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Volcanic gases, black smokers, and the Great Oxidation Event

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Abstract—This paper proposes that gradual changes in the composition of volatiles that have been added to the atmosphere-ocean system are responsible for the Great Oxidation Event (G.O.E.) ca. 2.3 Ga. Before ca. 2.3 Ga, the composition of these volatiles was probably such that 20% of the carbon gases could be reduced to organic matter and all of the sulfur gases could be reduced to pyrite. Since 2.3 Ga, the composition of these volatiles has been such that 20% of the carbon gases could be reduced to organic matter, but only a fraction of the sulfur gases could be reduced to pyrite. This change led to the oxygenation of the atmosphere and to a large increase in the SO_4^{-2} concentration of seawater. A considerable body of observational data supports these proposals. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The evidence for a major change in the oxidation state of the atmosphere between ca. 2.3 and 2.1 Ga was summarized briefly in 1999 (Holland, 1999). Since then, the discovery of the mass independent fractionation of sulfur, its variation with time in the geologic record (Farquhar et al., 2000), and the confirmation of this finding by Mojzsis et al. (2001), Farquhar et al. (2001a), and Bekker et al. (2002) now make a major change in the oxidation state of the atmosphere during the Paleo-proterozoic a virtual certainty. The appearance of O_2 in the atmosphere ca. 2.3 Ga could be explained easily if cyanobacteria evolved at that time. However, this explanation has been rendered very unlikely by the discovery of biomarkers in 2.7- to 2.8-Ga sedimentary rocks that are characteristic of cyanobacteria (Brocks et al., 1999). An alternative explanation involves a change in the redox state of volcanic gases as the trigger for the change in the oxidation state of the atmosphere. This was proposed by Kasting et al. (1993). They pointed out that the loss of H_2 from the top of a reducing atmosphere would have increased the overall oxidation state of the Earth and almost certainly that of the mantle. This in turn would have led to an increase in the f_{O_2} of volcanic gases and to a change in the redox state of the atmosphere. They proposed that an increase in reduced gas emissions by a factor of ~ 4 would be enough today to preclude the presence of a significant quantity of O_2 in the atmosphere, even if organic carbon was being buried at the same rate as today. In a more detailed analysis of the changes in the composition of volcanic gases that are required to maintain a reduced atmosphere Kump et al. (2001) concluded that the average f_{O_2} of volcanic gases had to be 2 log units below that of the FMQ buffer at and before the transition from a reducing to an oxidizing atmosphere. Such a low value of f_{O_2} in average volcanic gases is inconsistent with the data of Delano (2001) and Canil (1997, 1999) for the redox history of the Earth's mantle. This paper reexamines the issue. It proposes that the change in the average f_{O_2} of volcanic gases required to account for the transition of the atmosphere from an anoxy-

genic to an oxygenic state is much smaller than 2 log units and that there is no inconsistency between the required change and that allowed by other indicators of the f_{O_2} of volcanic gases in the past. The hypothesis explains a wide range of geologic and geochemical observations.

2. THEORETICAL FRAMEWORK

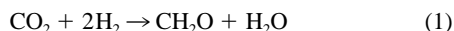
The oxidation state of the atmosphere at any given time depends in large part on the composition of the contemporary volcanic gases. With the exception of N_2 and the heavier rare gases, all of the constituents of volcanic gases are removed from the atmosphere-ocean system into sediments and into interplanetary space on a geologically short time scale. CO_2 and CO are removed from the atmosphere-ocean system by the deposition of organic matter and carbonate minerals. SO_2 and H_2S are removed by the deposition of sulfide and sulfate minerals. H_2 is removed by the reduction of CO_2 and CO to organic matter, by the reduction of SO_2 to sulfides, and by loss into interplanetary space. H_2 loss to interplanetary space from volcanic gases is significant only when the quantity of H_2 in the volcanic gases exceeds the quantity required to convert $\sim 20\%$ of the total quantity of ($\text{CO}_2 + \text{CO}$) to organic matter and all of the ($\text{SO}_2 + \text{H}_2\text{S}$) to a constituent of pyrite.

The proposition that the fraction of ($\text{CO}_2 + \text{CO}$) that is removed as organic carbon has always been close to 20% is counterintuitive. We have long been taught that the burial proportions of organic matter in sediments are influenced or even controlled by the exogenic system, the rates of carbon fixation, and the preservation of organic matter in sediments. However, although these processes do exert some effect on the burial proportions of organic matter, their effect seems to have been relatively minor. With a few notable exceptions, the isotopic composition of carbon in organic carbon and in carbonate minerals has been roughly constant during the past 3.5 Ga (e.g., Schidlowski, 1988; Strauss et al., 1992). Estimates of the average percentage of organic carbon in the total carbon of sedimentary rocks range from 15 to 23% (Holser et al., 1988a). The figure 20% used here is a reasonable average of the reported estimates. The demonstrated changes in biota, the likely changes in ocean productivity and in the preservation fraction of organic matter, and the almost certain changes in the

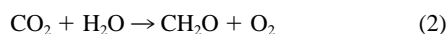
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composition of the atmosphere and of seawater during the past 3.5 Ga have apparently had only a relatively minor effect on the ratio of carbon burial as a constituent of organic matter to that in carbonate minerals.

The quantity of H_2 that is needed to convert volcanic ($CO_2 + CO$) to organic carbon (CH_2O) is, therefore, and has been during much of the geologic time the amount required to reduce ~20% of the total volcanic carbon gas content to CH_2O . This quantity is independent of the reduction path. In the presence of excess H_2 , it makes no difference whether reduction is carried out directly by organisms using photosystem I:



or indirectly by organisms using photosystem II:



In the latter case, the O_2 , which is generated by green-plant photosynthesis, is subsequently consumed by reaction with H_2 to yield H_2O :



The sum of Eqn. 2 and 3 is the same as Eqn. 1; two moles of H_2 are always needed to convert one mole of CO_2 to CH_2O .

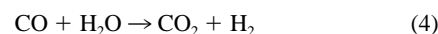
H_2 which remains in a batch of volcanic gas after the reduction of 20% of its contained ($CO_2 + CO$) to CH_2O , is available to convert the contained sulfur gases into a constituent of sulfide minerals. The dominant sulfide in marine sediments is pyrite. The quantity of H_2 required to remove the volcanic sulfur gases as a constituent of sulfides is therefore determined by the quantity of H_2 required to convert the volcanic sulfur into FeS_2 . If the amount of available H_2 is less than the amount required for this purpose, then only some of the volcanic sulfur is removed as a constituent of pyrite; the remaining sulfur is mainly removed as a constituent of sulfate minerals, dominantly gypsum and anhydrite. If the amount of available H_2 is greater than the quantity required to convert the volcanic ($SO_2 + H_2S$) to pyrite, then most of the excess H_2 escapes into interplanetary space.

The above treatment of a batch of volcanic gas is quite straightforward; but it remains to be shown how this treatment is related to the operation of the Earth system as a whole. Today both sulfur and carbon in rocks undergoing weathering are converted into gases and constituents of solutions. Most of the sulfides exposed to weathering are oxidized to sulfates. The SO_4^{-2} from these reactions joins SO_4^{-2} released by the solution of sulfate minerals, enters the oceans, and is removed from the oceans as a constituent of sulfides and sulfates. Organic matter that is exposed to weathering is largely oxidized to CO_2 . Carbonate minerals dissolve, and their contained carbon enters the oceans largely as HCO_3^- . In the oceans, carbon is in part deposited as a constituent of new carbonates. At steady state, the O_2 and CO_2 lost during weathering are regained during sedimentation. The total quantity of CH_2O , carbonates, pyrite, and sulfates is then the total quantity of these materials weathered plus the quantity that is added by volcanism and hydrothermal activity.

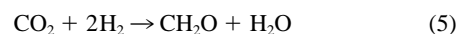
The total inventory of sulfur and carbon in the crust does not necessarily change significantly with time, because during the conversion of sedimentary rocks into high-grade metamorphic

and igneous rocks, these elements are released to a significant extent. Their release apparently accounts for a good deal of their quantity in volcanic gases and hydrothermal solutions. As long as the redox state of volcanic gases is such that H_2 is not present in excess, the redox state of subducted sediments is apt to be similar to that of volcanic gases. If, however, H_2 in volcanic gases is present in excess, some of this gas escapes into interplanetary space, and subducted sediments are more oxidized than the volcanic gases from which they were derived.

These qualitative considerations need to be converted into a quantitative treatment of the relationship between the composition of volcanic gases and the disposal of their constituents among the phases of sediments and into interplanetary space. A convenient approach consists of deriving a relationship between the composition of volcanic gases and the fraction, f , of their contained sulfur, which can be precipitated as a constituent of pyrite. Let us first convert all of the CO in a volcanic gas to CO_2 via the reaction



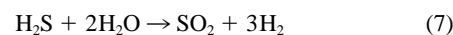
If the initial concentration of CO was ${}_o m_{CO}$, that of CO_2 ${}_o m_{CO_2}$, and that of H_2 ${}_o m_{H_2}$, the concentration of CO_2 at the end of the reaction is (${}_o m_{CO_2} + {}_o m_{CO}$), and that of H_2 is (${}_o m_{H_2} + {}_o m_{CO}$). Next let 20% of the total amount of CO_2 be converted to CH_2O via the reaction



At the end of this reaction

$$m_{H_2} = {}_o m_{H_2} + 0.6 {}_o m_{CO} - 0.4 {}_o m_{CO_2} \quad (6)$$

Next let all of the H_2S be converted to SO_2 via the reaction



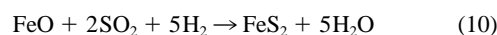
At the end of this reaction

$$m_{SO_2} = {}_o m_{SO_2} + {}_o m_{H_2S} \quad (8)$$

and

$$m_{H_2} = {}_o m_{H_2} + 0.6 {}_o m_{CO} - 0.4 {}_o m_{CO_2} + 3 {}_o m_{H_2S} \quad (9)$$

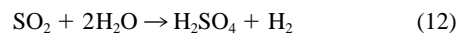
Next, let all of the SO_2 be removed as a constituent of FeS_2 via the reaction



At the conclusion of this reaction

$$m_{H_2} = {}_o m_{H_2} + 0.6 {}_o m_{CO} - 0.4 {}_o m_{CO_2} + 3 {}_o m_{H_2S} - 2.5 ({}_o m_{SO_2} + {}_o m_{H_2S}) \quad (11)$$

If not enough H_2 is present in the initial volatiles to convert all of the SO_2 to FeS_2 , let the remaining SO_2 be converted to H_2SO_4 via the reaction



and let the SO_4^{-2} be precipitated as a constituent of one or more sulfate minerals.

