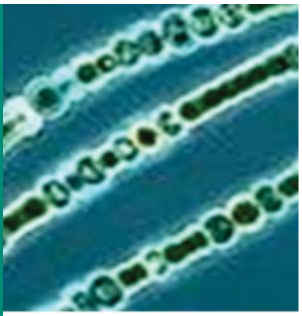
The Great Oxidation Event and Mineral Diversification



The evolution of oxygenic photosynthesis by cyanobacteria led to a dramatic rise of atmospheric oxygen at ~2.4 Ga.

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1811-5209/10/0006-0031$2.50 DOI: 10.2113/gselements.6.1.31

Before the Great Oxidation Event (GOE), at ~2.4 Ga, the mineralogical record of the near-surface continental environment indicates a low partial pressure of oxygen during weathering, which restricted many elements to a low oxidation state and limited the number of possible minerals formed from these elements. Calculations show that local pulses in the production of O_2 by photosynthesis could mobilize some metals (e.g. Mo and Re, but not U), but this O_2 would be completely consumed. After the GOE, many elements could occur in one or more oxidized forms in minerals in the near-surface environment. This development resulted in an explosive growth in the diversification of minerals.

Keywords: Archean, oxidation, weathering, Great Oxidation Event

THE RISE OF OXYGEN

The stretch of time between about 3.0 and 2.0 billion years before the present (Ga) is one of the most remarkable periods in Earth history. The sedimentary geologic record for this time contains rocks such as the great banded iron formations of Western Australia and the huge conglomerate-hosted gold and uranium deposits of the Witwatersrand, South Africa. These formations have long been recognized as indicating that near-surface atmospheric, continental, and marine conditions were very different from those of the present day. In recent years, detailed isotope studies have focused on the period of time referred to as the Great Oxidation Event (Holland 2006). It began at 2.45 Ga, the last time that the sulfur isotope record shows evidence of large mass-independent fractionation, and it probably continued until about 2.0 Ga, based on major excursions in the carbon isotope record of marine carbonates. During this time, an irreversible increase in the oxygen content of the near-surface atmosphere and the continental and marine environments occurred (Holland 2009; Sessions et al. 2009).

The mineralogical expression of the Great Oxidation Event (GOE) is the theme of this article. Studies of the mineralogical record of the near-surface continental environment before the GOE indicate severe environmental limitations on the diversity of minerals. The very low partial pressure of oxygen in the atmosphere typically restricted elements with possible multiple oxidation states to a single, low oxidation state, which in turn limited the number of possible minerals of such elements. In contrast, after the GOE and achievement of significant partial pressures of O_2 in the atmosphere, a vast array of new minerals became possible. Essentially any element with more than one possible oxidation state could then be present in one or more oxidized forms in minerals in the near-surface environment. This development resulted in an explosive growth in the diversification of minerals (Hazen et al. 2008).

THE MINERALOGICAL RECORD BEFORE THE GREAT OXIDATION EVENT

Evidence from Detrital Minerals

Minerals such as siderite ($FeCO_3$), uraninite (UO_2), and pyrite (FeS_2) alter rapidly on laboratory and geologic timescales in the present-day, near-surface environment containing abundant O_2. The Fe, U, and S in these minerals are all oxidizable under these conditions. However, several detailed studies have documented that these minerals occur as detrital phases in ancient, fluviatile, sedimentary rocks formed from sediments transported long distances in well-aerated waters before the GOE. After the GOE this did not happen. These observations, reviewed below, can be interpreted to place severe restrictions on the oxidation state of the weathering environment, and in turn on the evolution of the diversity of minerals before the GOE.

As an example, petrographic and sedimentological studies of three sets of sandstones from the Pilbara region in Western Australia, deposited between 3.250 and 2.715 Ga, have documented the occurrence of abundant detrital siderite in the heavy mineral fraction of one sandstone formation, minor detrital uraninite in two formations, and abundant pyrite in the heavy mineral fractions of all three formations (Rasmussen and Buick 1999). These minerals were transported and deposited by turbulent, well-aerated, braided river systems. Notably, none of these sandstones have been subject to hydrothermal mineralization. Detrital siderite in Archean sedimentary rocks has also been reported from the 3.2 Ga Moodies Group in the Barberton greenstone belt, South Africa (Hessler et al. 2004).

