for seawater carbonates (Alt and Teagle, 1999). Since low-temperature alteration of the oceanic crust leads to Na replacing Ca, and Si replacing Al, silicification, albitization, and carbonatization proceed hand-in-hand. For many elements, borehole fluid data (e.g., (Magenheim et al., 1995; Wheat et al., 2003) are probably more relevant to water-rock exchange at low temperatures than data on the rocks themselves. Overall, in contrast to the rather clean evidence from high-temperature hydrothermal vents at mid-ocean ridges, how much low-temperature alteration contributes to the ocean budget is still unclear.

3. Equilibria in Archean seawater

This section considers the balance of protons, electrons, and alkalinity together with the cycles of selected elements critical to Archean seawater. The two most important factors are: (1) because of the lack of oxygen in the pre-GOE atmosphere, SO_4^{2-} and NO_3^- , which dominate the redox chemistry of modern seawater, were essentially absent, and iron was overwhelm-

ingly in its Fe^{2+} form; and (2) despite recent attempts (Marty et al., 2018), the $[\text{Cl}^-]$ content of ancient oceans remains poorly known.

3.1. The charge balance

The alkalinity concept is central to our understanding of the evolution of the ocean/atmosphere system because, contrary to any other parameter of the carbonate system (pH, P_{CO_2} , $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$) and dissolved inorganic carbon or DIC aka ΣCO_2 , it is conservative upon exchange with the atmosphere. In addition, the record of chemical sediments (i.e. carbonates and oxides), provides a record of the oceanic sinks of alkalinity. As today, juvenile alkalinity (about 50% of the total (Gaillardet et al., 1999)) is produced upon weathering of silicates by CO_2 -rich meteoric water (Garrels and Mackenzie, 1971), while recycled alkalinity corresponds to the weathering of sedimentary carbonates. Both are eventually unloaded from the ocean as carbonate sediments.

A core factor of geochemical cycles is that in essentially all the natural fluids but rain, the abundance of $[\text{H}^+]$ is small with respect to those of major cations. Consequently, relatively minor transfers of electrolytes from the rock to the fluid, notably the most abundant Na and Cl, causes very large changes in pH.

In modern seawater, the charge deficit of anions (Cl^- , SO_4^{2-}) relative to cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) is mostly compensated by HCO_3^- and CO_3^{2-} . Ignoring borates, the present-day carbonate alkalinity

$$\text{Alk} \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \approx [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \quad (9)$$

is a small quantity of the order of $2 \times 10^{-3} \text{ meq L}^{-1}$, to be compared with 546 meq L^{-1} of Cl^- (Figure 3).

Figure 3. Charge balance (alkalinity) in modern seawater compared to what it might have been in the Archean world with only a small proportion of emerged continents. Concentrations for Archean seawater are only tentative and are shown for the sake of illustration: lower chlorinity, high Fe contents, lack of Mg because of a much reduced runoff. With much-reduced runoff, Mg^{2+} and Ca^{2+} are far less concentrated, while SO_4^{2-} is reduced and removed as iron sulfide. Phosphate (too dilute to be shown) is extremely low.

In pre-GOE times, the charge balance of the ocean must have been quite different. The seawater concentrations of Mg^{2+} , which is removed quantitatively at ridge crests (Edmond et al., 1979b), would have been reduced in proportion to the area of emerged continental expanses, while under low P_{O_2} conditions, SO_4^{2-} and NO_3^- were negligible. Accordingly, an approximate charge-balance condition of the Archean ocean is

$$[Na^+] + [K^+] + 2[Ca^{2+}] + 2[Fe^{2+}] \approx [Cl^-] + Alk \quad (10)$$

By virtue of the simple relationship $\frac{1}{2} Alk < DIC < Alk$, alkalinity strictly brackets the amount of CO_2 that can be dissolved in the ocean. Since maximum fluid eruption temperature is essentially determined at mid-ocean ridges by water thermal expansion and compressibility (Bischoff and Rosenbauer, 1985), alkalinity and, more generally, the composition of hydrothermal fluids are largely controlled by their chlorinity.