Now let f be the fraction of sulfur in the initial volatiles that is converted to FeS_2 . Then, at the end of the process outlined above,

$$m_{\text{H}_2} = 0 = {}_o m_{\text{H}_2} + 0.6 {}_o m_{\text{CO}} - 0.4 {}_o m_{\text{CO}_2} + 3 {}_o m_{\text{H}_2\text{S}} - 2.5 f({}_o m_{\text{SO}_2} + {}_o m_{\text{H}_2\text{S}}) + (1 - f)({}_o m_{\text{SO}_2} + {}_o m_{\text{H}_2\text{S}}) \quad (13)$$

After collecting terms, we obtain

$$f = \frac{{}_o m_{\text{H}_2} + 0.6 {}_o m_{\text{CO}} - 0.4 {}_o m_{\text{CO}_2} + 3 {}_o m_{\text{H}_2\text{S}}}{3.5 ({}_o m_{\text{SO}_2} + {}_o m_{\text{H}_2\text{S}})} + \frac{1}{3.5} \quad (14)$$

Volcanic gases added to the atmosphere can now be divided into four groups based on their f value:

Group 1. $f > 1.0$

Group 2. $f = 1.0$

Group 3. $1.0 > f > 0$

Group 4. $f < 0$

Volatiles in group 1 contain more H_2 than is required to reduce 20% of the carbon gases to organic matter and all of the sulfur to FeS_2 . Volatiles in group 2 contain just enough H_2 to effect this conversion. Volatiles in group 3 contain enough H_2 to reduce 20% of the carbon gases to organic matter but not enough H_2 to convert all of the sulfur gases to FeS_2 . Volatiles in group 4 do not contain enough H_2 to reduce 20% of their contained carbon gases to organic matter. Reducing atmospheres, i.e., those in which O_2 is essentially absent and the partial pressure of reduced gases such as methane is significant, require f values > 1.0 , i.e., conditions under which the volatiles that are added to the atmosphere fall in group 1.

The approach developed in this paper combines individual chemical analyses of gases from well-studied volcanoes to yield values for the average composition of gases from these volcanoes. These averages are used to compute the f value for each volcano. The entire set of f values is then used to estimate the average f value of volcanic gases as a whole. The same result can be achieved by using estimates of the total volcanic flux of each of the important volatiles to calculate the world average of f . At present, however, the uncertainties in these flux estimates are very large (e.g., Holser et al., 1988; Arthur, 2000), and it is difficult to choose and to combine these estimates in calculating the values of f for volcanic gases as a whole (see Appendix). The approach based on the composition of gases from well-studied volcanoes circumvents this problem. It yields a rather coherent set of f values for individual volcanoes and produces a more reliable estimate of the global f value of volcanic gases.

3. THE AVERAGE f VALUE OF VOLATILES TODAY

It is likely that volcanic gases and gases in black smokers are quantitatively the most important source of volatiles that are being added to the atmosphere-ocean system today. Fortunately, useful approximations of their average f value can be extracted from the available data.

3.1. The Average f Value of Volcanic Gases

Symonds et al. (1994) and Giggenbach (1996) have published excellent summaries of the available data for the composition of many volcanic gases, and Allard (1983) has compiled a good deal of the isotopic evidence bearing on the origin

of hydrogen, carbon, sulfur, nitrogen, and the rare gases in volcanic exhalations. Figure 1 shows the location of the volcanoes for which a relatively large body of gas analyses are available. Although their number is small compared to the total number of active volcanoes, the group contains representatives from spreading centers, above subduction zones, and at hot spots. The average f values of their gases are shown in Fig. 2. They scatter a great deal, but 16 of the 21 average f values fall between 0.2 and 0.7. The average of the set falls close to 0.5. Estimates of the total Phanerozoic inventory of sulfide and sulfate sulfur in Phanerozoic rocks (Holser et al., 1988b) are uncertain, but they suggest that sulfide sulfur accounts for ~67% of the total sulfur, implying an average value of 0.67 for f as defined above (Holser et al., 1988b). This value agrees with an equally uncertain average value of f derived from the mean isotopic composition of sulfur in Phanerozoic sulfides and sulfates. The average value of $\delta^{34}\text{S}$ in sedimentary sulfates during the Phanerozoic is approximately +18‰. The average value of $\delta^{34}\text{S}$ in sulfide minerals is ca. -7‰. The average $\delta^{34}\text{S}$ of mantle sulfur is close to 0‰. These data suggest that the fraction of sulfide sulfur in the Phanerozoic crust is ~0.72 (data from Holser et al., 1988b). For the Neogene alone, the value of f calculated in this fashion is 0.60. Altogether, these estimates suggest that the mean value of f in present-day volcanic gases is slightly lower than the average value of f for the total sulfur inputs during the Phanerozoic. The difference may not be real, but it can be explained by the composition of hydrothermal fluids that are added to the atmosphere-ocean system.

3.2. The Average f Value of Hydrothermal Fluids

It is difficult to make precise estimates of the relative importance of the volcanic and hydrothermal contributions to the carbon and sulfur fluxes to the atmosphere-ocean system. Marty and Tolstikhin (1998) proposed that the global magmatic flux of CO_2 is $\sim 6 \times 10^{12}$ mol/yr. This estimate is not significantly different from an earlier value proposed by the author (Holland, 1978). Of this total flux, $\sim (2.2 \pm 0.9) \times 10^{12}$ mol/yr are derived from hydrothermal fluxes at midocean ridges. An estimate of the average composition of black smoker fluids at MORs is shown in Table 1. The f value of these fluids is 0.9. The inclusion of the likely contribution from such fluids to the f value of all volatiles added to the atmosphere-ocean system increases the estimated global f value to ~0.65.

In most terrestrial geothermal fluids, the $\text{CO}_2/\text{H}_2\text{S}$ ratio is so high that their f value is negative (Ellis, 1979; Ellis and Mahon, 1977). It is likely, therefore, that their overall effect is to lower the f value of the worldwide volatile input. The body of available data for these fluids is not large enough to make a meaningful estimate of this reduction. It is perhaps best to adopt a value of 0.6 ± 0.1 for the average value of f in the input of volcanic gases and hydrothermal solutions during the Phanerozoic.

4. THE AVERAGE f VALUE OF VOLATILES BEFORE THE G.O.E

4.1. The f Value of Volcanic Gases

As shown in Fig. 3, the f_{O_2} of volcanic gases today ranges from slightly lower than the quartz-fayalite-magnetic (QFM)

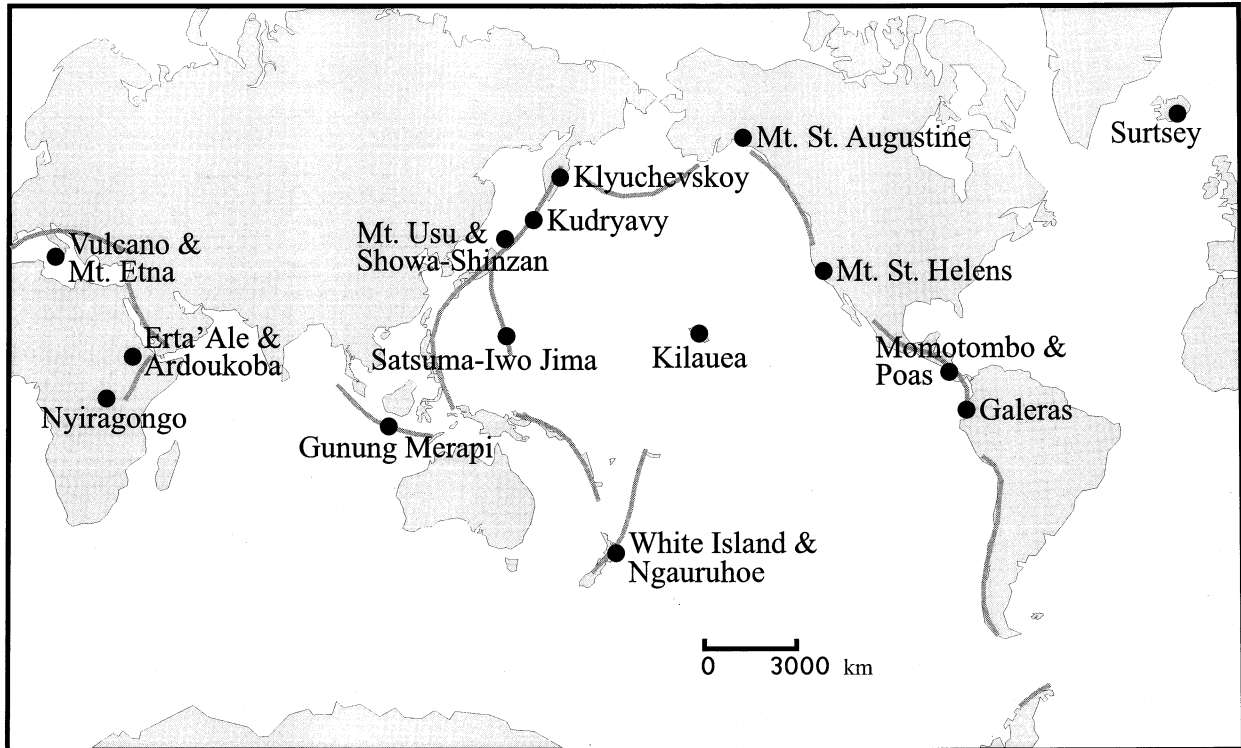


Fig. 1. Location of the volcanoes discussed in the text.

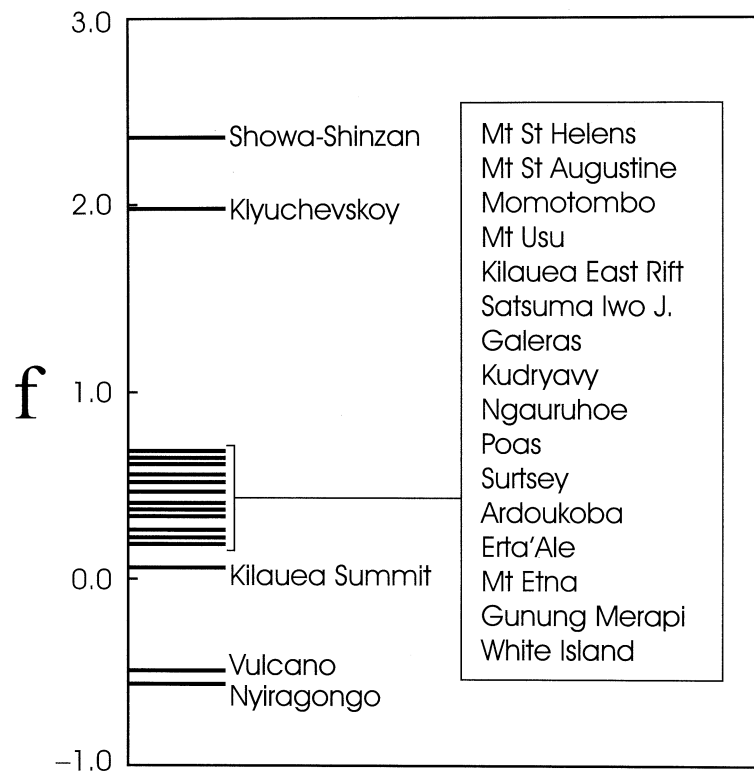


Fig. 2. The average value of the function f in volcanic gases from the volcanoes located in Fig. 1.