A second example involves the long-studied Witwatersrand conglomerates, which, although fluviatile in origin, have been affected by metamorphism and hydrothermal activity. Despite the long-standing controversy over the relative importance of detrital sedimentary versus hydrothermal processes in the origin of the uraninite, pyrite, and gold in these deposits, substantial evidence supports a modified placer origin (Frimmel 2005). Textural, isotopic, and compositional characteristics of the uraninite, pyrite, and gold in the deposits point to deposition as detrital grains

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in the host sediments. The strongest evidence includes (1) the rounded shape of the particles (Fig. 1), (2) ages greater than those of the host rock as indicated by isotopic dating, and, (3) for the rounded uraninite grains, a great variation in the Th/U ratio, consistent with derivation from a variety of sedimentary provinces, and a much higher Th content than would be expected from hydrothermal alteration (Hazen et al. 2009). Furthermore, the Witwatersrand sediments have been subject to intense weathering, whereas detrital uraninite grains in the modern Indus River are part of a system that has not been subject to intense chemical weathering (Maynard et al. 1991). Additional examples of Archean placer uraninite and pyrite deposits similar to those of the Witwatersrand but with only minor amounts of gold are widespread (Frimmel 2005). In contrast, the Proterozoic (2.1 Ga) gold deposits of the Tarkwaian System of Ghana, although hosted by quartz-pebble conglomerates similar to those in the Witwatersrand, contain detrital hematite and magnetite associated with the gold instead of pyrite (or siderite), with no uraninite reported (Frimmel 2005).

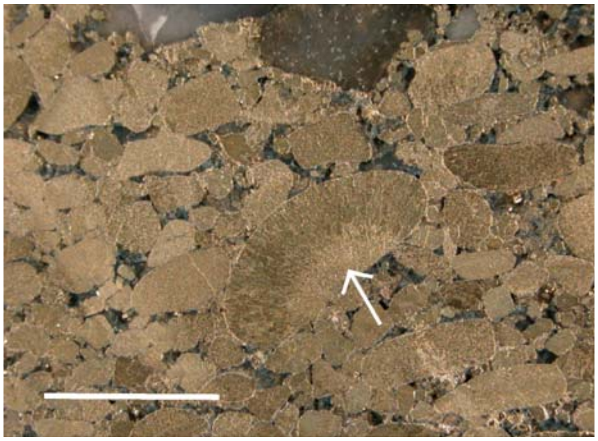

Figure 1 Coarse sedimentary rocks from the Witwatersrand contain rounded, detrital clasts of pyrite. The truncated, well-rounded, oolitic pyrite (arrow) is consistent with a near-surface oxygen fugacity of $<10^{-60}$ bars. Scale bar = 0.5 cm.
From Frimmel (2005), reprinted with permission from Elsevier

The above examples provide strong evidence that, during the Archean, siderite, uraninite, and pyrite underwent prolonged transport as detrital minerals in aqueous near-surface continental environments, which we have every reason to believe were in contact with the Archean atmosphere. The characteristics of these transport and depositional processes suggest that kinetic inhibition of oxidation is not the reason for the survival of these minerals. Siderite reacts quickly on a laboratory timescale (Berner 1981). Uraninite oxidation may proceed rapidly, particularly if a surface layer of altered uraninite is formed (De Pablo et al. 1999), and pyrite weathers rapidly in the presence of oxygen (Anbar et al. 2007). Instead, it seems more likely that the survival of siderite, uraninite, and pyrite in the near-surface Archean environment was due to a lack of a thermodynamic driving force for their destruction. In other words, the combined atmospheric and aqueous-solution chemical conditions during weathering were such that these minerals were stable.

Implications for the Archean Atmosphere

The conditions required for a lack of a thermodynamic driving force for the oxidation of pyrite and siderite are shown in Figure 2. The relative stabilities of these minerals depend on the partial pressures (fugacities) of O_2, S_2, and CO_2 gases. Preserving siderite from oxidation or sulfidation requires values of log f_{O_2} (i.e. the logarithm of the oxygen fugacity) less than about –73 to –60 at 25°C and 1 bar, depending on the partial pressure of CO_2 (Fig. 2). Aqueous solutions that will not oxidize either siderite or pyrite require similar, low values of log f_{O_2}.

The above conditions are also consistent with the preservation of uraninite from oxidation in either rainwater-like or river water–like aqueous solutions (Fig. 3). Depending on the pH of the solutions, uraninite (containing U^{4+}) could oxidize to aqueous UO_2^{2+}, soddyite, or uranophane (all containing U^{6+}) over a range of log f_{O_2} values, but a maximum of about –44 is indicated (Fig. 3). This value would be higher if the uraninite were impure, but lower if aqueous complexes of UO_2^{2+} were considered or if the concentration of aqueous Ca^{2+} or SiO_2 were higher than in Figure 3b.

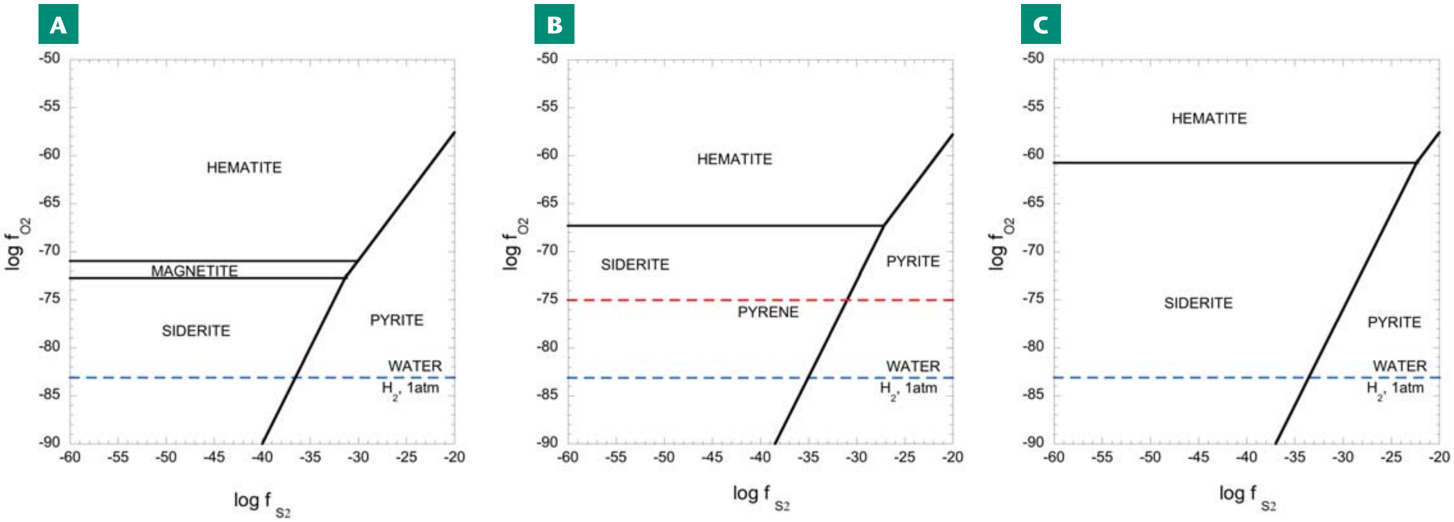

Figure 2 Stabilities of minerals in the Fe–S–C–O system at 25°C and 1 bar as functions of the logarithms of the fugacities of the gaseous species O_2 and S_2 where the logarithm of the fugacity (in bars) of CO_2 is fixed at (**A**) –3.0, (**B**) –1.5, and (**C**) 0.0, respectively, to cover a range of values consistent with suggestions in the literature for the period 2.0 to 3.0 Ga (Hessler et al. 2004). The solid lines separate fields of mineral stability labeled with the name of the stable mineral. The dashed line labeled "pyrene" represents the upper stability limit of this polyaromatic hydrocarbon. The dashed line labeled "water" represents the lower stability limit of liquid water relative to 1 atm of H_2 gas.

Values of log f_{O_2} less than about –73 to –60 (at 25°C and 1 bar) in the near-surface Archean environment have long been suggested in the geochemical literature (Garrels et al. 1973; Krupp et al. 1994; Frimmel 2005). Although seemingly low, these values are consistent with upper limits deduced from atmospheric models (Kasting 1993; Catling and Claire 2005), paleosols (Rye and Holland 1998), and models inferred from sulfur isotope data (Pavlov and Kasting 2002). However, atmospheric models have also suggested a lower limit of P_{O_2} equal to about 10^{-15} bars (Kasting and Walker 1981). This lower limit may be applicable to the lower atmosphere right down to the boundary with an aqueous phase such as seawater, below which it could be 10^{-63} bars (Kasting and Walker 1981). We assume that the aqueous weathering environment on the continents during the Archean can be represented similarly.

The quantitative chemical implications of weathering conditions on land in the Archean have not been sufficiently explored. Specifically, what role do reactions with minerals in multicomponent systems play? Reducing conditions are presumably influenced by the supply of reductants, such as H_2 and CO from volcanic sources (Catling and Claire 2005), although these must have reacted with exposed rocks via aqueous solutions during weathering processes. In addition, after the rise of oxygenic photosynthesis, there would probably have been a period of time during which weathering and atmospheric reductants competed with the O_2 released by photosynthesis. The implications of these processes are explored below through model calculations that simultaneously consider weathering, volcanic gases, and O_2 released by photosynthesis.

WEATHERING IN THE ARCHEAN ATMOSPHERE

Weathering Reactions

How rainwater from an Archean atmosphere reacted with volcanic gases and continental crust is of interest from at least three standpoints: the types of minerals that may have resulted, the evolution of water chemistry, and the oxidation state of the near-surface environment. Insight into the chemical complexities of such processes can be obtained from models of the irreversible chemical mass transfer associated with the reactions (Helgeson 1979). An example is shown in Figure 4. In these calculations, the minerals enstatite, ferrosilite, diopside, anorthite, albite, and magnetite provide an approximation to a basaltic crustal composition. Excess amounts of these minerals are permitted to react irreversibly with model rainwater with a starting composition similar to that of the present day (Berner and Berner 1996), except that it has initial values of log f_{O_2} = –70 and log f_{CO_2} = –1.5 (cf. Fig. 2). Simultaneously, the rainwater is reacted with a mixture of H_2, H_2S, SO_2, CO_2, and CO, representing the composition of volcanic gases, based on discussions in the literature (Zolotov and Shock 2000; Catling and Claire 2005). The reactions produce a Na–Mg–Ca–HCO_3 water and minerals such as pyrite, kaolinite, chalcedony, siderite, calcite, and lizardite (Fig. 4a, b; lizardite is not expected to form during weathering but is included here as a proxy for a more complex Fe–Mg–Al-type clay mineral for which we do not have an adequate thermodynamic characterization). The iron dissolved during weathering reaches a maximum molar value of about $10^{-4.3}$, or 3 ppm, when siderite begins to precipitate. Thus, as anticipated by Garrels et al. (1973), depending on the extent of reaction, significant quantities of Fe^{2+} could be produced during weathering and possibly transported in Archean rivers to the oceans.

The full reaction path can be followed as a function of log f_{O_2} and pH in Figure 4c. Of interest here is that the changes in log f_{O_2} are small. The oxidation state of the system stays roughly constant (about ±2 units of log f_{O_2}). The pH, however, evolves towards more alkaline conditions depending on the extent of reaction. In practice, for real flow-through systems, the extents of reaction are probably limited, perhaps less than about log ξ = –2. For limited extents of reaction, the aqueous-solution chemistry is near to both the H_2S–SO_4^{2-} and the NH_4^+–N_2 lines of equal activity (Fig. 4c). Therefore aqueous solutions during Archean weathering could have significant amounts of either the reduced or oxidized S and N species when the log f_{O_2} values are around –70.

Overall, the weathering reactions shown in Figure 4 indicate that the Archean near-surface weathering environment during reactions involving rainwater, volcanic gases, and basaltic rocks does not result in significant changes in oxidation state. Nor are minerals other than kaolinite,

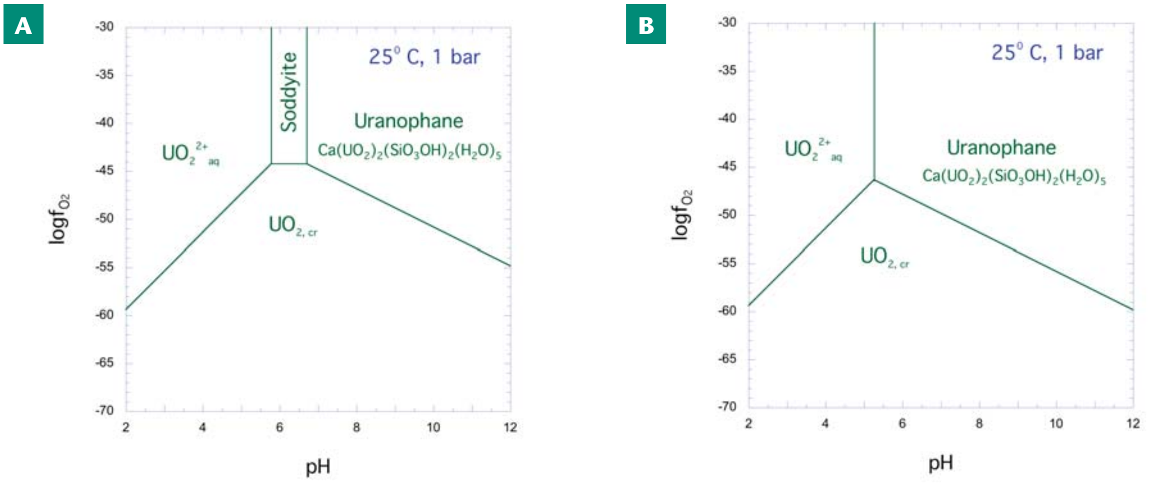

Figure 3 Stability of uraninite ($UO_{2,\,cr}$) relative to uranyl minerals and aqueous UO_2^{2+} as a function of the logarithm of the fugacity of O_2 gas and the pH of the aqueous phase (from Hazen et al. 2009). The solid lines correspond to the boundaries for equilibrium between two minerals or between a mineral and an aqueous species, with the activities (i.e. effective concentrations) specified as follows: (**A**) low concentrations of Ca and silica: $a_{Ca^{2+}} = 10^{-4}$, $a_{SiO_{2,aq}} = 10^{-6}$, $a_{UO_2^{2+}} = 10^{-6}$; (**B**) high concentrations of Ca and silica: $a_{Ca^{2+}} = 10^{-3}$, $a_{SiO_{2,aq}} = 10^{-4}$, $a_{UO_2^{2+}} = 10^{-6}$.

pyrite, and silica, and minor amounts of siderite (depending on the extent of weathering) to be expected. This situation could presumably have prevailed for a prolonged period, until perturbed by the rise of oxygenic photosynthesis.

Effects of Oxygenic Photosynthesis

Much discussion in the literature has focused on the apparent gap in time between the beginning of oxygenic photosynthesis and the development of an oxygenated atmosphere, a gap that may be several hundred million years or much longer (Holland 2006; Knoll and Beukes 2009). A possible explanation for this gap is that the O_2 steadily produced by photosynthesis was consumed entirely by a sufficiently reducing near-surface environment (e.g. Catling and Claire 2005 and others). This scenario has not been tested quantitatively in a way that includes weathering processes. Anbar et al. (2007) recently suggested that widespread oxidative weathering by O_2 started at about 2.5 Ga, based on anomalous spikes in the Mo and Re concentrations in marine shales of that age. These scenarios can be investigated by expanding the scope of the reaction path calculations on weathering described above to include input of O_2 gas as a reactant. In the model, O_2 can be added steadily, along with the other reactants, to simulate gradual oxygenic photosynthesis, or rapidly, to simulate a pulse representing localized oxygenic photosynthesis.

The steady addition of 10^{-3} moles of O_2 per kilogram of rainwater corresponds to a reaction path that reaches a maximum log f_{O_2} of only –66 (Fig. 5a). Mineralogically, this value corresponds to the production of less pyrite and siderite than mentioned in Figure 4. Consequently, a steady production of O_2 by photosynthesis could indeed be completely consumed by weathering in the near-surface environment. In contrast, a pulse of the same amount of O_2 added much more rapidly relative to the rates of reaction of the rainwater with the volcanic gases and basaltic rock results in a rapid excursion in log f_{O_2} that reaches values as high as about –60 (Fig. 5b). The reaction path shown crosses the boundary for oxidation of MoS_2 and reaches the boundary for oxidation of ReS_2. It stops short of the boundary for oxidizing uraninite. Such a pulse could indeed mobilize Mo and Re, but not U, during weathering. Mo and Re could then be transported to the oceans as the soluble oxyanions MoO_4^{2-} and ReO_4^- and reduced again and precipitated in marine shales. Mineralogically, even less pyrite and siderite and a small amount of hematite (about 10^{-3} moles) are produced. However, the maximum log f_{O_2} reached is still so low that O_2 does not accumulate in the atmosphere.

The above calculations strongly suggest that production of O_2 by oxygenic photosynthesis could proceed steadily in the near-surface environment without any accumulation of O_2 in the atmosphere. In the shallow marine environment, a pulse of O_2 could have resulted in a "rain" of ferric hydroxide precipitates, contributing to the formation of banded iron formations. On the continents, a pulse in the production of O_2 could mobilize Mo and Re during weathering without mobilizing U, but not contribute any measurable O_2 to the atmosphere. Neither scenario would necessarily lead to the introduction into the geologic record of any significant amount of oxidized minerals of metals other than Fe. That diversification had to wait until oxygenic photosynthesis completely dominated reductants released to the near-surface environment from biological and nonbiological sources. It is assumed here that such a domination had been achieved by 2.0 Ga.

THE EXPLOSION OF MINERALOGICAL DIVERSITY AFTER 2.0 Ga

As soon as molecular O_2 started to accumulate in the atmosphere and reached 1% of the present atmospheric level, weathering reactions proceeded very much like they do today. Fe and U in particular oxidized readily. In the near-surface environment in contact with such levels of O_2, siderite and pyrite oxidized to iron oxides. Trendall and coworkers estimated that "90 percent of the tonnage of all known iron formations was probably deposited between ca. 1.9 and 2.6 Ga" (Holland 2005). These great banded iron formations could represent the removal of dissolved Fe^{2+} from the shallow marine environment in response to oxidation of the atmosphere. From the standpoint of the diversification of minerals, however, iron oxides were not new, just hugely abundant compared to other times in Earth history. The main change for iron minerals after the GOE was the cessation of deposition of detrital siderite and pyrite and the end of riverine transport of Fe^{2+} to the oceans.

In contrast, uranium presents a dramatically different picture. Deposition of detrital uraninite ceased after the GOE, but the oxidation of uraninite exposed at the surface of the Earth in an O_2-bearing atmosphere resulted over time in the appearance of approximately 200 uranyl minerals that were unlikely to have existed prior to the GOE (Hazen et al. 2009). These colorful minerals include hydrous uranyl oxides and silicates, such as soddyite, weeksite, curite, sklodowskite, and uranophane. Uraninite alteration also commonly leads to the complex mixed-phase material "gummite," a fine-grained mixture of soddyite, curite, kasolite, uranophane, boltwoodite, and clarkeite. Oxidized uranium can also precipitate as the uranium carbonate rutherfordine and a large suite of uranyl phosphate minerals, such as autunite and saléeite (Fig. 6).

Even the amount of uraninite exposed at Earth's surface for weathering was probably greatly increased by the development of an oxygenated atmosphere. Prior to the GOE, uraninite (rich in Th) was formed in magmatic environments and was then exposed at the surface after uplift and erosion. After the GOE, major hydrothermal U deposits, such as the unconformity-type deposits of northern Australia (1.6 Ga) and western Canada (1.8 Ga) formed, and when these were exposed by uplift and erosion the full variety of secondary and tertiary uranium minerals could develop. The unconformity-type deposits were formed from shallow, hydrothermal circulation systems in Earth's crust involving fluids with unusually high log f_{O_2} values. These physicochemical conditions were probably achieved through the interaction of the hydrothermal fluids with sulfate-bearing evaporites, which were not present in any significant abundance in the geologic record until after the GOE (Komninou and Sverjensky 1995).

Thus, just for one chemical element, U, a huge increase in the number and variety of minerals occurred after the GOE. Similar considerations must also apply to other elements with multiple oxidation states, such as Cu, which occurs in 321 oxide and silicate minerals (Hazen et al. 2008), and the elements B, V, Mn, Se, Te, As, Sb, Bi, Ag, and Hg. Finally, a host of biologically mediated minerals proliferated in association with the development of microbial life (Dove 2010 this issue).

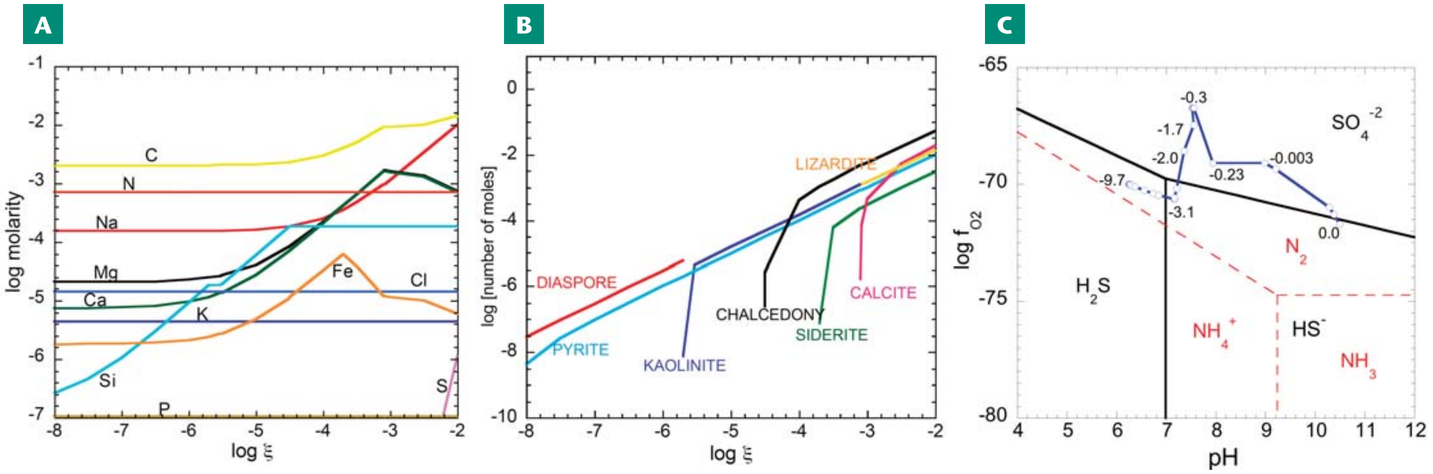

FIGURE 4 Weathering model in which Archean rainwater reacts with basaltic minerals and volcanic gases. In (**A**) and (**B**) the logarithms of the number of moles of total dissolved elements and minerals produced per kilogram of water (respectively) are plotted as a function of the extent of reaction progress represented by the logarithm of ξ (equal to the number of moles of silicate minerals destroyed per kilogram of water). In (**C**), the computed reaction path is illustrated by the blue line marked with values of log ξ, as a function of the logarithm of the fugacity of O_2 and pH.

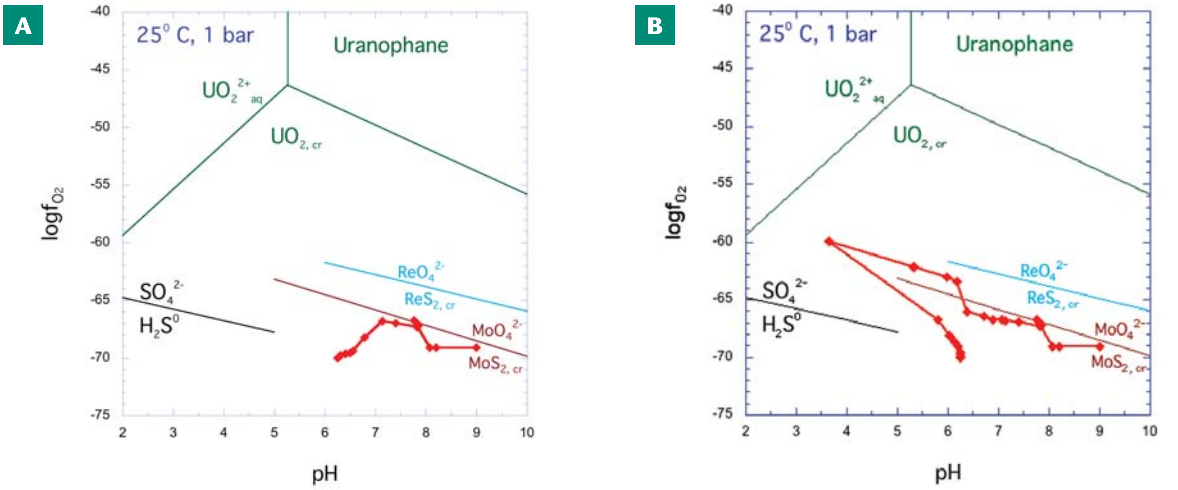

FIGURE 5 Weathering models in which Archean rainwater reacts with basaltic minerals, volcanic gases, and O_2 from photosynthesis. The solid lines without dots represent equilibrium boundaries between minerals and aqueous species as functions of the logarithm of fO_2 and pH, and are consistent with activities of dissolved Ca, silica, and uranyl cation given by $a_{Ca^{2+}} = 10^{-3}$, $a_{SiO_{2,aq}} = 10^{-4}$, and $a_{UO_2^{2+}} = 10^{-6}$, respectively. Reaction paths are shown in red starting at pH = 6 and finishing at pH = 9. (**A**) Reaction path for a steady addition of 0.001 moles of O_2 per kilogram of H_2O. The maximum fO_2 achieved is about 10^{-67} bars, so the reaction path does not cross the boundaries for oxidation of MoS_2, ReS_2, or UO_2. Consequently, no Mo, Re, or U is mobilized. All the O_2 added is destroyed during weathering. (**B**) Reaction path for a pulse of O_2 from localized photosynthesis. The amount added is the same as in A, but the rate of addition is much faster. Note that the reaction path crosses the boundary for oxidation of MoS_2, reaches the corresponding boundary for ReS_2, but does not cross the boundary for oxidation of UO_2. This pulse of O_2 could mobilize Mo and some Re, but not U. Also, no O_2 accumulates in the atmosphere because the maximum fO_2 achieved is only about 10^{-60} bars.

CONCLUDING REMARKS

The mineralogical expression of the Great Oxidation Event is dramatic. Before the GOE, detrital siderite, pyrite, and uraninite were transported and deposited in sedimentary systems that must have been in contact with the Archean atmosphere. Thus there was probably no thermodynamic driving force for the destruction of these minerals. In other words, the combined chemical conditions in the atmosphere and in aqueous solutions were such that these minerals were stable, suggesting values of log f_{O_2} of –60 to –67 at 25°C and 1 bar. These conditions are also consistent with the preservation of uraninite from oxidation in either rainwater-like or river water–like aqueous solutions in the Archean.

Irreversible reaction path models indicate that reaction of such an Archean atmosphere with rainwater, volcanic gases, and basaltic rocks does not result in significant changes in the oxidation state during weathering. Kaolinite, pyrite, silica, and minor amounts of siderite can be expected until perturbed by the rise of oxygenic photosynthesis. Consequently, the Archean environment placed severe environmental limitations on the diversity of minerals. The very low partial pressure of oxygen during weathering restricted elements with possible multiple oxidation states to a single low oxidation state, which in turn limited the number of possible minerals of such elements.

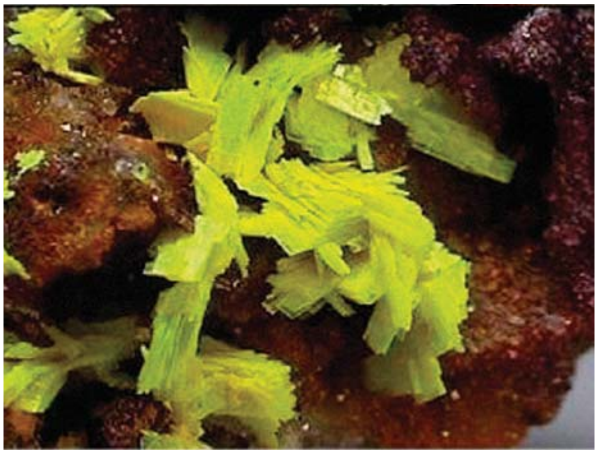

FIGURE 6 Bright yellow saléeite [$Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$] crystals are typical of the dramatic effect of the Great Oxidation Event on uranium mineral diversification. PHOTO COURTESY OF JOHN VEEVAERT, TRINITY MINERAL CO.

Calculations further suggest that even with a low but steady production of O_2 by photosynthesis in the Archean near-surface environment, no O_2 would accumulate in the atmosphere. A local pulse in the production of O_2 could mobilize Mo and Re without mobilizing U, but would not contribute to any measurable O_2 in the atmosphere. Both scenarios would lead to Fe-minerals as the only oxidized minerals in the geologic record. The calculations presented here suggest that the Archean atmosphere could persist until a drastic change in the production of O_2 relative to the available amount of biologic and abiologic reductants.

In contrast, after the GOE and the achievement of a measurable partial pressure of molecular O_2 in the atmosphere, a vast array of new minerals became possible. Essentially any element with more than one possible oxidation state could then be present in one or more oxidized forms in minerals in the near-surface environment. This development resulted in an explosive growth in the diversification of minerals.

ACKNOWLEDGMENTS

The authors are extremely grateful for encouragement from and discussions with R. M. Hazen. We also appreciate discussions with M. W. Claire, H. J. Cleaves, G. D. Cody, R. L. Cohen, S. D. Domagal-Goldman, C. Flynn, M. Fogel, R. J. Hemley, J. J. Hemley, C. M. Jonsson, C. L. Jonsson, B. Myssen, and D. Rumble. We also wish to thank H. Frimmel and J. Veevaert for the pyrite and saléeite figures. Financial support was provided by a joint National Science Foundation–NASA Astrobiology Institute Collaborative Research Grant to the Johns Hopkins University and the Carnegie Institution for Science and by the NASA Astrobiology Institute at the Carnegie Institution for Science.

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