The carbonate content of Archean meteoric water and, therefore, weathering intensity are unknown. However, a high- CH_4/CO_2 atmosphere (Haqq-Misra et al., 2008; Thibon et al., 2019; Zahnle et al., 2019) does not support strong alkalinity transport in the runoff. Moreover, at the time of the GOE, little alkalinity had been stored as sedimentary carbonates. From this follows that alkalinity in the runoff was restricted to the fraction corresponding to silicate weathering (juvenile alkalinity). Finally, the extent of emerged land was small, which should have further reduced the flow of alkalinity to the ocean. It is thus surmised that seawater alkalinity was quite low, much lower than today.

3.2. The proton balance and the chlorine question

A weaker drainage of ancient continents must have been equivalent to a reduced neutralizing capacity of the fluids emitted by high-temperature vents at mid-ocean ridges. In a landmark paper written in the wake of the discovery of the Galapagos hydrothermal vents, Edmond et al. (1979a) reformulated the then classic description of weathering processes. ‘Reverse weathering’ (Sillén, 1961) assumes that cations produced upon continental weathering are reprecipitated in the ocean as authigenic clay, a process that replenishes seawater with the protons lost on continental surfaces. Edmond et al. (1979a) demonstrated, however, that although runoff is depleted in protons by weathering, seawater is ‘back-titrated’ at high temperatures at mid-ocean ridges, where protons are produced in abundance, rather than by the for-

mation of authigenic clay (Isson and Planavsky, 2018) which, even on the seafloor, cannot be regarded as a significant proton source (Wheat et al., 2004).

Alteration of albite to paragonite mica in the greenschist facies is a good example:

A critical element of explanation is that any rock-water reaction at temperature T similar to this reaction is ruled by the van t'Hoff's equation

$$\frac{d \ln K}{d T} = \frac{\Delta H_r}{RT^2} \quad (12)$$

This equation, which relates the equilibrium constant K of the reaction, its enthalpy change ΔH_r , and the gas constant R , indicates that, at silica saturation, the ratio $[\text{Na}^+]/[\text{H}^+]$ of the above equation quickly decreases with temperature. Figure 4 plots $[\text{M}^{n+}]/[\text{H}^+]^n$ derived from Arnorsson et al.'s (1983) equations in order to account for Icelandic geothermal fluids between 50 and 300°C. For instance, the 300°C value is consistent with the $[\text{Na}^+]$ concentration (300-500 mM kg⁻¹) and the pH reported for several hydrothermal vent fields of the global mid-ocean ridge system (German and Von Damm, 2006; Von Damm, 1990a). As indicated above, changes in equilibrium constants are dominated by changes in $[\text{H}^+]$.

Figure 4. Effect of temperature on $[M^{n+}]/[H^+]^n$ ratios in hydrothermal fluids. Increased acidity of the fluids at high temperature overwhelms the effect of temperature on equilibrium constants. Equations established on Iceland geothermal fields and taken from Arnorsson et al. (1983). These equations incorporate the effect of ionic strength. Water-rock temperature interaction (weathering) at low temperatures is a proton sink in contrast to high-temperature processes which produce low-pH solutions.

An additional proton source is the inorganic oxidation of Fe^{2+} to Fe^{3+} , regardless of the reaction involved. Braterman et al. (1983; 1984) pointed out that dissolved Fe^{2+} , partially hydrolyzed as $Fe(OH)^+$, absorbs UV radiation in the 200–400 nm range and forms $FeO(OH)$:

Likewise, Thibon et al. (2019) observed that CO_2 is reduced to CH_4 by dissolved Fe^{2+} according to the magnetite-forming reaction:

The ferrihydrite- Fe^{2+} equilibrium has the same effect:

Consequences of the charge balance on electrolyte concentration can be simply described using Shikazono's (1978) equations. The water/rock reactions listed above, or alternative equivalent reactions, can all be written in the form of $[M^{n+}]/[H^+]^n = K_M(T)$, where M stands for any metal and K for equilibrium constants. For the sake of simplicity, activity coefficients and complexation constants have been ignored. The charge balance can be written at the first order as

$$K_{Na}[H^+] + K_K[H^+] + 2K_{Mg}[H^+]^2 + 2K_{Fe}[H^+]^2 + 2K_{Ca}[H^+]^2 + \dots = Alk + [Cl^-] \approx [Cl^-] \quad (16)$$