Table 1. The concentration and f value of gases in average black smokers and the maximum concentration of gases observed in black smokers (von Damm et al., 1995; von Damm, pers. comm., 2001).

	Average	Maximum
CO ₂	20 mmol/kg	200 mmol/kg
H ₂ S	7 mmol/kg	110 mmol/kg
H ₂	2 mmol/kg	40 mmol/kg
CH ₄	<1 mmol/kg	
f	0.90	1.04

buffer to slightly higher than the Ni-NiO (NNO) buffer. If the hypothesis outlined at the beginning of this paper is correct, the average value of f_{O_2} in volcanic gases before the Great Oxidation Event (G.O.E.) was sufficiently lower than today, so that the f value of volatile inputs to the atmosphere-ocean system was >1.0 . It must now be shown that the required decrease in the average f_{O_2} of volcanic gases is within the geologically permitted range.

The required decrease in the f_{O_2} of volcanic and hydrothermal gases is defined by the required increase in their hydrogen-to-water ratio. Most volcanic gases are analyzed after they have cooled somewhat below their initial preeruption temperature. During cooling, H₂ reacts with SO₂ to produce H₂S by the reverse of Eqn. 7. ${}_i m_{H_2}$, the preeruption H₂ concentration in volcanic gases, is therefore close to

$${}_i m_{H_2} = {}_o m_{H_2} + 3 {}_o m_{H_2S} \quad (15)$$

where ${}_o m_{H_2}$ and ${}_o m_{H_2S}$ are as above the concentrations of these gases in the analyzed samples. It is easy to calculate the value

of ${}_i m_{H_2}$ in analyzed gas samples that would be required to raise or to lower their f value to 1.0. Let the function Φ be defined as the ratio

$$\Phi = \frac{({}_i m_{H_2})_{f=1}}{({}_i m_{H_2})_{f,now}} \quad (16)$$

where $({}_i m_{H_2})_{f,now}$ is the value of ${}_i m_{H_2}$ in an analyzed gas sample before eruption, and where $({}_i m_{H_2})_{f=1}$ is the value of ${}_i m_{H_2}$ in the same gas sample, but with its H₂ concentration raised so that the f value of the gas is 1.0. Figure 4 shows the value of Φ for the average composition of gases from the volcanoes represented in Fig. 2. For 13 of the 20 volcanoes in Fig. 4, the value of Φ is between 1.4 and 3.4. The average value of Φ is 2.4. Since the value of f_{O_2} varies as the inverse of $(f_{H_2})^2$ at a constant value of f_{H_2O} , an increase of Φ by a factor of 2.4 implies a decrease in f_{O_2} by a factor of 5.8, i.e., a decrease of 0.76 log units. This is much smaller than the decrease of 2 log units proposed by Kump et al. (2001). The difference is due largely to two factors. Kump et al. (2001) used the data for the composition of volcanic gases in Holland (1978) rather than the much larger compilations which have become available since then. In addition, their treatment of the sulfur budget is in error, because they assumed that even in the absence of atmospheric O₂, sulfur leaves the oceans as sulfate rather than as sulfide (J. F. Kasting, pers. comm., 2001).

The most direct evidence for the f_{O_2} of volcanic gases in the past is provided by the concentration of Cr and f_{O_2} in basaltic rocks. Canil (1997, 1999) and Delano (2001) have shown that the f_{O_2} of mantle melts has changed little during the past 3.96 Ga. Delano (2001) has proposed that since 3.96 Ga, the oxygen

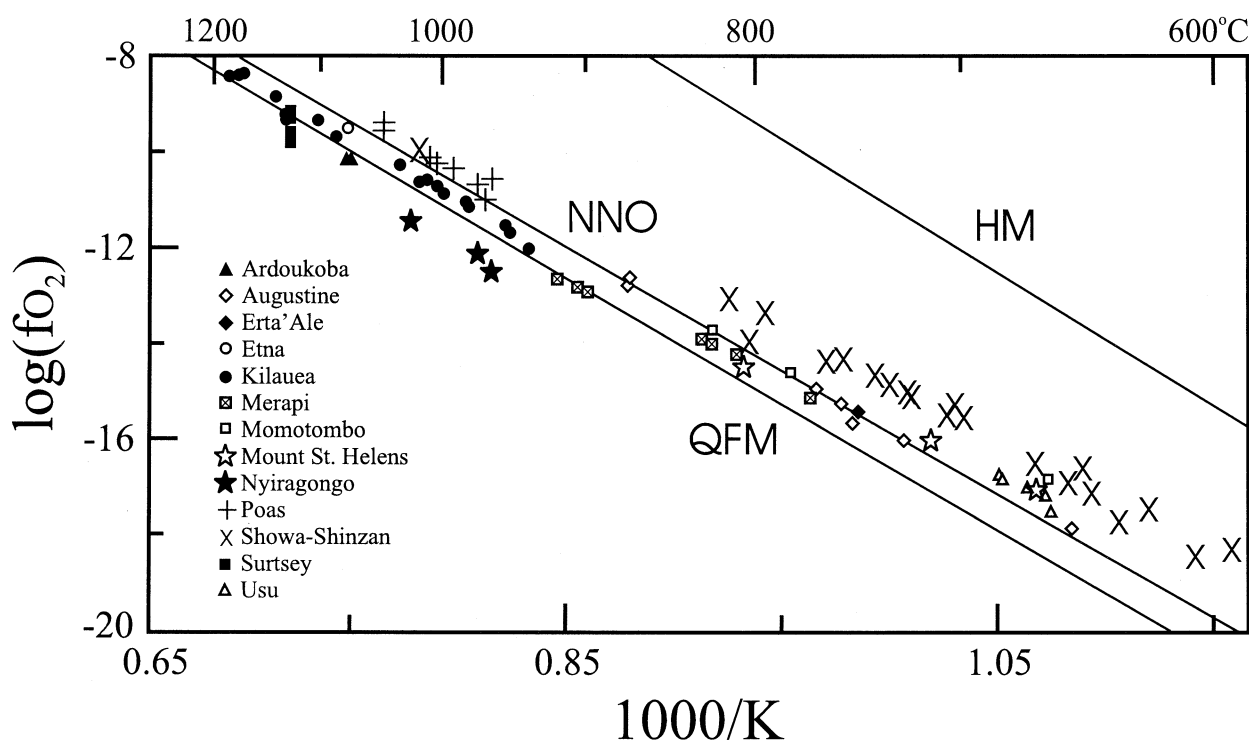


Fig. 3. Plot of $\log f_{O_2}$ vs. inverse temperature for volcanic gas compositions in Symonds et al. (1994). The quartz-fayalite-magnetite (QFM), Ni-NiO (NNO), and hematite-magnetite (HM) oxygen buffers are shown for reference.

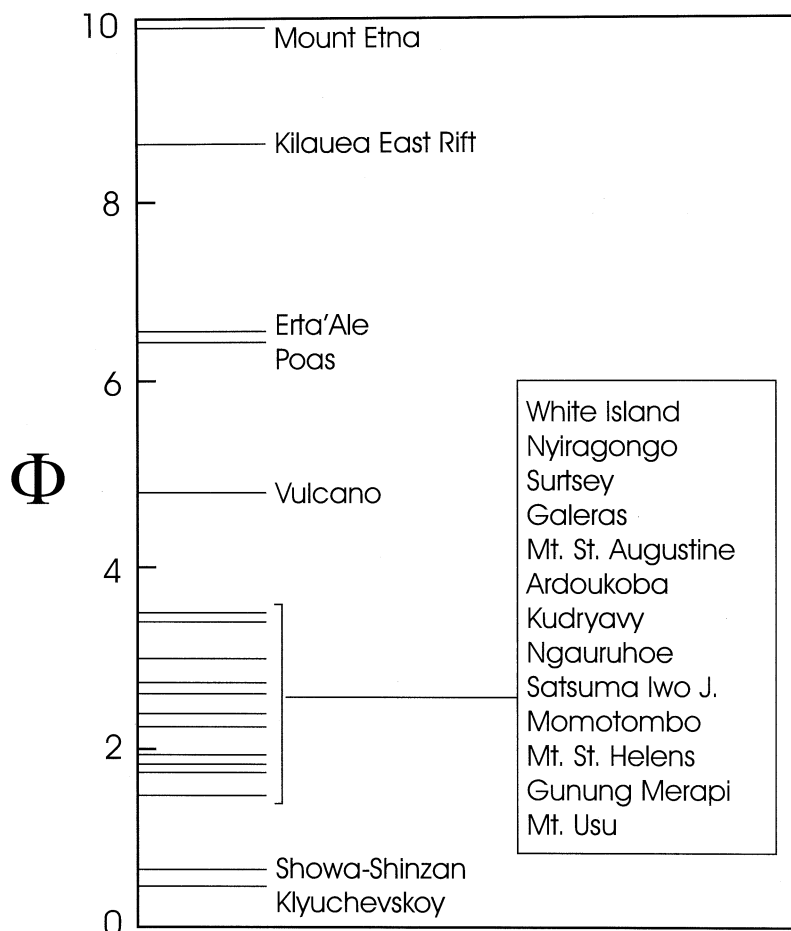


Fig. 4. The values of the function Φ for the volcanoes located in Fig. 1.

fugacity of these melts has been no more than 0.5 log units lower or higher than today (see Fig. 5). The lower limit of f_{O_2} permitted by these data is somewhat higher than the value estimated above for the f_{O_2} of volcanic gases before the G.O.E. It seems likely, however, that the f value of volcanic gases before the G.O.E. was close to 1.0 even without a change in their f_{O_2} (see below). If so, the oxidation state of volcanic gases required to maintain an anoxic atmosphere was well within the limits indicated by the Delano (2001) data.