which shows that $[H^+]$ in hydrothermal solutions is controlled by temperature through the reaction constants, and by $[Cl^-]$. Once these two parameters are set, this equation may be solved for $[H^+]$, and then for $[Mg^{2+}]$, $[Fe^{2+}]$, $[Ca^{2+}]$, and $[Na^+]$, using the appropriate thermodynamic data or equations such as those derived from Icelandic hydrothermal systems (Arnórsson et al., 1983). For set eruption temperature and chlorinity, greenschist facies mineral assemblages actually buffer the composition of hydrothermal vent solutions through geologic time. The compositions calculated for hydrothermal fluids (Bowers and Taylor, 1985; Michard, 1982) compare reasonably well with those measured on the samples collected on the East Pacific Rise. Although the fluxes associated with the loss of seawater into the mid-ocean ridge depends on how well seawater composition is known, the hydrothermal inputs are unlikely to have substantially changed through time under the effect of parameters other than seawater chlorinity.

An important outcome of Eqn.6 is the relationship:

$$d \log [M^{n+}] = n d \log [Cl^-] \quad (17)$$

where $n = 1$ for $[H^+]$, $[Na^+]$, and $[K^+]$, and $n = 2$ for $[Mg^{2+}]$, $[Ca^{2+}]$, and $[Fe^{2+}]$, etc (Shikazono, 1978). In other words, $[Cl^-]$ variations strongly affect the relative abundances of heterovalent cations. In addition to the standard Na/K geothermometer, the $[Fe^{2+}]/[K^+]$ ratio may be a good temperature diagnostic. Arnórsson et al. (1983) show that, on the condition of no brine separation, heterovalent ratios such as $[Na]^2/[Mg]$ and $[Al]^2/[Mg]$ may be good proxies of the chlorinity of hydrothermal fluids and therefore of seawater (Arnórsson et al., 1983) (Figure 5). How these chlorinity proxies are imprinted on the metamorphic rock record is at this stage the major stumbling block.

Figure 5. Effect of chlorine on the composition of solutions calculated from Arnorsson et

al.'s (1983) equations. Units in mol L⁻¹ (M). This plot illustrates the potential of using hydro-
thermal fluid reconstructions and ratios of heterovalent cations to infer the chlorinity of an-
cient seawater.

3.3. The electron balance

Ever since the GOE, H₂O and O₂ have been the dominant redox couple of the
ocean/atmosphere system. Not so, however, on the early Earth devoid of oxygen. The geo-
chemical, pedological, and sedimentological features used to document the low level of oxy-
gen in the pre-GOE atmosphere are multiple and often consistent (see (Lyons et al., 2014) for
a review), but the strongest evidence so far supporting lack of ozone and therefore low O₂
levels in the Archean atmosphere comes from the photolytic fractionation of sulfur isotopes
(Farquhar et al., 2000). In the absence of O₂, the existence of large amounts of ferric iron
precipitated from Fe²⁺-rich seawater requires the availability of abundant electron acceptors
and the options are few.

One solution to this issue is the coupling of iron oxidation with biological activity (Holland,
1973):

The very low abundance of P in BIF, however, argues against BIF precipitation being fueled
by biological activity (Klein and Beukes, 1989; Thibon et al., 2019).

A second solution is the photolytic oxidation of Fe²⁺ mentioned above. However, as noted
before (Braterman et al., 1983; Braterman et al., 1984; Konhauser et al., 2007) and regardless
of the fate of hydrogen gas, iron photolysis quickly brings the pH of seawater down to values
at which the reaction direction is reverted and photooxidation stops. An additional difficulty
is that this reaction only takes place in the uppermost layers of the ocean. Ferrous iron must,

therefore, be replenished by deep water rising to the surface, a mechanism unlikely to be efficient.

These problems led Thibon et al. (2019) to suggest that the electron liberated by oxidation of seawater Fe^{2+} is used to reduce HCO_3^- , and eventually atmospheric CO_2 , to methane. Under such conditions, the CH_4/CO_2 ratio of the atmosphere is buffered by dissolved Fe^{2+} and coexisting Fe^{3+} -bearing sedimentary minerals (Figure 6), magnetite or any other oxyhydroxide. The coefficients of this equation show that, at the interface between the atmosphere and seawater buffered by magnetite, the CH_4/CO_2 ratio is extremely sensitive to both $[\text{Fe}^{2+}]$ and pH. The CH_4/CO_2 ratio of the atmosphere in equilibrium with magnetite and Fe^{2+} increases with increasing pH and $[\text{Fe}^{2+}]$. Zahnle et al. (2019) show that 5000 ppmv CH_4 or more in the atmosphere provide an adequate source of H^+ capable of ionizing Xe and force its escape, thereby accounting for the remarkable isotopic fractionation of this heavy rare gas. An equimolar $\text{CH}_4\text{—CO}_2$ atmosphere (Haqq-Misra et al., 2008) requires pH of 5.6, 6.6, and 7.6 for $[\text{Fe}^{2+}] = 10^{-2}$, 10^{-4} , and 10^{-6} M, respectively (Figure 6).

Figure 6. The CH_4/CO_2 ratio of the atmosphere in equilibrium with magnetite and Fe^{2+} for different oceanic values of Fe^{2+} and pH. Red lines represent constant $[\text{Fe}^{2+}]$ values and blue lines constant pH values.

The outcome is essentially unchanged if hematite (Fe_2O_3) or ferrihydrite or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ are preferred to magnetite, i.e. the conditions for an equimolar $\text{CH}_4\text{—CO}_2$ atmosphere are not drastically different from those required for magnetite. Using thermodynamic data at 25°C (Anderson, 2005; Lemire et al., 2013), the following relationships are obtained:

$$\text{pH} = 6.0 - \frac{1}{2} \log[\text{Fe}^{2+}] \quad (19)$$

for magnetite, and

$$\text{pH} = 5.7 - \frac{1}{2} \log[\text{Fe}^{2+}] \quad (20)$$

for ferrihydrite. These equations compare well with that of greenalite saturation at $\log [\text{SiO}_2] = -2.760$ (see Fig. 12 in Tosca et al. (2016)):

$$\text{pH} = 5.5 - \frac{1}{2} \log[\text{Fe}^{2+}] \quad (21)$$

Seawater with a pH of ~ 7 can easily host Fe^{2+} at the millimolar concentration levels proposed by Thibon et al. (2019). The reason why equations 19-21 are so similar is that the ratio $[\text{Fe}^{2+}]/[\text{H}^+]^2$ only depends on temperature regardless of the nature of the primary mineral precipitating out of seawater to form the BIF precursors.

4. Implications for some of the pre-GOE geochemical cycles

Pre-GOE carbonates are scarce and have undergone diagenetic and metamorphic processes, often to a severe extent (see above). Given the lack of sulfate in the contemporaneous seawater, the $^{87}\text{Sr}/^{86}\text{Sr}$ record by pre-GOE samples of barite, a mineral often perceived as an alternative marker of the marine environment (e.g., (Satkoski et al., 2017), is more ambiguous than the record of sedimentary carbonates. The timing of the divergence of the marine Sr

isotope record from the mantle evolution curve is therefore still an open question. Nevertheless, Derry and Jacobsen (1988) suggested that Sr isotopes in chemical sediments are best explained by a higher hydrothermal to river water flux ratio during the Early Proterozoic. Likewise, rare-earth elements and Sr isotopes in 2.52 Ga old Campbellrand carbonates were interpreted by a weaker continental erosion flux with respect to hydrothermal fluxes than today (Kamber and Webb, 2001).

4.1. Chlorine

Seawater composition clearly changes with the evolving composition of the atmosphere and with growing continental expanses. It also responds to changing concentrations of chlorine (Coogan et al., 2019), an element that has so far largely eluded extensive observation and well-constrained modeling (Eggenkamp, 2014; Holland, 1984). An original estimate of the chlorinity of Archean seawater was proposed by Marty et al. (2018) as an end-member of the correlation between $\text{Cl}/^{36}\text{Ar}$ and $\text{K}/^{36}\text{Ar}$ in fluids extracted from a single inclusion in quartz. These fluids share many geochemical characteristics with Red Sea brines (Schmidt et al., 2015). The Cl/K ratio of the most diluted sample (~54) is indistinguishable from the ratio in modern seawater. The error bar due to uncertainties on equilibration temperature is, however, no better than a factor of two for $[\text{Cl}^-]$, which translates into a fourfold uncertainty on $[\text{Mg}^{2+}]$, $[\text{Ca}^{2+}]$, and $[\text{Fe}^{2+}]$. More worrisome is the observation that these fluid inclusions contain fair amounts of unsupported ^{40}Ar . As suggested by the authors, ^{40}Ar excess may have been introduced from the country rocks. A minimum value of the low-salinity component $^{40}\text{Ar}/^{36}\text{Ar}$ can be inferred from the intercept of the $^{40}\text{Ar}/^{36}\text{Ar}$ vs $\text{K}/^{36}\text{Ar}$ array. The alignment is good ($r^2=0.99$) but the intercept is far too high ($^{40}\text{Ar}/^{36}\text{Ar} > 2800$) for original equilibration of this component with the atmosphere. The approach is nevertheless very promising, and provided this problem can be tackled with appropriate geochemical and mineralogical tools, the unknown that is ancient seawater chlorinity may be within reach.