It is likely that the f_{O_2} of the upper mantle has increased slightly with time. H_2 is continually lost from the mantle as a constituent of volcanic gases. Before the G.O.E., some of this H_2 escaped into interplanetary space. The Earth as a whole therefore became slightly more oxidized until the H_2 escape rate from the Earth was reduced to today's insignificant value after the onset of the G.O.E. (Kasting et al., 1993). Unfortunately, it is still very difficult to assess the effect of pre-G.O.E. H_2 escape on the oxidation state of the mantle. The argument can be made that the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio in the upper mantle probably changed by a few percent due to H_2 escape (Kasting et al., 1993; Catling et al., 2001); but even if this is correct, the influence of such a small change on the f_{O_2} of mantle melts is difficult to determine. The major effect of a small increase in the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio of the mantle is to increase the proportion

of the spinel phase. Secondary effects are produced by changes in the composition of the minerals in the buffer assemblage. These are the changes that increase the f_{O_2} of mantle melts. Unfortunately, the magnitude of these changes is not well known, and the buffering effects of carbon-fluid equilibria (CCO) are not well constrained (Blundy et al., 1991).

Changes other than those in the H_2 concentration of volcanic gases have probably also contributed to changes in the mean f value of volcanic gases. In Fig. 6, the composition of the volcanic gases which were used in the computation of their current f values are plotted as a function of $\Sigma\text{C}/\text{H}_2\text{O}$, the ratio of the total concentration of carbon gases to H_2O and $\Sigma\text{S}/\text{H}_2\text{O}$, the ratio of the total concentration of sulfur gases to H_2O . The average f value of these gases is listed next to each data point. The rectangle represents the best estimate of the ratio of carbon to water and sulfur to water in the Earth's crust plus oceans. Although the position of the rectangle is somewhat uncertain, it is clear that the ratio of sulfur to carbon in volcanic gases today is ~ 4 times greater than the ratio of sulfur to carbon in the crust plus oceans. Sulfur apparently cycles through the mantle considerably more rapidly than carbon. This may be related to the precipitation of CaSO_4 in the oceanic crust during the cycling of seawater through MORs. Currently, an undetermined fraction of this CaSO_4 is redissolved and returned to the oceans

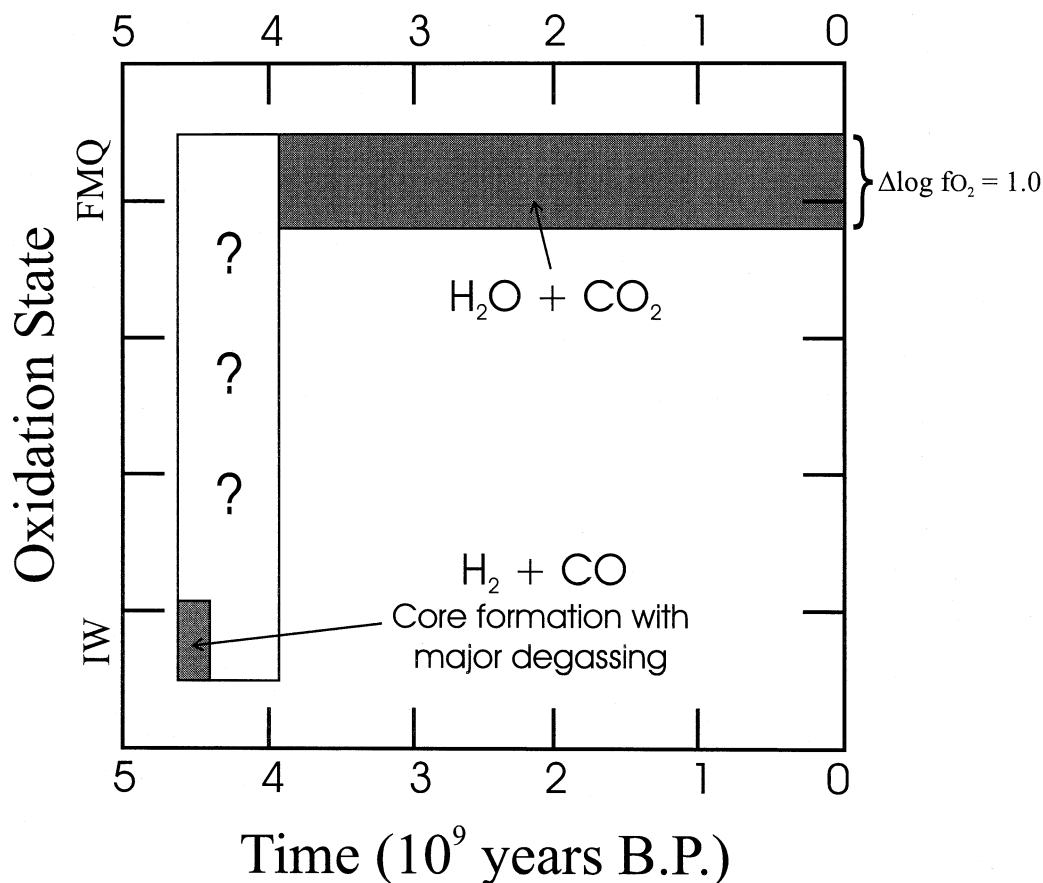


Fig. 5. The Delano (2001) summary of the redox state of the mantle during Earth history based on the Cr content of basalts, slightly modified.

during the cycling of seawater on the flanks of MORs, where the temperature of the cycled seawater is considerably lower than at the ridge crests. CaSO_4 which escapes dissolution is carried down into subduction zones, can participate in magma production, and can reappear at the surface as a constituent of volcanic gases. The most recent estimate of the high-temperature flux of seawater on-axis (0–1 Ma) is $(5.6 \pm 1.7) \times 10^{13}$ kg/yr (Butterfield et al., 2001). The present annual high-temperature flux of seawater SO_4^{-2} into MORs is, therefore,

$$28 \frac{\text{mmol}}{\text{kg}} \times (5.6 \pm 1.7) \times 10^{13} \frac{\text{kg}}{\text{yr}} = (1.6 \pm 0.5) \times 10^{12} \text{ mol/yr.}$$

The present-day flux of S from volcanoes as estimated by Williams et al. (1992) and Arthur (2000) is $\sim 0.3 \times 10^{12}$ mol/yr. A somewhat different value of $\sim 1.0 \times 10^{12}$ mol/yr is obtained by dividing the CO_2 emission rate of Marty and Tolstikin (1998) by the CO_2/SO_2 ratio used by Williams et al. (1992) for average volcanic gases. In either case, CaSO_4 precipitated at and near MOR crests from cycled seawater could account for all or nearly all of the sulfur in volcanic gases. The isotopic composition of sulfur in volcanic gases in rift volcanoes is close to 0‰, the composition of juvenile sulfur. The value of $\delta^{34}\text{S}$ in volcanic gases from subduction zones is

usually positive, indicating that a significant part of their sulfur is derived from sources that contain oceanic sulfate (Allard, 1983; Poorter et al., 1991).

There is a good deal of evidence (Canfield et al., 2000) that the concentration of SO_4^{-2} in seawater was very low, probably < 1 mmol/kg before the G.O.E. If so, the precipitation of CaSO_4 in the oceanic crust was negligible before the G.O.E., and the sulfur content of gases emitted from volcanoes in areas of convergent plate margins was almost certainly lower than today. The effect of a lower $\Sigma\text{S}/\text{H}_2\text{O}$ content of volcanic gases on their f value is shown in Fig. 7. The diagram has been drawn for a value of $m_{\text{H}_2}/m_{\text{H}_2\text{O}}$ of 2.4×10^{-2} , the ratio for the FMQ buffer at 1400K. On the left side of this diagram, $i m_{\text{H}_2}/m_{\text{H}_2\text{O}}$ is > 0.4 times their $\Sigma\text{C}/\text{H}_2\text{O}$ ratio. Lowering the $\Sigma\text{S}/\text{H}_2\text{O}$ ratio of volcanic gases on this side of the diagram raises their f value. At very low $\Sigma\text{C}/\text{H}_2\text{O}$ values, a reduction of $\Sigma\text{S}/\text{H}_2\text{O}$ from 1.0×10^{-2} to 0.5×10^{-2} increases the value of f from 1.0 to 1.7. On the right side of the diagram, where the chosen $i m_{\text{H}_2}/m_{\text{H}_2\text{O}}$ value of 2.4×10^{-2} is $< 0.4 \Sigma\text{C}/\text{H}_2\text{O}$, a decrease in the $\Sigma\text{S}/\text{H}_2\text{O}$ ratio of volcanic gases lowers their f value.

Most of the gases in Fig. 6 that are emitted from volcanoes associated with convergent plate margins fall within the left side of Fig. 7. Before the G.O.E., the f value of gases from volcanoes in this setting was therefore probably higher than today. The f value of gases from volcanoes at divergent plate

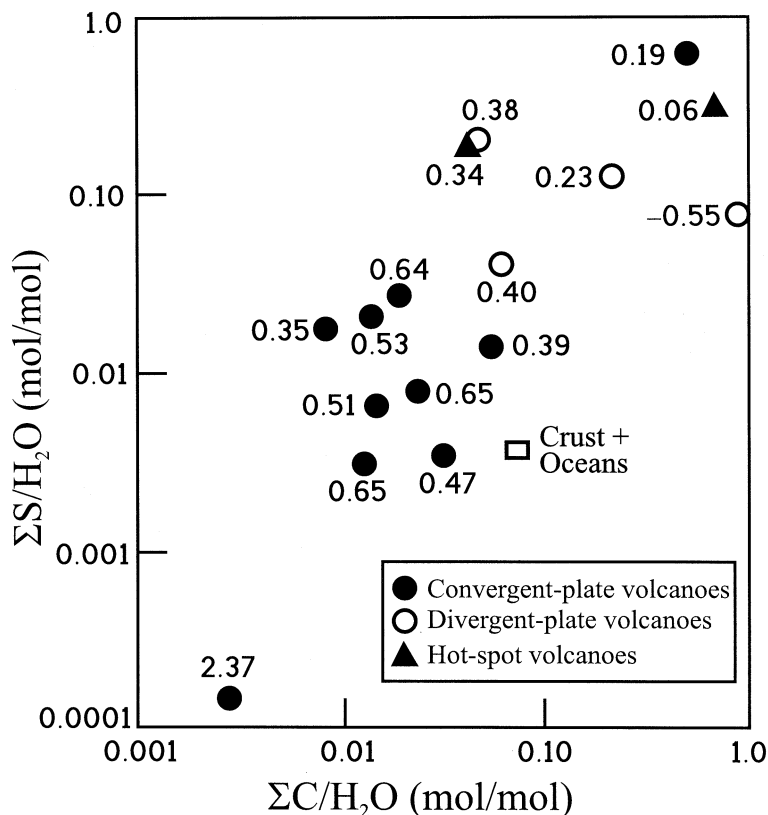


Fig. 6. The ratio of sulfur to water in average gas emitted from the volcanoes sited in Fig. 1 plotted against their total carbon-to-water ratio. The figures next to the data points represent the f value of the volcanic gas compositions. The rectangle represents the ratios in the crust plus the oceans.

and hot spots was probably not much lower or perhaps not lower at all before the G.O.E. If this is correct, the average f value of volcanic gases before the G.O.E. was greater than today's value of ~ 0.5 simply due to their lower $\Sigma S/H_2O$ ratio. This suggests the following sequence of events. Before ca. 2.3 Ga, the average value of the ratio $i_{m_{H_2}}/m_{H_2O}$ was $> 2.4 \times 10^{-2}$, but not necessarily much greater, and the f value of average volcanic gases was > 1.0 . By ca. 2.3 Ga, the ratio of $i_{m_{H_2}}/m_{H_2O}$ had decreased to 2.4×10^{-2} , and the f value of average volcanic gases had decreased to 1.0. After the appearance of atmospheric O_2 , the loss of H_2 from the atmosphere decreased to a negligibly small rate. The average value of $i_{m_{H_2}}/m_{H_2O}$ in volcanic gases has therefore decreased very little since then. However, the rise of the SO_4^{2-} content of seawater led to faster S cycling and an increase in the $\Sigma S/H_2O$ ratio of volcanic gases. If correct, this sequence of events implies that the value of $i_{m_{H_2}}/m_{H_2O}$ in volcanic gases before the G.O.E. could have been within the limit set by the Delano (2001) data for the Cr content of basaltic rocks during the past 3.96 Ga. The increment is significantly less than the factor of 5.8 that seems to be required if the $\Sigma S/H_2O$ ratio before the G.O.E. was the same as today.

4.2. The f Value of Hydrothermal Fluids

During the course of Earth history, the rate of internal heat generation has decreased significantly. During the Archean, the

rate of seafloor spreading was almost certainly more rapid and the temperature of the upper mantle almost certainly higher than today. It therefore seems likely that the temperature of black smokers was also higher than today. This suggestion is not contradicted by the calculations of Jupp and Schultz (2000), who dealt only with the behavior of pure water in hydrothermal vent systems. The concentrations of Fe^{+2} and H_2S in black smoker fluids are both strongly temperature dependent (e.g., Nishima, 1989; Seyfried et al., 1991). Predictions of their concentration based on thermodynamic calculations agree with direct observations by von Damm et al. (1995, 1997) and von Damm (2000). The input of Fe^{+2} and H_2S from black smokers to the oceans was therefore almost certainly greater during the Archean than it is today. This inference is supported by the abundance of banded iron formations in the Archean and Paleoproterozoic and by the presence of excess Fe in Precambrian sandstones and shales as shown by their elevated Fe/Ti ratios (Kump and Holland, 1992).

The gas concentrations in average Archean black smoker fluids may have been similar to their maximum concentration in present-day black smokers. Their f value of 1.04 is slightly greater than that of average black smokers (see Table 1). It is unlikely that the f value of Archean black smokers was much greater than 1.04. Since the CO and SO_2 content of black smoker fluids is very small, their f value derived from Eqn. 14 is approximately equal to

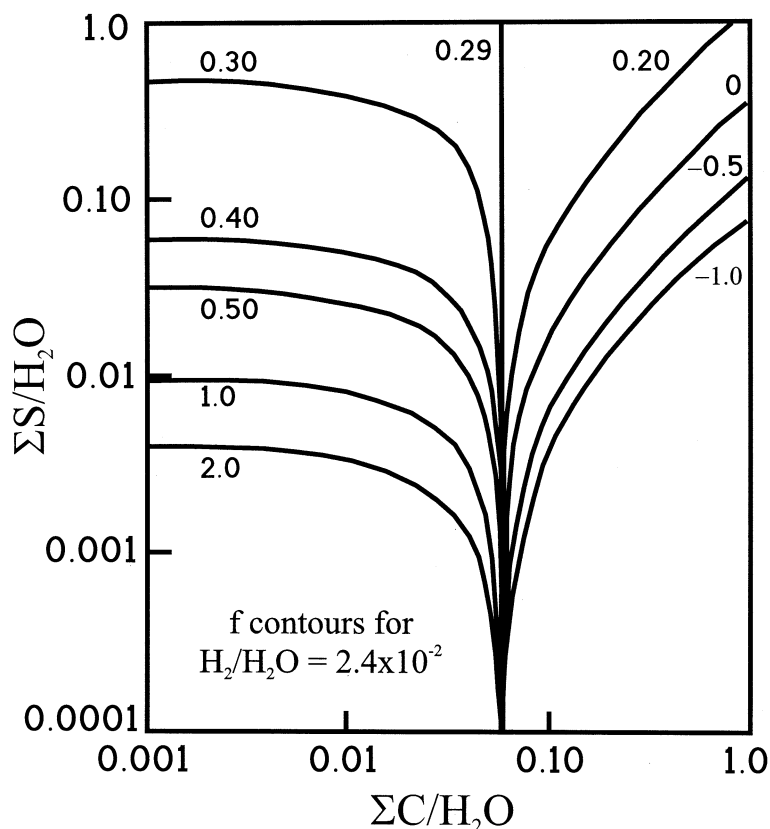


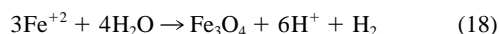
Fig. 7. Contours of the function f for volcanic gases in which the initial ratio of $m_{\text{H}_2}/m_{\text{H}_2\text{O}}$ is 2.4×10^{-2} , on the value of the ratio in gases buffered by FMQ at 1400 K. The contours are based Eqn. 14. Note that at high temperatures, i.e., before cooling, ${}_o m_{\text{CO}}$ and ${}_o m_{\text{H}_2\text{S}}$ can be neglected.

$$f = 0.29 \left(\frac{m_{\text{H}_2}}{m_{\text{H}_2\text{S}}} \right) - 0.11 \left(\frac{m_{\text{CO}_2}}{m_{\text{H}_2\text{S}}} \right) + 1.14 \quad (17)$$

Even if the $\text{CO}_2/\text{H}_2\text{S}$ ratio of black smokers was very much smaller than in the maximum-gas analysis in the right hand column of Table 1, the f value of the fluids was unlikely to have exceeded 1.25. The f value of black smoker gases has, therefore, probably decreased only modestly with time. This decrease, together with the decrease proposed for the f value of volcanic gases, can probably account for the average value of f for volcanic and hydrothermal inputs today.

4.3. Other Sources of Reduced Gases

At least two other sources have contributed reduced gases to the atmosphere-ocean system: the oxidation of Fe^{+2} emitted by black smokers and serpentinization. Fe^{+2} emitted by black smokers before the G.O.E. was removed from seawater largely by the precipitation of FeS_2 , FeCO_3 , Fe^{+2} silicates, iron oxides, and oxyhydroxides. The last two were probably the most important of these precipitates. They are largely represented by magnetite in BIFs. The process of magnetite precipitation can be described by the equation



which shows that both H^+ and H_2 are generated during the precipitation of Fe_3O_4 .

The generation of Fe_3O_4 during serpentinization reactions also generates H_2 and H^+ . However, H^+ is removed by reaction of the serpentinizing fluids with Mg-silicates. The resulting fluids are therefore often alkaline (Kelley et al., 2001). Little is known about the magnitude of these sources of H_2 . After the G.O.E. the deposition of hydrothermal Fe occurred mainly as a constituent of hematite. The deposition of hematite generated more H_2 per mole of Fe, or what is equivalent, used more O_2 . However, the hydrothermal input of Fe has almost certainly decreased with time; the effect of the precipitation of Fe-oxides on the redox state of the oceans has therefore almost certainly decreased as well. The abundance of near-surface ultramafics and the generation of H_2 during serpentinization have also probably decreased with time.

5. EVIDENCE FROM THE SEDIMENTARY RECORD

If a decrease in the mean f value of volatiles was responsible for the G.O.E., the marine geochemistry of C, N, and S before, during, and after the G.O.E. should reflect this change.

5.1. Carbon

Fig. 8 is a summary by Karhu and Holland (1996) of a good deal of data for the isotopic composition of carbon in marine carbonate sediments, in carbonates associated with BIFs, and in organic carbon. Data obtained since then have confirmed the

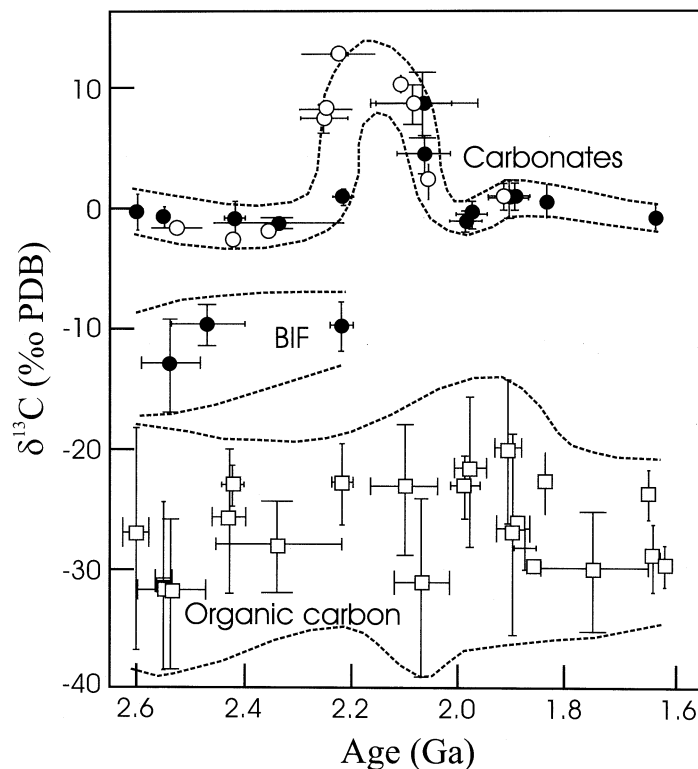


Fig. 8. The isotopic composition of carbon in marine carbonates, in carbonates associated with BIFs, and in organic carbon between 2.6 and 1.6 Ga (Karhu and Holland, 1996).

trend of $\delta^{13}\text{C}$ in carbonate sediments. Additional positive carbon isotope excursions have been found in carbonates of the Transvaal Supergroup, South Africa (Buick et al., 1998; Melezhik et al., 1999; Bekker et al., 2001), but it is not clear whether these excursions reflect global or only local processes. The data in Fig. 8 show that there was a major positive worldwide excursion in the $\delta^{13}\text{C}$ value of marine carbonates. The excursion started after the beginning of the G.O.E. and lasted for ~ 150 Ma. The $\delta^{13}\text{C}$ of marine carbonates then returned to its pre-G.O.E. value close to 0‰. The nearly constant $\delta^{13}\text{C}$ value of marine carbonates close to 0‰ and the roughly constant value of the $\delta^{13}\text{C}$ value of organic carbon before the G.O.E. indicate that the fraction of carbon gases added to the atmosphere that was reduced to organic carbon has been roughly constant. The large positive $\delta^{13}\text{C}$ excursion between ca. 2.20 and 2.05 Ga indicates that the fraction of carbon gases reduced to organic carbon during this period was much larger than before. The $\delta^{13}\text{C}$ of ~ 0 ‰ after the large positive excursion indicates that by 2.00 Ga, the fraction of carbon gases reduced to organic carbon had returned to its pre-2.20 Ga value. At the peak of the excursion, the $\delta^{13}\text{C}$ of carbon in carbonates was $\sim +12$ ‰; the $\delta^{13}\text{C}$ of carbon in organic matter was ~ -24 ‰. If the average input $\delta^{13}\text{C}$ to the atmosphere was -5 ‰, $\sim 50\%$ of the carbon in the exogenic cycle was removed as organic C. The total amount of “excess” O_2 produced by the burial of “excess” organic carbon during the $\delta^{13}\text{C}$ excursion can only be estimated roughly. It seems to have been about $(2.0 \pm 0.6) \times 10^{22}$ gm, i.e., between ~ 12 and 22 times the O_2 content of the present-day atmosphere.

Today, the rate of burial of organic carbon is controlled in large part by the availability of PO_4^{3-} , NO_3^- , and Fe. In the pre-G.O.E. ocean, the concentration of Fe was considerably greater than today, as shown by the elevated Fe content of pre-G.O.E. carbonate sediments (Veizer, 1978). It is unlikely, therefore, that Fe was a limiting nutrient in the pre-G.O.E. ocean. The role of N as a limiting nutrient is more difficult to evaluate. The average isotopic composition of N in marine organic matter differs significantly from that of the atmosphere. The average value of $\delta^{15}\text{N}$ in present-day marine organic matter is $\sim +6$ ‰ (see Fig. 9), while that of the atmosphere is close to 0‰. In large part, the difference between these values is almost certainly due to the effect of the denitrification of NO_3^- . In early Archean kerogens, the average value of $\delta^{15}\text{N}$ was apparently close to 0‰ (Beaumont and Robert, 1998, 1999). The very negative $\delta^{15}\text{N}$ values in kerogens from the 3.45-Ga Warrawoona Formation in Australia have been confirmed by Pinti and Hashizume (2001). These authors pointed out that some modern vent-related chemosynthetic organisms have negative $\delta^{15}\text{N}$ values and suggested that the negative values of $\delta^{15}\text{N}$ in Archean kerogens reflect their similarity to modern vent organisms rather than the marine chemistry of N. It is not clear, however, that the Archean kerogens analyzed to date are the remains of chemosynthetic rather than photosynthetic organisms. The largest shift in the average value of $\delta^{15}\text{N}$ of kerogens analyzed by Beaumont and Robert (1998) occurs between 2.7 and 2.1 Ga (see Fig. 9). This shift could well be related to the G.O.E., because the oxygenation of the upper parts of the oceans at that time was almost certainly accompa-

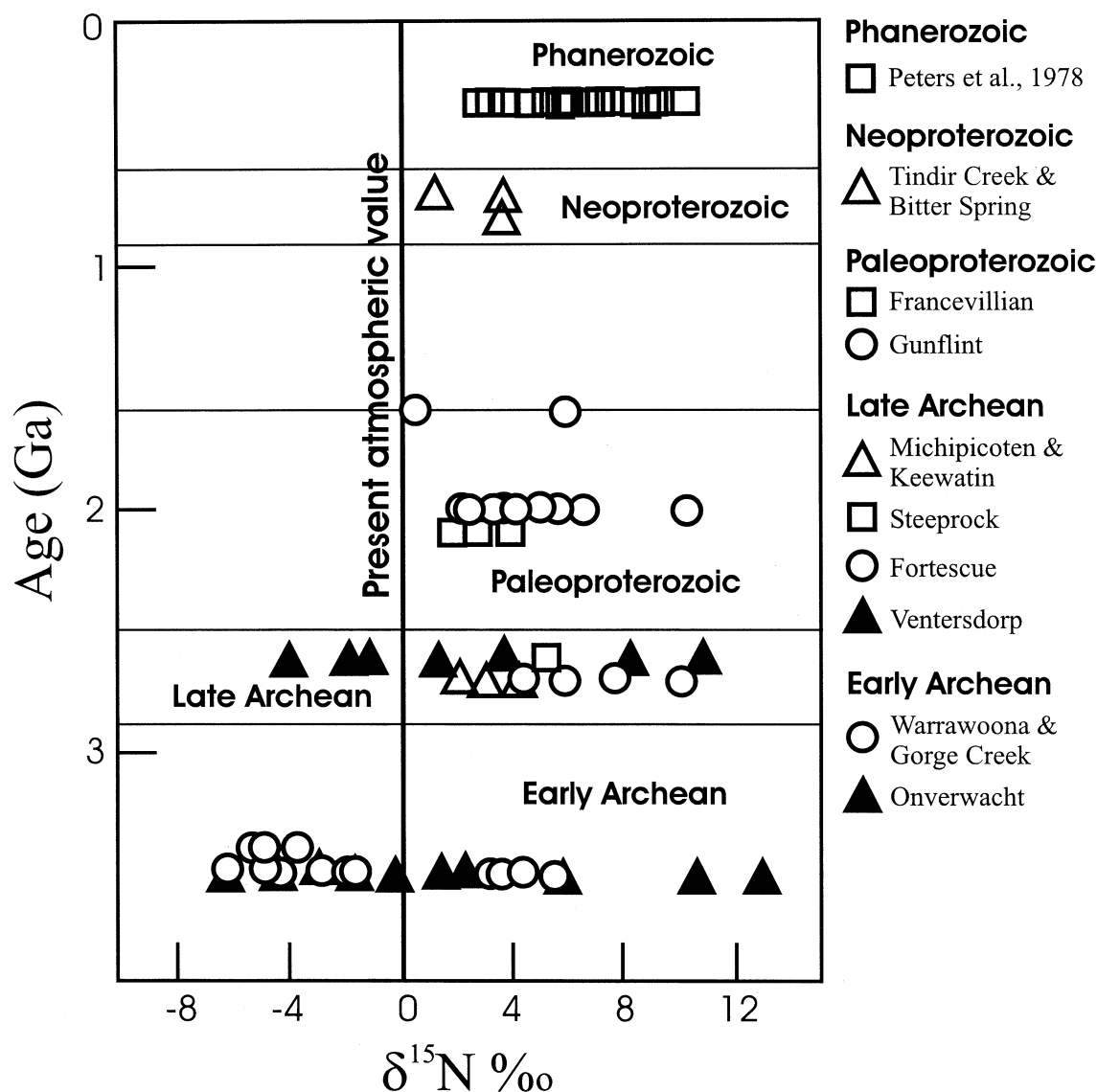


Fig. 9. The isotopic composition of nitrogen in kerogen since 3.5 Ga (Beaumont and Robert, 1998).

nied by a shift in the marine chemistry of N from NH_4^+ -dominated to NO_3^- -dominated. However, the range of $\delta^{15}\text{N}$ values in kerogens of any given age is so large, that the dating of the major shift in the average $\delta^{15}\text{N}$ value of kerogens requires a much larger number of analyses than are currently available. The time gap between the age of the upper Archean and the Paleoproterozoic samples analyzed by Beaumont and Robert (1998) is too large to determine whether the shift in the average value of $\delta^{15}\text{N}$ in marine kerogen occurred before, during, or shortly after the G.O.E.

In the absence of O_2 in the water column, NH_4^+ must have been the dominant combined-N species. This cation probably cycled efficiently between photosynthesizers, decomposers, and the water column. Losses of NH_4^+ by conversion to N_2 were probably minor. It is likely, therefore, that NH_4^+ was not a limiting nutrient at that time. The situation changed drastically when the concentration of O_2 in the water column reached $\sim 15 \mu\text{m}$. Nitrifying chemoautotrophs were then able to oxidize

NH_4^+ to NO_2^- and, subsequently, to NO_3^- . These oxidized N-species were convertible to N_2 in anaerobic settings by anaerobic microorganisms (denitrifiers). At a time when the deeper parts of the oceans were anoxic, this process could have constituted a major drain on the concentration of the fixed-N species (Falkowski and Berman-Frank, 2001) and could have imposed strong limits on the total rate of photosynthesis in the oceans.

The time at which the O_2 content of seawater in the photic zone reached the level at which nitrifying autotrophs became important parts of the marine N cycle is not known. It could have been during the early Archean, if cyanobacteria had already developed by then. However, the data in Fig. 9 suggest that denitrification did not shift the average $\delta^{15}\text{N}$ value of marine kerogen to its present value until some time between 2.7 and 2.1 Ga. N-limitation of photosynthesis may therefore have been severe only during the transition of the atmosphere from an anoxygenic to an oxygenated state ca. 2.3 Ga. Since the

oxygenation of the oceans as a whole, nitrogen species do not seem to have limited the rate of marine photosynthesis on a geologic time scale. The entire matter of the role of N species as limiting nutrients is not, however, settled and continues to be a subject of considerable controversy.

Of the three limiting nutrients, N, Fe, and PO_4^{-3} , the last is the constituent of seawater most likely to have limited the rate of photosynthesis and the rate of carbon burial before the G.O.E. Since the fraction of the carbon gases added to the atmosphere that were reduced to organic matter and buried with marine sediments was nearly constant before the G.O.E., the rate of PO_4^{-3} supply to the oceans must have scaled with the rate of addition of carbon gases to the atmosphere. This is not unreasonable. The rate of chemical weathering is proportional to the rate of CO_2 addition to the atmosphere. PO_4^{-3} is released during chemical weathering, largely by the dissolution of apatite. It is not surprising, therefore, that PO_4^{-3} addition to the oceans was coupled to the rate of carbon gas addition to the atmosphere. It is, however, somewhat puzzling that the fraction of ($\text{CO}_2 + \text{CO}$) buried as a constituent of organic matter today is so nearly equal to the pre-G.O.E. fraction, given the great complexity of the marine geochemistry of phosphorus (e.g., Slomp, 1997; Colman and Holland, 2000).

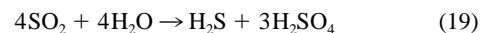
The large positive $\delta^{13}\text{C}$ excursion in carbonate sediments between ca. 2.22 and 2.06 Ga suggests that during this period, PO_4^{-3} was exceptionally available for photosynthesis and carbon burial. Several changes probably contributed to this greater availability. As the O_2 content of the atmosphere rose, the oxidation of FeS_2 during weathering must have increased dramatically. The H_2SO_4 generated during FeS_2 oxidation must have increased the total rate of chemical weathering and, hence, the rate at which PO_4^{-3} was delivered to the oceans. At the same time, H_2S and HS^- in the near-surface oceans were probably oxidized to SO_4^{-2} . This process lowered the pH of river and seawater and perhaps made PO_4^{-3} more available for photosynthesis. The combination of these effects may have been responsible for much of the increase in the $\delta^{13}\text{C}$ value of marine carbonates between 2.22 and 2.06 Ga. The deposition of the geologically oldest phosphorites and phosphatic BIFs followed hard on the beginning of the G.O.E. In Finland, uraniferous phosphorites belonging to the Jatuli Group of the Karelian Supergroup or to the basal parts of the Svecofennian Supergroup were deposited between 2.1 and 1.9 Ga (Äikäs, 1989). In Western and Central India, the middle part of the Paleoproterozoic Aravalli Supergroup contains economic stromatolitic phosphorite deposits (Verma, 1984). Unfortunately, these sediments are not well dated, and it is not yet clear whether they were deposited shortly before, during, or after the G.O.E. The appearance of phosphorites does not prove that PO_4^{-3} became more available during the rise of atmospheric O_2 , but their development is one of its expected consequences.

The decrease in the $\delta^{13}\text{C}$ value of carbonates following the peak of the positive excursion suggests that the PO_4^{-3} flux to the oceans decreased after ca. 2.10 Ga, and/or that PO_4^{-3} was being removed more efficiently from the oceans. Both processes probably contributed to the decrease in the $\delta^{13}\text{C}$ of carbonates after ca. 2.10 Ga. The FeS_2 content of sediments deposited after the G.O.E. was lower than that of pre-G.O.E. sediments, because some of the S^{-2} in the older sediments had been converted to SO_4^{-2} , which did not contribute to the gen-

eration of H^+ during weathering. In the oceans, the increase in the O_2 content, at least above the thermocline, must have been accompanied by the deposition of $\text{Fe}(\text{OH})_3$, which is an excellent scavenger for PO_4^{-3} (e.g., Colman and Holland, 2000). Although quantitative data are still lacking, the likely decrease in the PO_4^{-3} input to the oceans and the more efficient removal of PO_4^{-3} from the oceans probably accounted for a large part of the decrease in the burial rate of organic carbon and the return of the $\delta^{13}\text{C}$ of marine carbonates to values close to 0‰ at the end of the G.O.E.

The magnitude of the $\delta^{13}\text{C}$ excursion is a measure of the excess O_2 generated during the G.O.E. (Karhu and Holland, 1996). Some of this excess accumulated in the atmosphere and in the surface oceans. The majority was probably used in the oxidation of FeS_2 during weathering. This resulted in a large increase in the SO_4^{-2} concentration of the oceans and in the deposition of gypsum and anhydrite in evaporitic settings. It is interesting and perhaps significant that the duration of the G.O.E. was roughly equal to the cycling time of sediments, i.e., ca. 200 Ma.

The hypothesis advanced in this paper demands that all or nearly all of the sulfur in volatiles added to the ocean-atmosphere system before the G.O.E. was removed as a constituent of sulfides, mainly pyrite. This seems to be true. Anhydrite is known only as a replacement mineral before 2.3 Ga. The earliest significant anhydrite deposits are ca. 2.2 Ga (Chandler, 1988; Master, 1990). Barite is reasonably common in Archean and early Proterozoic sediments. Its quantity is very small compared to that of contemporaneous pyrite, but its presence does indicate that SO_4^{-2} has been present in surface ocean water during the past 3.45 Ga. This is not surprising. Volcanic SO_2 reacts with H_2O at temperatures below $\sim 400^\circ\text{C}$ and disproportionates to H_2S and H_2SO_4 :



No O_2 is required to generate H_2SO_4 via this reaction. The presence of barite in Archean sediments is not, therefore, proof of the presence of O_2 in the atmosphere at that time. The isotopic composition of sulfur in ca. 3.47-Ga barites from North Pole, Australia (Shen et al., 2001) lends strong support to the proposition that microbial sulfate reduction had already evolved at that time. Most of the SO_4^{-2} generated inorganically by reactions such as Eqn. 19 and photochemically (Farquhar et al., 2001a) was apparently reduced to S^{-2} and was then removed by precipitation as a constituent of sulfide minerals. Microbial sulfate reduction and fractionation of sulfur isotopes becomes rapid and efficient at SO_4^{-2} concentrations >1 mmol (Canfield et al., 2000). The isotopic fractionation of sulfur observed in Archean pyrite such as that in the ~ 2.5 -Ga McRae shale in Western Australia (Kakegawa et al., 1999) does not, therefore, require that the concentration of SO_4^{-2} in seawater was "more than one-third the present concentration" and does not demand that the atmosphere was oxidic at ~ 2.5 Ga.

The spread in the value of $\delta^{34}\text{S}$ in pyrite during the Precambrian decreases with increasing age (Fig. 10). The spread is quite small until ca. 2.7 Ga, increases irregularly thereafter with decreasing age, shows a significant increase during the G.O.E. (ca. 2.3 Ga), and reaches its full present-day range ca. 0.7 Ga. The complexity of this record probably owes something to the

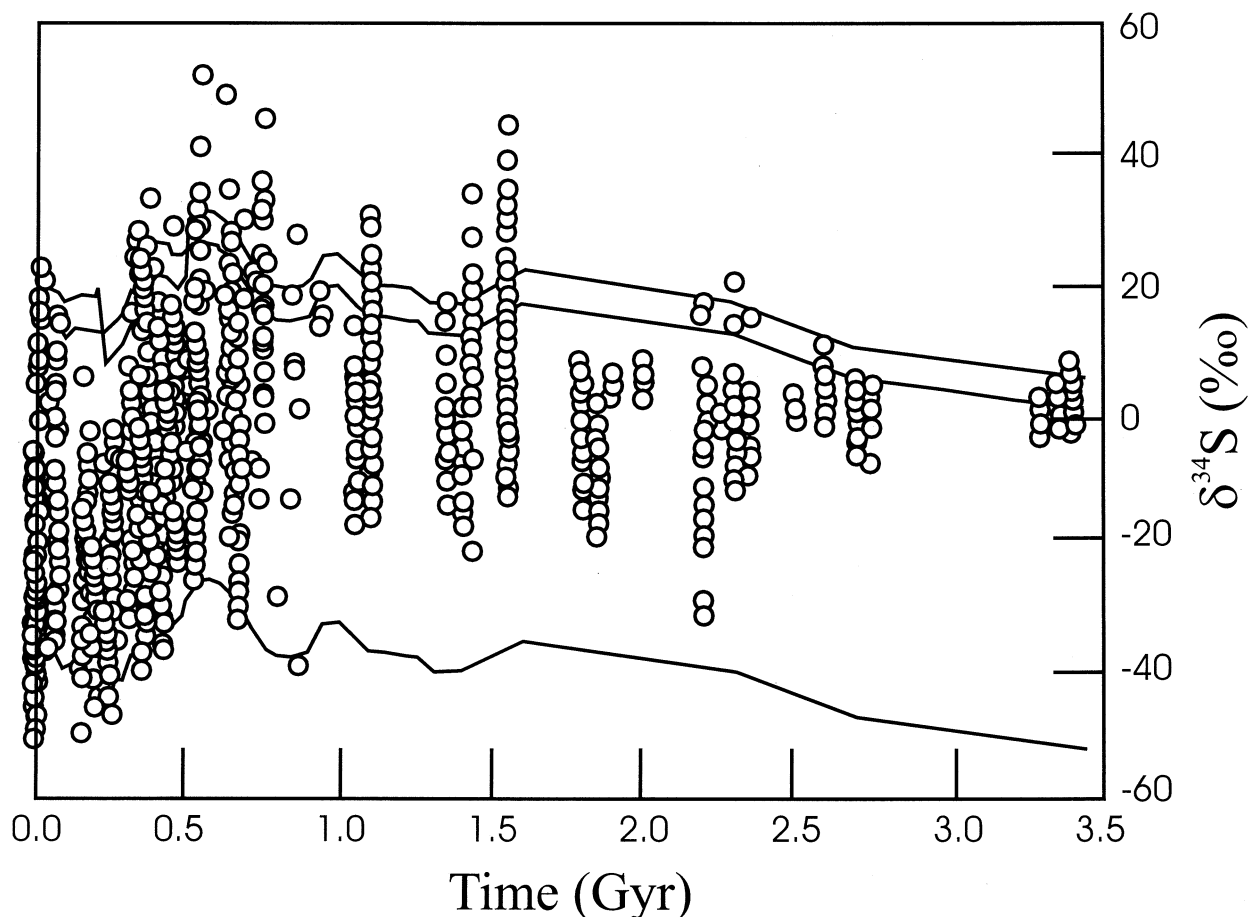


Fig. 10. The isotopic composition of sedimentary sulfides of probable biologic origin during the past 3.5 Ga (Canfield, 1998).

presence of cyanobacteria in the photic zone during at least the past 2.7 Ga. The generation of O_2 in the upper part of at least some of the oceans must have led to the oxidation of H_2S and HS^- to SO_4^{2-} in the photic zone and to an increase in the rate of SO_4^{2-} reduction within the oceans. In spite of this likely source of SO_4^{2-} in the photic zone, the concentration of SO_4^{2-} in the oceans as a whole was apparently sufficiently low before the G.O.E., that gypsum and anhydrite were deposited very rarely, if ever, in evaporitic settings. The Precambrian geochemistry of sulfur is therefore consistent with the hypothesis proposed in this paper. However, the factors that control the $\delta^{34}S$ value of marine sulfides are so many and so varied that reconstructions of the chemistry of the atmosphere and oceans based on the isotopic data of sulfur are still rather uncertain.

6. CONCLUSIONS

This paper proposes that the change in the composition of the atmosphere from anoxygenic to oxygenated ca. 2.3 Ga was due to a gradual increase in the oxidation state of volcanic gases and hydrothermal inputs. It is shown that the required increase in the f_{O_2} of volcanic gases was <0.5 log units, which is in keeping with the limits set by the Cr and V content of volcanic rocks erupted during the past 3.96 Ga.

The proposed model for the evolution of the atmosphere is consistent with what is known about the geochemistry of carbon, nitrogen, sulfur, and phosphorus, and with the likely escape rate of H_2 from the atmosphere before the G.O.E. However, the proposed explanation for the evolution of the atmosphere is not yet rigorously quantitative and should be regarded as an attractive and likely rather than as a proven model.

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APPENDIX 1

DESCRIPTION OF MASS BALANCE CALCULATIONS

Mass balance calculations are the traditional way to calculate the increase in the H₂/H₂O ratio of volcanic gases that is required to assure that the Earth’s atmosphere remains anoxic. The uncertainties in the mass balance data are, however, quite large, and calculations based on them are probably less certain than those presented in the body of this paper. Mass balance calculations are included here for the sake of completeness and to show that there is no serious disagreement between the results obtained with the two methods.

1. The Rate of Oxygen Use During Weathering

The rate of O₂ use during weathering is dominated by the oxidation of C^o, FeS₂, and “FeO,” the quantity of ferrous iron in phases other than FeS₂. The data needed to calculate the O₂ use during the weathering of average rock are summarized in Table A1.

The figures in column 1 represent the concentration of C^o, FeS₂, and “FeO” in average rocks undergoing weathering. The figures in column 2 represent the annual rate of O₂ use via the three reactions. The total rate of rock weathering today is taken to be $(2.0 \pm 0.2) \times 10^{16}$ gm/yr, and the reactions are assumed to go to completion during weathering.

Table A1.

The rate of O₂ use during weathering; data from Holland (1978). See text for explanation.

Reaction	1	2
1. C ^o + O ₂ → CO ₂	0.45 ± 0.1%	$(7.5 \pm 2.5) \times 10^{12}$ mol/yr
2. FeS ₂ + 15/2O ₂ + 7/2H ₂ O → Fe(OH) ₃ + 2H ₂ SO ₄	0.6 ± 0.2%	$(7.0 \pm 3.6) \times 10^{12}$
3. “FeO” + 1/4O ₂ → 1/2Fe ₂ O ₃	1.5 ± 0.6%	$(1.0 \pm 0.6) \times 10^{12}$
Total rate of O ₂ use =		$(15.5 \pm 6.7) \times 10^{12}$

Table A2.

The rate of O₂ production during sedimentation; data from Holland (1978).

Reaction	1	2
1. CO ₂ → C ^o + O ₂	0.6 ± 0.1%	$(10.0 \pm 3.3) \times 10^{12}$ mol/yr
2. Fe(OH) ₃ + 2H ₂ SO ₄ → FeS ₂ + 15/2SO ₂ + 7/2H ₂ O	0.6 ± 0.2%	$(7.0 \pm 3.6) \times 10^{12}$
3. “FeO” + 2SO ₂ → FeS ₂ + 5/2O ₂	0.2 ± 0.1%	$(0.8 \pm 0.4) \times 10^{12}$
4. SO ₂ + 1/2O ₂ + H ₂ O → H ₂ SO ₄	0.3 ± 0.1%	$-(0.3 \pm 0.1) \times 10^{12}$
5. 1/2Fe ₂ O ₃ → “FeO” + 1/4O ₂	1.5 ± 0.6%	$(0.9 \pm 0.4) \times 10^{12}$
Total rate of O ₂ production =		$(18.4 \pm 7.8) \times 10^{12}$

The total rate of O₂ use calculated in this fashion is $(15.5 \pm 6.7) \times 10^{12}$ mol O₂/yr.

2. The Rate of Oxygen Production During Sedimentation

The rate of O₂ production during sedimentation is dominated by the reverse of the three reactions in Table A1. The numbers are not, however, the same, because carbon and sulfur are added to sediments by volcanic and hydrothermal gases. The composition of average rock undergoing weathering is determined by the relative proportion of igneous and high-grade metamorphic rocks vs. sedimentary and low-grade metamorphic rocks (Holland, 1978). The former group comprises ~25%, the latter ~75% of the rocks being weathered today. Since the composition of modern sediments is similar to that of sedimentary rocks undergoing weathering, the O₂ generation during the deposition of new sediments can be calculated as shown in Table A2. O₂ generated by the deposition of C^o is 4/3 the rate of O₂ consumption via C^o oxidation of average rock exposed to weathering. O₂ generated via the deposition of FeS₂ consists of two parts. The first is simply the reverse of the oxidation reaction in Table A1, which adds $(0.6 \pm 0.2)\%$ FeS₂ to the new sediments. An additional $(0.2 \pm 0.1)\%$ FeS₂ is generated by reactions involving volcanic and hydrothermal inputs. Reaction 3 in Table A2 describes the addition of FeS₂ by the reduction of volcanic SO₂. Approximately half of the volcanic and hydrothermal sulfur is removed as a constituent of sulfates by the conversion of SO₂ to H₂SO₄. Reaction 4 in Table A2 shows that the O₂ loss via this reaction is approximately equal to $(0.3 \pm 0.1) \times 10^{12}$ mol/yr. The reduction of Fe₂O₃ to “FeO” via reaction 5 yields a gain of O₂ essentially equal to the rate of O₂ loss in Table A1. The inclusion of hydrothermal gases modifies the figure for the total O₂ generation in Table A2 only slightly.

The net excess of O₂ production during sedimentation over O₂ consumption during weathering is $\sim(2.9 \pm 1.0) \times 10^{12}$ mol/yr. The uncertainty in this figure is taken to be the sum of the uncertainties in reactions 3 and 4 of Table A2 plus the uncertainty in the estimate of the contribution of igneous and high-grade metamorphic rocks to the composition of average rock undergoing weathering.

The figures in Table A2 and the estimated O₂ excess production can be compared with figures derived from the quantity and composition of volcanic and hydrothermal inputs. The comparison is summarized in Table A3. The figures for C^o and S in column 1 are derived from the figures in Tables A1 and A2. They represent the increments of these elements that are added during sedimentation. The figure for O₂ in column 1 is the net rate of O₂ generation from Table A2.

The figure for C^o in column 2 is derived from an estimated flux of volcanic and hydrothermal (CO₂ + CO) of 6.0×10^{12} mol/yr (Marty and Tolstikhin, 1998) and assumes that 20% of this carbon is reduced to C^o and buried with sediments. The uncertainty in the estimated burial rate of C^o is large as shown, for instance, by the wide range of estimates for the total volcanic carbon flux in compilations such as those of Arthur (2000).

The figure for the rate of S addition to sediments in column 2 is derived from the same estimate of the total carbon flux and assumes a CO₂/SO₂ ratio of 6 in volcanic gases (Williams et al., 1992). As Symonds et al. (1994) have pointed out, the ratio of CO₂/SO₂ in

Table A3.

Comparison of the results of weathering and sedimentation calculations with the results based on volcanic and hydrothermal gas data; see text for explanation.

Process	1 from weathering and sedimentation calculations	2 from volcanic and hydrothermal fluxes
1. C ^o added	$(2.5 \pm 1.0) \times 10^{12}$ mol/yr	$(1.2 \pm 0.8) \times 10^{12}$ mol/yr
2. S added to sediments as FeS ₂ and sulfates	$(1.2 \pm 0.6) \times 10^{12}$	$(1.0 \pm 0.8) \times 10^{12}$
3. O ₂ added to atmosphere	$(2.9 \pm 1.0) \times 10^{12}$	÷
4. H ₂ added to atmosphere	÷	$(4.8 \pm 3.6) \times 10^{12}$
Φ	$1.4^{+0.3}_{-0.2}$	$1.7^{+0.5}_{-0.4}$

volcanic gases is highly variable. The estimate of the rate of addition of S to sediments in column 2 is therefore quite uncertain.

The data in Fig. 6 suggest that the ratio of $\Sigma C/H_2O$ is highly variable. The average value of this ratio seems to be (0.03 ± 0.02) . If we take the total C input to be 6×10^{12} mol/yr, the annual input of H₂O is then $(2.0 \pm 1.5) \times 10^{14}$ mol/yr. Since many volcanic gases have an f_{O_2} close

to FMQ, the corresponding H₂ input is $\sim(4.8 \pm 3.6) \times 10^{12}$ mol/yr, a quantity that can oxidize $(2.4 \pm 1.8) \times 10^{12}$ mol O₂/yr. The differences between the figures in column 1 and column 2 of Table A3 are clearly large, but the individual numbers agree within the stated uncertainties.

The value of Φ based on weathering and sedimentation calculations can be calculated readily. When $f = 1$, all of the volcanic sulfur is removed as FeS₂. The rate of O₂ generation due to the sulfur cycle is therefore $(1.6 \pm 0.8) \times 10^{12}$ mol/yr, the total O₂ generation rate is $(19.5 \pm 7.8) \times 10^{12}$ mol/yr, and the difference between the rate of O₂ generation and the rate of O₂ use during weathering is $(4.0 \pm 1.0) \times 10^{12}$ mol/yr rather than $(2.9 \pm 1.0) \times 10^{12}$ mol/yr. The value of Φ is therefore ~ 1.4 . The addition of hydrothermal gases to the calculations does not change the value of Φ significantly, but does increase its likely uncertainty.

The value Φ for calculations based on volcanic and hydrothermal data in column 2 of Table A3 can be estimated in a similar manner. The rate of O₂ generation due to the burial of C^o and the disposal of volcanic S is $(1.6 \pm 1.0) \times 10^{12}$ mol/yr. If all of the S were removed as a constituent of FeS₂, the rate of O₂ generation would become $(2.7 \pm 1.0) \times 10^{12}$ mol/yr. The value of Φ is therefore ~ 1.7 . This value of Φ and the value in column 1 of Table A3 are clearly > 1.0 . They are somewhat lower than the value of Φ estimated in the body of the paper based on analyses of volcanic gases, but perhaps not significantly lower. All three values of Φ suggest that rather small changes in the H₂/H₂O ratio of volcanic gas inputs would be sufficient to generate an anoxygenic atmosphere. The large uncertainties in all of these calculations should, however, be borne in mind before assigning a great deal of weight to the numbers in Tables A1, A2, and A3.