4.2. Protons

The oceanic inputs correspond to the high-temperature fluids of mid-ocean ridge hydrothermal systems and other volcanic sources and the precipitation of magnetite or ferrihydrite in BIF, whereas the main output is accounted for by the low-temperature alteration on the flanks of mid-ocean ridges. Low-temperature exchange between seawater and the oceanic crust is poorly constrained simply because reliable proxies are rare. Most pre-GOE samples were profoundly altered at different times and the complex overprinting of weathering, diagenesis, alteration, and metamorphism is difficult to disentangle. A robust statement emerges, however, from the previous discussion: $[\text{Cl}^-]$ is the gatekeeper of charge balance and equilibrium constants at high temperatures favor preferential release of protons and increase $[\text{H}^+]$ by orders of magnitude in fluids relative to the increase of any other cations. On the input side, the runoff was smaller in pre-GOE times than today due to scant land surfaces and low atmospheric P_{CO_2} and therefore had a proportionately smaller neutralizing capacity. The seawater pH must, therefore, have been lower than today and the chlorinity higher. The effect is particularly severe since, from equation 17, a decrease of one unit of pH in high-temperature hydrothermal fluids requires a $[\text{Cl}^-]$ increase by a factor of 10.

4.3. Electrons

Precipitation of Fe^{3+} -bearing minerals (ferrihydrite and magnetite) liberates electrons that must be removed either by producing organic material (Holland, 1973) or by the reduction of volcanic CO_2 into CH_4 , thus liberating more protons (equations 13-15). Fe^{2+} solubility in seawater increases with decreasing pH.

4.4. Iron

Contrary to the modern ocean in which ferric iron is insoluble and seawater is devoid of iron, Fe^{2+} was massively transferred from the low-temperature sites of water-rock interaction to

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12 580 the high-temperature hydrothermal vent fluids at ridge crests and injected into the ocean. In-
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jection of hydrothermal fluids into the ocean was suggested on a global scale by Derry and
Jacobsen (1988) and the record of mixing events demonstrated through the rare-earth element
patterns of late Archean Campbellrand carbonates (Kamber and Webb, 2001). Iron is re-
moved, after partial oxidation, by BIF precipitation and, to a lesser extent, traps runoff car-
bonate as siderite and ankerite on continental shelves.

4.5. Sodium and potassium

The higher $[\text{Na}^+]/[\text{H}^+]$ and $[\text{K}^+]/[\text{H}^+]$ ratios of hydrothermal fluids at low temperature relative to high-temperature fluids essentially reflect their higher pH and not necessarily a net loss of alkali elements. High-temperature hydrothermal vents from mid-ocean ridges add excess K^+ to the ocean (Edmond et al., 1979b) which, in accordance with mineralogical observations, is removed by low-temperature alteration (Alt et al., 1996; German and Von Damm, 2006; Magenheimer et al., 1995). Because the Na-K substitution is isovalent, the Na/K ratio is expected to be dominated by its dependence on temperature. This is illustrated by the broad acceptance of Na-K thermometry of hydrothermal solutions (Fournier and Truesdell, 1973; Giggenbach, 1988). Sodium itself in hydrothermal fluids has not received much attention, presumably because of its very long residence time in seawater (Broecker and Peng, 1982). Today, Na^+ is slightly depleted in both low- and high-temperature hydrothermal fluids with respect to seawater (Elderfield and Schultz, 1996; German and Von Damm, 2006; Von Damm, 1990a), a deficit compensated for by runoff. In an ancient world with little subaerial expanses, the Na cycle would be out of balance, which may indicate that the metamorphic assemblage reacting with hydrothermal fluids could be very different from its modern equivalent or that a diagenetic input may have been overlooked. Ancient seawater may have had less Na and more divalent Ca and Fe.

4.6. Magnesium and calcium

A recent discussion of the global modern cycle of these elements can be found in Higgins and Schrag(2015). From the perspective taken here, the fluxes of double-charged elements between high- and low-temperature hydrothermal systems should be larger than for single-charged elements. Magnesium is the most intriguing of all the major elements, since it is efficiently removed from seawater at temperatures in excess of 50°C and does not seem to have any obvious major source other than runoff. In hydrothermal vents, the Ca-Mg substitution is

also isovalent. The Ca/Mg ratio is more scattered than the Na/K ratio (Fournier and Truesdell, 1973; Giggenbach, 1988), most likely as a result of carbonatization and the production of clay minerals. A minor source may be submarine felsic intra-oceanic arc volcanics (de Ronde et al., 2019), which have been shown to have lost most of their Mg, but the scarcity of these rocks and their rather low initial Mg abundance is unlikely to make them a strong oceanic source. Because of smaller continental inputs, Archean seawater must have been more depleted in Mg than its modern equivalent. Magnesium in sediments may be an alternative measure of the surface of continents above sea level. Likewise, high-temperature hydrothermal alteration adds Ca^{2+} excess to the ocean. This excess is removed in part by low-temperature hydrothermal reactions, in part by carbonate precipitation on continental shelves. High chlorinity favors low pH and high Ca/Na ratios (Figure 5) in hydrothermal fluids, which may help resolve the imbalance of the sodium cycle.

4.7. Phosphorus

Phosphorus is taken up by both hydrothermal vents from mid-ocean ridges and low-temperature alteration of the oceanic crust. Alt et al. (1996) find no measurable downcore variation of P_2O_5 in DSDP Hole 504B. Gernon et al. (2016) argue that palagonitization of volcanic glass leads to release of phosphorus into seawater, but Kruber et al.'s data (2008) on the most immobile elements in glasses from the Mohs Ridge and associated palagonite clearly show that this assessment is incorrect. The $\text{P}_2\text{O}_5/\text{TiO}_2$, $\text{P}_2\text{O}_5/\text{MnO}$, $\text{P}_2\text{O}_5/\text{Y}$, $\text{P}_2\text{O}_5/\text{REE}$, and $\text{P}_2\text{O}_5/\text{Th}$ in paragonite are 150, 34, 30, 60, and 12% higher, respectively, than in glass. This requires P gain, not loss, during glass palagonitization.

4.8. Alkalinity

High-temperature hydrothermal fluids bring zero to negative alkalinity to the modern ocean (Von Damm, 1990a), while acidity fluxes from low-temperature upper ocean crust alteration

do not balance riverine fluxes of alkalinity (Spivack and Staudigel, 1994). To a large extent, alkalinity fluctuations therefore reflect the effect of weathering and the surface area of continental surfaces. pH and seawater alkalinity control atmospheric P_{CO_2} through one of the standard equations of the carbonate system (Broecker and Peng, 1982; Zeebe and Wolf-Gladrow, 2001):

$$P_{\text{CO}_2} = \frac{Alk}{K_1 k_{\text{CO}_2}} \times \frac{[\text{H}^+]^2}{[\text{H}^+] + 2K_2} \quad (22)$$

in which K_1 and K_2 are the dissociation constants of carbonic acid, and k_{CO_2} the CO_2 solubility constant in seawater. For ancient seawater, the two conditions used by Halevy and Bachan (2017) who assumed both a significant atmospheric P_{CO_2} and carbonate saturation to infer the evolution of seawater pH through geological times over-constrain the system. The pre-GOE continental input of alkalinity must have been small compared to its modern equivalent, while mid-ocean ridges released abundant protons. In agreement with conclusions from the Fe^{2+} /magnetite equilibrium, seawater alkalinity must have been small or even negative. The pre-GOE alkalinity balance not only explains, but requires the scarcity of carbonates in the pre-GOE geological record, which is consistent with the rather small fluxes of detrital material represented by mudstones. Morse and Mackenzie (1998) concluded, however, that the alkalinity of the Archean ocean was higher than in the Phanerozoic. Their conclusion was based on a high atmospheric P_{CO_2} , on the assumption that the surface of the ocean was saturated in carbonates, on assumed high seawater $[\text{Na}^+]$ and $[\text{Cl}^-]$, and unlimited P availability.

Until the GOE, BIF were the main sedimentary sink of oceanic cations. To a large extent, the removal of Fe added by high-temperature vents through BIF precipitation, plus conversion of CO_2 to CH_4 , played during the Archean the role that carbonates play in the modern world for removing excess positive charges and therefore for controlling altogether the alkalinity of Archean seawater.

5. Conclusions

The main points arrived at in this work can be summarized as follows:

1. Dissolved chlorine is the gatekeeper of pre-GOE charge balance in seawater. Several indices point to seawater $[\text{Cl}^-]$ being higher and the pH lower in the Archean than today but evidence is still tenuous.
2. Prior to GOE, BIF were the main sedimentary sink of seawater cations, a role played in the modern ocean by carbonate sedimentation.
3. The chemistry of pre-GOE seawater differs from modern seawater by the presence of soluble Fe^{2+} , which may have permitted the reduction of HCO_3^- to methane.
4. The very low P contents of BIF is inconsistent with a control of iron oxidation by biological activity.
5. The timing of the rise of continents above sea level indicated by the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ record depends on which genetic significance is assigned to pre-GOE barite in a sulfate-free ocean.
6. The low P contents of ancient sediments and the Sr isotope record of carbonates indicate that Archean subaerial expanses occupied about 7% of the Earth's surface prior to the GOE, i.e. about 20% of their modern equivalent. The reliability of these estimates would benefit from better understanding of P distribution among sedimentary sinks and diagenetic and metamorphic overprinting. Smaller subaerial exposures imply that the proton sinks and alkalinity sources of weathering were much weaker than today. As a consequence, seawater had a lower pH and therefore less carbonate and less alkalinity.
7. The Na and Mg cycles in the pre-GOE ocean seem to have been out of balance and require the identification of missing inputs.

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8. Seawater iron concentration is controlled by its $[\text{Fe}^{2+}]/[\text{H}^+]^2$ ratio, temperature, and chlorinity. Lower pH rendered Fe^{2+} more soluble than in the modern ocean. Buffering of seawater $[\text{Fe}^{2+}]$ by ferrihydrite, magnetite, or greenalite from Fe^{2+} -rich seawater is consistent with methane being a major component of the ancient terrestrial atmosphere. This new reaction pathway for the formation of Paleoproterozoic BIF helps resolve the problem of the formation of Archean BIF, which cannot be attributed to extensive O_2 production by biological activity. Seawater Fe^{2+} and BIF played the same role as Ca^{2+} and CaCO_3 in the modern ocean.

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Figure captions

Figure 1. A simple box-model representation of the pre-GOE ocean. Runoff is a first-order input (left), chemical sediments (carbonates and oxyhydroxides) a first-order output (right). Interaction between seawater and the oceanic crust at high (mid-ocean ridge crests) and low (mid-ocean ridge flanks and marine volcanoes) temperature combines outputs of seawater and inputs of hydrothermal fluids. This model can be evaluated for the modern ocean using the numbers in Table 1.

Figure 2. The evolution of phosphorus concentrations in ~8000 samples of marine sediments from the geological record (Reinhard et al., 2017). The red circles represent the average of the data binned by 100 My slices. The blue shaded area is the 1 σ confidence interval. The white dotted line is an exponential fit to the average values. Phosphorus rises continuously by, on average, 34% per Gy. The GOE (~2.4 Ga) does not seem to be associated with a sharp increase of phosphorus and therefore does not mark a sudden rise of continents above sea level.

Figure 3. Charge balance (alkalinity) in modern seawater compared to what it might have been in the Archean world with only a small proportion of emerged continents. Concentrations for Archean seawater are tentative and are shown for the sake of illustration: lower chlorinity, high Fe contents, lack of Mg because of a much reduced runoff. With much-reduced runoff, Mg^{2+} and Ca^{2+} are far less concentrated, while SO_4^{2-} is reduced and removed as iron sulfide. Phosphate (too dilute to be shown) is extremely low.

Figure 4. Effect of temperature on $[\text{M}^{n+}]/[\text{H}^+]^n$ ratios in hydrothermal fluids. Increased acidity of the fluids at high temperature overwhelms the effect of temperature on equilibrium constants. Equations established on Iceland geothermal fields and taken from Arnorsson et al. (1983). These equations incorporate the effect of ionic strength. Water-rock temper-

ature interaction (weathering) at low temperatures is a proton sink in contrast to high-temperature processes which produce low-pH solutions.

Figure 5. Effect of chlorine on the composition of solutions calculated from Arnorsson et al.'s (1983) equations. Units in mol L⁻¹ (M). This plot illustrates the potential of using hydrothermal fluid reconstructions and ratios of heterovalent cations to infer the chlorinity of ancient seawater.

Figure 6. The CH₄/CO₂ ratio of the atmosphere in equilibrium with magnetite and Fe²⁺ for different oceanic values of Fe²⁺ and pH. Red lines represent constant [Fe²⁺] values and blue lines constant pH values.

Table captions

Table 1. Upper panel: fraction f_{LT} of the low-temperature hydrothermal fraction of off-axis hydrothermal fluids and mass fluxes Φ . The value $f_{LT} = 0.4$ is consistent with Hasenclever et al.'s (2014) estimate. The modern runoff value of $3.73 \cdot 10^{16} \text{ kg a}^{-1}$ was taken from (Wu et al., 2016). The flux of Ca carbonates of $4.0 \cdot 10^{12} \text{ kg a}^{-1}$ was taken from (Mackenzie and Morse, 1992) and the adopted calcite/dolomite molar ratio of 3.5 is consistent with Milliman's (1993) estimates. A Φ_H value of $1.0 \cdot 10^{14} \text{ kg a}^{-1}$ (total hydrothermal water flux) is consistent with Hasenclever et al.'s (2014) estimate for 40,000 km of fast-spreading ridges similar to the East Pacific Rise and with Palmer and Edmond's (1989) estimate from Sr isotopes. Lower panel, inputs (first three columns): concentrations of high- and low-temperature hydrothermal solutions. The 21°N site on the East Pacific Rise (Von Damm, 1990b) is representative of the high-temperature component because its Cl content indicates little liquid-vapor separation. Likewise, fluids from hole 504B, ODP leg 137 extrapolated at Mg=0 (Magenheim et al., 1995) can be chosen as the low-temperature end-member. Lower panel, outputs: runoff values from Berner and Berner (2012) and sedimentary carbonate composition (ch) from

Mackenzie and Morse (1992). The last two columns compare the calculated and measured seawater compositions.

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Figure 1

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Table 1.

	f_{LT}	Φ_H	Φ_{riv}	Φ_{ch}		
factor	0.4	$1.00 \cdot 10^{14}$	$3.73 \cdot 10^{16}$	$4.0 \cdot 10^{12}$		
	1	1	1.094	0.3945		
gat/kg	C_{HT}^i	C_{LT}^i	C_{riv}^i	C_{ch}^i	C_{sw}^i calc	C_{sw}^i meas
Alk	0	0	0.001	25.7	0.0023	0.0024
Ca ²⁺	0.0156	0.0102	0.00038	10	0.011	0.01
Mg ²⁺	0	0	0.00014	2.9	0.011	0.01
Na ⁺	0.432	0.336	0.00026	0	0.5	0.48
Sr ²⁺	$8.10 \cdot 10^{-5}$	$9.70 \cdot 10^{-5}$	$8.90 \cdot 10^{-7}$	$2.29 \cdot 10^{-2}$	$8.99 \cdot 10^{-5}$	$8.60 \cdot 10^{-5}$
K ⁺	0.0232	0.00625	$3.25 \cdot 10^{-5}$	0	0.0297	0.0104
Rb ⁺	$2.80 \cdot 10^{-5}$	$1.07 \cdot 10^{-6}$	0	0	$1.72 \cdot 10^{-5}$	$1.30 \cdot 10^{-6}$
Li ⁺	$8.91 \cdot 10^{-4}$	$7.30 \cdot 10^{-5}$	0	0	$5.64 \cdot 10^{-4}$	$2.60 \cdot 10^{-5}$

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: