

Why the atmosphere became oxygenated: A proposal

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This paper is dedicated to the memory of Peter Deines (1936–2009).

Abstract

The increase in the oxidation state of the atmosphere during Earth history is well documented, but not the reasons for this process. The course of atmospheric evolution has been dominated by the effects of photosynthesis and by the composition of volcanic gases. The $\text{H}_2/\text{H}_2\text{O}$ ratio of volcanic gases has remained essentially constant during most of Earth history. It is here proposed that their $\text{CO}_2/\text{H}_2\text{O}$ and $\text{SO}_2/\text{H}_2\text{O}$ ratios have increased with time. A simple model for the degassing and the recycling of CO_2 , SO_2 , and H_2O can account for many of the major steps in the oxygenation of the atmosphere.

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1. INTRODUCTION

It is now generally, though not universally, agreed that the Earth's atmosphere was essentially free of O_2 until ca. 2.45 Ga (billion years ago), and that O_2 levels have increased irregularly since then, somewhat as shown in Fig. 1. The reasons for this oxygenation are not well understood (Canfield, 2005). The importance of volcanic gases (i.e. gases emitted by volcanoes) and green plant photosynthesis in determining the oxidation state of the present atmosphere was outlined previously (Holland, 2002), and it was shown that the average composition of volcanic gases early in Earth history must have been rather different from that of average volcanic gases today to account for the reducing composition of the Archean atmosphere. A simple explanation for the progressive oxidation of the atmosphere during Earth history involves a gradual decrease in the H_2 content of average volcanic gases, while their CO_2 and SO_2 content has remained essentially constant. At significantly higher H_2 concentrations in volcanic gases, enough H_2 would have been available to reduce the ca. 20% of volcanic CO_2 that have been reduced to CH_2O during most of the past 3.8 Ga, as well as to reduce all volcanic sulfur to FeS_2 , and to provide an excess of H_2 . The H_2 excess would have been balanced by H_2 escape into interplanetary space.

At the time when this explanation for the progressive oxygenation of the atmosphere was advanced (Holland, 2002), the constraints on the redox history of volcanic gases were sufficiently loose to make the explanation tenable. Since then it has been shown that changes in the O_2 fugacity of volcanic gases during the past 3.8 Ga have almost certainly been too small to accommodate the required decrease in the H_2 content of average volcanic gases (Canil, 2002; Lee et al., 2003; Li and Lee, 2004).

This paper proposes an alternative explanation for the progressive oxidation of the atmosphere. It posits that, while the $\text{H}_2/\text{H}_2\text{O}$ ratio in volcanic gases has not changed significantly, the $\text{CO}_2/\text{H}_2\text{O}$ and the $\text{SO}_2/\text{H}_2\text{O}$ ratio in volcanic gases have increased with time. It is proposed that during the Archean these ratios were so much lower than today, that the quantity of H_2 was sufficient to reduce 20% of the volcanic CO_2 to CH_2O , to reduce all the sulfur gases to FeS_2 and to supply a significant excess of H_2 to the atmosphere. The progressive increase in the $\text{CO}_2/\text{H}_2\text{O}$ and $\text{SO}_2/\text{H}_2\text{O}$ ratio of volcanic gases since then has led to the oxidation of the atmosphere, because the quantity of H_2 required to reduce 20% of the CO_2 to CH_2O and to reduce all the sulfur gases to FeS_2 began to exceed the supply of H_2 in volcanic gases. By the time this happened, oxygenic photosynthesis had developed. O_2 therefore appeared as a significant constituent of the atmosphere, and a progressively larger fraction of the volcanic sulfur gases was removed

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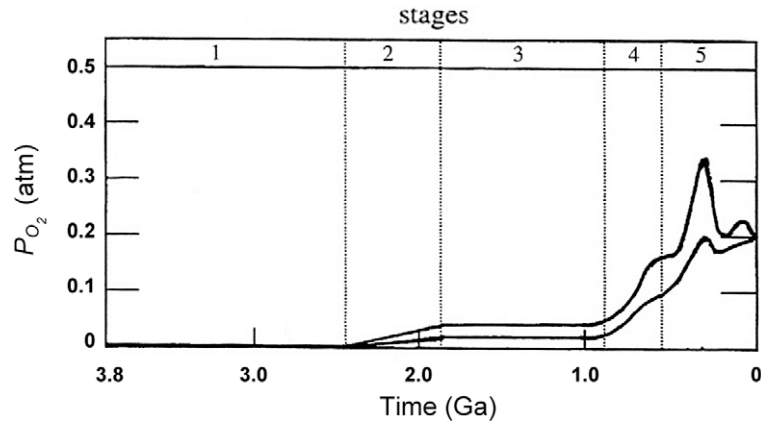


Fig. 1. The probable evolution of oxygen in the Earth's atmosphere (Holland, 2006). The two curves represent the likely upper and lower bounds on the O₂ content of the atmosphere. O₂ levels before 2.45 Ga were almost certainly less than 10⁻⁵ atm (Pavlov and Kasting, 2002).

into the solid earth as a constituent of gypsum (CaSO₄·2H₂O) and anhydrite (CaSO₄).

The rationale for proposing a gradual increase in the CO₂/H₂O and SO₂/H₂O ratio of volcanic gases is illustrated in the highly simplified representation of the Earth system in Fig. 2. Volcanic gases are mixtures of primordial and recycled gases. The presence of ³He in present day volcanic gases is the strongest evidence for the presence of primordial gases in today's mix (Porcelli and Turekian, 2004). However, recycled gases dominate the CO₂, SO₂ and H₂O output of volcanoes today. The recycling history of carbon and sulfur compounds differs from that of H₂O. Carbon and sulfur compounds in volcanic gases are removed into the solid earth in large part as solids: carbon as a constituent of carbonates (mainly CaCO₃ and CaMg (CO₃)₂) and organic matter (CH₂O), sulfur as a constituent of sulfides (mainly FeS₂) and sulfates (mainly CaSO₄ and CaSO₄·2H₂O). The rate of recycling of these phases by metamorphism and magmatism during subduction depends on their concentration in the subducted materials. Their concentration in subducted materials was almost certainly low early in Earth history and has increased with time as their quantity in the crust increased.

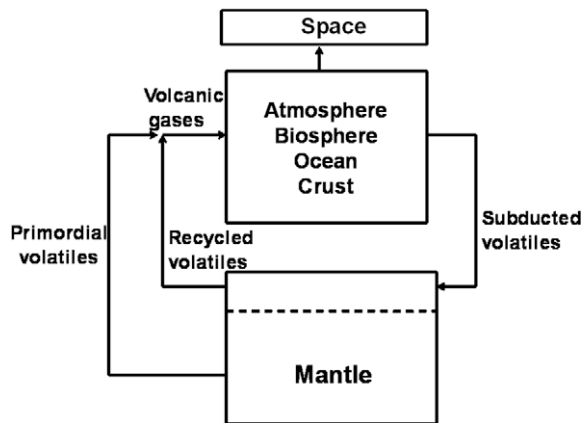


Fig. 2. A simplified model of the degassing of the mantle and the recycling of crustal volatiles.

The recycling rate of water follows a different pattern. The water content of subducted material depends largely on the water content of the subducted sediments and on the water content of the subducted oceanic crust. The total water content in subducted materials has probably depended only weakly on the volume of the contemporary oceans. A progressive increase in the carbon and sulfur content of subducted material coupled with a near-constancy of its water content must have led to a progressive increase in the CO₂/H₂O and SO₂/H₂O ratio of volcanic gases generated by the release of these volatiles from the subducted material. It is proposed that this increase, together with the near-constancy of the H₂/H₂O ratio in volcanic gases, and the continued reduction of CO₂ to CH₂O account for much of the progressive oxidation of the atmosphere.

Many of the parameters and functional relationships that determine the operation of the simplified Earth system of Fig. 2 are poorly defined, and it can be argued that attempts to go beyond a qualitative description of the evolution of this system are premature. Nevertheless, there are sufficient data to construct a useful first-order quantitative model of the system, which can be modified to accommodate at least some of the neglected complexities of Earth history (Zhang and Zindler, 1993; Hayes and Waldbauer, 2006; Claire et al., 2006).

2. A FIRST-ORDER MODEL

The release of primordial volatiles from the degassing mantle must be related to their quantity, i.e. the number of mols, M_M , in the mantle by an expression such as

$$\frac{dM_M}{dt} = -aM_M e^{-\lambda t} \quad (1)$$

where the term $e^{-\lambda t}$ represents the effect of the progressive slowing of the Earth system and where "a" is a parameter that depends on a number of geologic processes. If "a" and λ are time invariant, it follows that

$$\ln \frac{M_M}{M_M^0} = \frac{a}{\lambda} (e^{-\lambda t} - 1) \quad (2)$$

where M_M^O = initial number of mols of the volatile in the mantle and t = time elapsed since the beginning of degassing.

An expression of this type should describe the primordial degassing of CO_2 , SO_2 , and H_2O . The rate of recycling, R , of carbon and sulfur is probably governed by an expression such as

$$R = bM_C e^{-\lambda t} \quad (3)$$

where M_C represents the number of mols of carbon and of sulfur in the crust and “ b ” is a parameter that depends on a number of geologic processes. The term $e^{-\lambda t}$ again represents the slowing of the Earth system with time. The volcanic flux, F , of CO_2 and SO_2 is the sum of their degassing and recycling rates:

$$F = \{aM_M + bM_C\}e^{-\lambda t} \quad (4)$$

Since

$$M_C = M_M^O - M_M \quad (5)$$

$$F = M_M^O \left\{ b + (a - b) e^{\frac{a}{b}(e^{-\lambda t} - 1)} \right\} e^{-\lambda t} \quad (6)$$

The volcanic flux of H_2O is taken to be independent of the ocean volume. Hence the volcanic flux of water is described by the equation

$$F = \{aM_M + b\}e^{-\lambda t} \quad (7)$$

$$= M_M^O \left\{ a e^{\frac{a}{b}(e^{-\lambda t} - 1)} + \frac{b}{M_M^O} \right\} e^{-\lambda t} \quad (8)$$

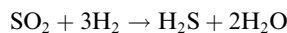
Note that the values of a and b for the fluxes of CO_2 , SO_2 , and H_2O are not the same. The flux calculations are anchored by the values of the present-day fluxes. Representative values of these are compiled in Tables 1 and 2 together with estimates of the quantity of the volatiles in

Table 2
Hydrothermal fluxes of CO_2 , H_2S , H_2 , and CH_4 (data kindly supplied by M. Mottl).

	Average concentration (mmol/kg)	Maximum concentration (mmol/kg)	Estimated annual flux (10^{12} mol/yr)
CO_2	14	285	0.57
H_2S	4.5	110	0.18
H_2	0.9	40	0.03
CH_4	1.3	16	0.05

the crust, the depleted (degassed) mantle, and the undepleted mantle. The figures for the present day fluxes and their crustal quantities are reasonably well known, probably to within a factor of two. Differences of opinion regarding the present day volcanic H_2 flux are quite large and deserve further discussion. Hayes and Waldbauer (2006) use Giggenbach’s (1996) value of ca. 0.01 for the $\text{H}_2/\text{H}_2\text{O}$ ratio in volcanic gases. Taking the arc magmatic-water flux to be 17×10^{12} mol/yr, they obtain a volcanic hydrogen flux of 0.17×10^{12} mol/yr. This neglects other volcanic areas. Jarrard’s (2003) value for the volcanic H_2O flux is 102×10^{12} mol/yr. My estimate (Holland, 2002) was a little lower, 80×10^{12} mol/yr. A reasonable value for the volcanic H_2 flux is therefore ca. 0.9×10^{12} mol/yr.

In most volcanic gases H_2S is the product of the reaction of SO_2 with H_2 during cooling:



To avoid having to deal with two sulfur gases, I have backreacted the H_2S in volcanic gas analyses (Giggenbach, 1996) to regenerate the original quantity of SO_2 and H_2 . Hayes and Waldbauer (2006) have used a volcanic SO_2 flux of $0.16\text{--}0.28 \times 10^{12}$ mol/yr from arc volcanoes. If this is

Table 1

Upper part: literature data for the parameters needed for the computation of the curves in Fig. 3. The arrows mark the figures that were used in the computations. Lower part: values of parameters a and b that were used in the computation of the curves in Fig. 3.

	CO_2	SO_2	H_2O	H_2
Present day volcanic flux (10^{12} mol/yr)	ca. 3.6 (1) 2.3±0.6 (2) 3.0 (3)	0.33-1.32 (7) 1.0 (3) [#]	80 (3) [#] 102 (9)	0.8-3.9 (7) [*] 2.4 (3) [#]
Present day quantity in atmosphere, ocean and sedimentary rocks	8.5 (1) 7.64(4) 7±1 (2) 5.7 (5)	0.43 (5) 0.425 (4)	83 (3) 89 (10)	None
Present day quantity in degassed (upper) mantle (10^{21} mol)	18_{-6}^{+9} →5.5 (6)	→12.0 (3) 14±4 (8)	→33 (2, 3) 143 (8, 11)	None
Original quantity in degassed (upper) mantle (10^{21} mol)	25_{-6}^{+9} (2) →11.6	→12.4 (3)	→116 (3)	None
a (yr^{-1})	0.274×10^{-9}	1.23×10^{-11}	0.462×10^{-9}	
b (yr^{-1})	1.24×10^{-9}	6.68×10^{-9}	$bM_M^O = 228 \times 10^{12}$	

1. Hayes and Waldbauer (2006); 2. Zhang and Zindler (1993); 3. Holland (2002); 4. Holser et al. (1988); 5. Lerman et al. (2007); 6. Jambon (1994); 7. Canfield et al. (2006); 8. Saal et al. (2002); 9. Jarrard (2003); 10. Lecuyer et al. (1998); 11. Data supplied by M. Mottl in 2008.

* The H_2 flux has been calculated after converting all the volcanic H_2S to SO_2 .

[#] These values include hydrothermal fluxes.

scaled up as was the H₂ flux, one obtains a total SO₂ flux of 0.8–1.4 × 10¹² mol/yr. This agrees with my figure in Table 1. Hayes and Waldbauer (2006) use a range of 1.0–0.05 for the H₂S/SO₂ ratio in volcanic gases. This translates into an H₂S flux of 0.04–1.4 × 10¹² mol/yr. If this is backreacted to SO₂ and H₂, the reaction adds 0.12–4.2 × 10¹² mol/yr to the total H₂ flux. Their (recalculated) H₂ flux is therefore ca. (1.0–4.9) × 10¹² mol/yr, a range which brackets my estimate of 2.4 × 10¹² mol/yr.

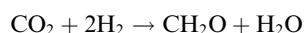
Sleep and Bird (2007) adopted Hayes and Waldbauer's (2006) figure of 0.17 × 10¹² mol/yr for the volcanic H₂ flux. They added 0.06 × 10¹² mol/yr H₂ from hot basaltic vents and 0.19 × 10¹² mol/yr H₂ from serpentine vents to yield a total H₂ flux of 0.42 × 10¹² mol/yr. This is surely a minimum figure. If the volcanic contribution of H₂ is increased as above by a factor of about 5, Sleep and Bird's (2007) H₂ flux becomes 1.1 × 10¹² mol/yr. They cite no figures for their H₂S fluxes, but it seems likely that there would be no significant difference between their total reconstituted H₂ flux and mine, also none between theirs and my earlier, much maligned range of (4.8 ± 3.6) × 10¹² mol/yr for the total H₂ flux (Holland, 2002).

The hydrothermal fluxes are based on a new compilation by M. Mottl. The concentration range of the volatiles in high temperature hydrothermal vents is very large. The average values in Table 2 are therefore rather uncertain. Fortunately the hydrothermal fluxes are not a major part of the total present day volatile fluxes. In the calculations of the past fluxes the same present day fluxes were used as in Holland (2002).

The concentration of the volatiles in the depleted and undepleted mantle, and the changes in the release rates to the crust are still poorly constrained (see below). Flux calculations have therefore been made with a range of values

of this parameter. For any given set of values of M_M at present, M_M^0 , and λ the values of “ a ” can be calculated from Eq. (2). With these values and estimates of the present day fluxes, the parameters “ b ” for CO₂ and SO₂ can be calculated from Eq. (4) and for H₂O from Eq. (7).

The total hydrogen supply rate today is approximately 0.03 times the H₂O flux. Since the oxygen fugacity of volcanic gases has not changed significantly during much of Earth history, the H₂/H₂O ratio has been nearly constant and close to its present value. The H₂ demand has depended on the fraction of CO₂ that has been reduced to CH₂O and the fraction of SO₂ that has been reduced to FeS₂. The first reaction consumes two mols of H₂ per mol of CO₂ reduced via photosystem I to organic matter, CH₂O



The isotopic composition of carbon in marine carbonates (Shields and Veizer, 2002) indicates that ca. 20% of volcanic CO₂ has been reduced to CH₂O during much of geologic time. Hence the H₂ demand for this reaction has been 0.4 times F_C , the CO₂ flux. If all the emitted volcanic SO₂ is reduced to FeS₂ by reaction with “FeO”,



The H₂ demand for this process equals 2.5 times F_S , the SO₂ flux. The total H₂ demand, D_{H_2} , is then

$$D_{\text{H}_2} = 0.4F_C + 2.5F_S \quad (9)$$

The calculated values of the H₂ supply and the H₂ demand during Earth history are shown in Figs. 3 and 4. The two sets of curves are very different. The H₂ supply decreases continuously, because both the degassing rate and the recycling rate have decreased with time. On the other hand, the H₂ demand first rises sharply, because the

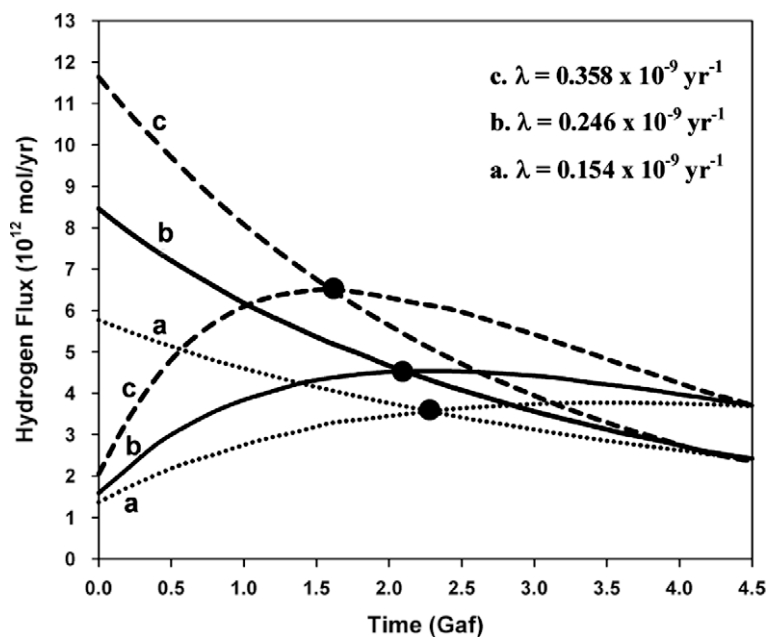


Fig. 3. The variation of the H₂ supply and the H₂ demand as a function of time for three values of the decay constant λ . Time is measured in billions of years forward (Gaf) from the origin of the Earth. The parameters used in the calculations are listed in Tables 1–3.

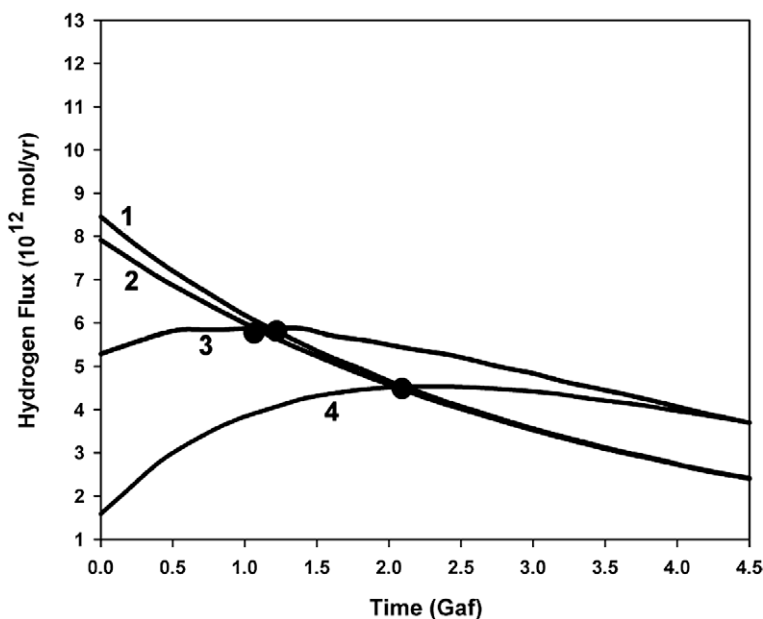
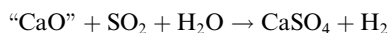


Fig. 4. The variation of the H₂ supply and H₂ demand as a function of time for several values of the fraction of volatiles that have been released from the depleted mantle. Time is measured in billions of years forward (Gaf) from the origin of the Earth. The parameters used in the calculations are listed in Tables 1–3.

decrease in the degassing rate of CO₂ and SO₂ is more than offset by the increase in their recycling rate. The H₂ demand curve then flattens out, and finally decreases due to the gradual slowing of the Earth system. As a result, the curves for the H₂ demand and the H₂ supply intersect. Early in Earth history, to the left of the intersection, the supply of H₂ exceeded the H₂ demand. Hence excess H₂ was present in the Earth's atmosphere. Its partial pressure, together with that of CH₄ and other hydrocarbons, was such that the rate of H₂ escape into interplanetary space was equal to the rate of excess volcanic H₂ input. To the right of the intersection of the H₂ demand with the H₂ supply curves, the H₂ demand exceeded the H₂ supply. Not enough volcanic H₂ was available to reduce all of the volcanic SO₂ to FeS₂. The atmosphere therefore became oxidizing, and part of the volcanic SO₂ was ultimately removed as a constituent of gypsum (CaSO₄·2H₂O) and/or anhydrite (CaSO₄). In terms of the H₂ budget



This reaction acted both to reduce the H₂ demand for FeS₂ production and to generate additional H₂ to balance the H₂ budget. The fraction of volcanic SO₂ that must have been oxidized to SO₃ can be determined from the calculated volcanic SO₂ flux and the gap between the calculated H₂ supply and the H₂ demand curves in Figs. 3 and 4. The fraction is zero at the crossover point. It has now reached a value of ca. 0.4 (Holland, 2002). This value is consistent with the average $\delta^{34}\text{S}$ value of pyrite and of gypsum/anhydrite today. The H₂ demand curve has not quite coincided with the H₂ supply curve, because O₂ has built up in the atmosphere. However, the average build-up rate of O₂ (0.013×10^{12} mol/yr) has been so slow, that its effect would be barely visible if it were included in Figs. 3 and 4. The

three sets of curves in Fig. 3 explore the effect of differences in the value of λ on the supply and demand of H₂. For the curves marked "a" the value of λ is 0.154×10^{-9} /yr. This implies that the Earth has slowed by a factor of 2.0 during the past 4.5 Ga. For the curves marked "b" the value of λ is 0.246×10^{-9} /yr reflecting a slowing by a factor of 3.0; for the curves marked "c" the value of λ is 0.358×10^{-9} /yr and the slow-down is by a factor of 5.0. A value of 4 is perhaps closest to the secular decrease in the rate of heat generated by the radioactive decay of the Earth's K, U, and Th (Davies, 1980). The crossover intersection for a λ value of 0.246×10^{-9} /yr occurs close to a forward age of 2.1 Ga, i.e. 2.45 Ga ago. This is close to the time of the appearance of O₂ in the atmosphere as indicated by the end of the major mass independent fractionation of sulfur in crustal rocks (Farquhar et al., 2000; Farquhar and Johnston, 2008). For values of λ smaller than 0.246×10^{-9} /yr the crossover intersection occurs later in Earth history; for larger values of λ it occurs earlier. Fig. 4 shows that differences in the choice of the fraction of water degassed from the upper mantle affects the H₂ supply curve only little. Significant reductions in the retention of carbon and sulfur in the degassed upper mantle shift the intersection of the hydrogen supply and demand curves closer to the origin of the Earth.

3. TESTING AND REFINING THE MODEL

3.1. The Archean CO₂ flux

The composition of early Archean sedimentary rocks offers a test of the model between ca. 3.8 and 3.0 Ga. Condie's (1993) compilation of the chemical composition of igneous and sedimentary rocks permits an estimate of the approximate loss of MgO and CaO during the conversion

Table 3
Additional construction parameters used in Figs. 3 and 4.

λ (yr ⁻¹)	$(\frac{M_M^{\text{Present}}}{M_M^0})_{\text{CO}_2}$	$(\frac{M_M^{\text{Present}}}{M_M^0})_{\text{SO}_2}$	$(\frac{M_M^{\text{Present}}}{M_M^0})_{\text{H}_2\text{O}}$
Fig. 3			
a. 0.154×10^{-9}	0.474	0.965	0.284
b. 0.246×10^{-9}	0.474	0.965	0.284
c. 0.358×10^{-9}	0.474	0.965	0.284
Fig. 4			
1. 0.246×10^{-9}	–	–	0.284
2. 0.246×10^{-9}	–	–	0.500
3. 0.246×10^{-9}	0.200	0.800	–
4. 0.246×10^{-9}	0.474	0.965	–

Table 4
Composition of Archean juvenile continental crust, graywackes and cratonic shales (Condie, 1993).

	MgO (%)	CaO (%)
Map model for the average composition of juvenile upper continental crust		
$t > 3.5$ Ga	3.40	3.51
3.5–2.5 Ga	2.57	3.58
Restoration model for the average composition of juvenile upper continental crust		
$t > 3.5$ Ga	4.06	3.81
3.5–2.5 Ga	2.89	3.80
Average	3.23 ± 0.73	3.67 ± 0.15
Average chemical composition of graywackes		
Early Archean	3.50	2.50
Late Archean	3.30	2.60
Average	3.40 ± 0.10	2.55 ± 0.05
Average chemical composition of Archean cratonic shales	3.88	0.64

of average igneous rocks to the graywackes which dominate early Archean sedimentary suites. The data in Table 4 show that very little MgO but a significant quantity of CaO was lost during this conversion. If we take the MgO loss during early Archean weathering to be zero, and the CaO loss to be 1.1%, then the CO₂ that was demanded to precipitate the CaO loss as a constituent of CaCO₃ was 0.20 mol/kg of parent rock.

The CO₂ flux that was needed to generate such sediments at the present weathering rate of ca. 2×10^{13} kg/yr would therefore have been 4×10^{12} mol/yr. This is close to the CO₂ flux predicted by the model for the values of the several parameters that were used in the computations for Figs. 3–5. Higher fluxes are predicted for larger values of λ .

Limestones are scarce in early Archean sedimentary sequences. This is not surprising within the framework of the proposed model. If intense mantle degassing and the release of volatiles from infalling objects added large quantities of CO₂ to the atmosphere during and shortly after the accretion of the Earth (Allègre, 2008), much of this CO₂ must have been blown off and/or returned to the mantle, presumably largely as a constituent of carbonates, before the onset of the present regime. If this is correct, the point of zero time in Figs. 3–5 coincides with the time of this onset.

3.2. The Archean SO₂ flux

An interesting check on the validity of the proposed evolution of the Archean sulfur cycle is offered by Cameron and Garrels' (1980) paper on the composition of Precambrian shales from the Canadian Shield. Fig. 6 shows their data for 406 shales from eight stratigraphic sections between 3.0 and 2.5 Ga. Five groups of shales contain only very small quantities of organic carbon and pyrite; the data for the remaining three groups fall close to a line with a C/S weight ratio of 1.02, i.e. a molar C/S ratio of 2.72. The average isotopic composition of sulfur, $\delta^{34}\text{S}$, of the entire set is

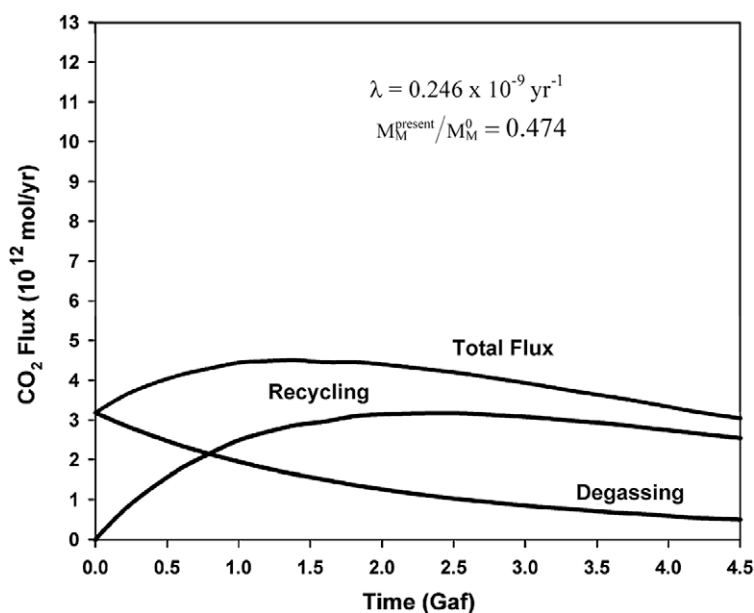


Fig. 5. The evolution of the degassing, recycling, and total CO₂ flux for the indicated values of the model parameters.

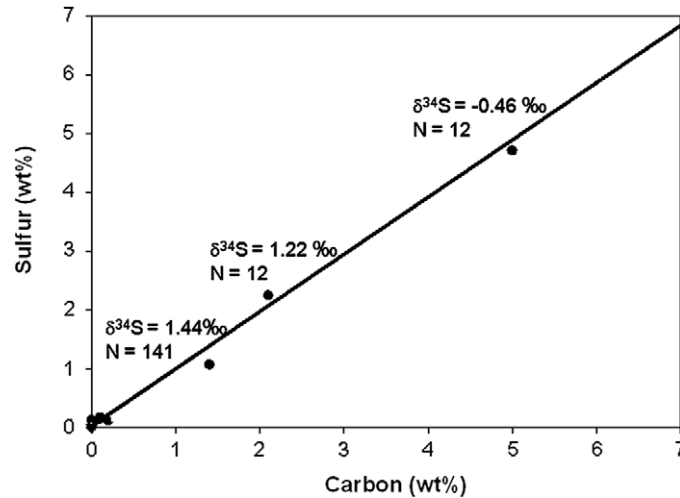


Fig. 6. The sulfur and carbon content of late Archean shales (Cameron and Garrels, 1980).

$1.31 \pm 0.3\%$. This suggests that nearly all late Archean sulfides were deposited in reducing environments, although seven sulfides in South African late Archean sediments have a slightly higher average $\delta^{34}\text{S}$ value, $4.3 \pm 1.6\%$ (Watanabe et al., 1997).

The isotopic composition of carbon in late Archean carbonates and organic residues indicates that organic carbon accounted for 16–20% of the total carbon inventory. Hence Fig. 6 indicates that the ratio of total carbon to total sulfur in late Archean sedimentary rocks was 15.3 ± 1.7 mol/mol. Figs. 5 and 7 suggest that the ratio of the degassing input of carbon to that of sulfur decreased from 19 to 10 during Earth history. At $t = 1.8$ Gaf, i.e. during late Precambrian time, the estimated ratio is ca. 14 mol/mol. The agreement between the predicted and the observed values of the ratio of the volcanic CO_2 and SO_2 inputs is reassuring.

3.3. The Archean excess hydrogen flux

The calculated Archean excess flux of hydrogen, i.e. the difference between the H_2 supply and the H_2 demand, de-

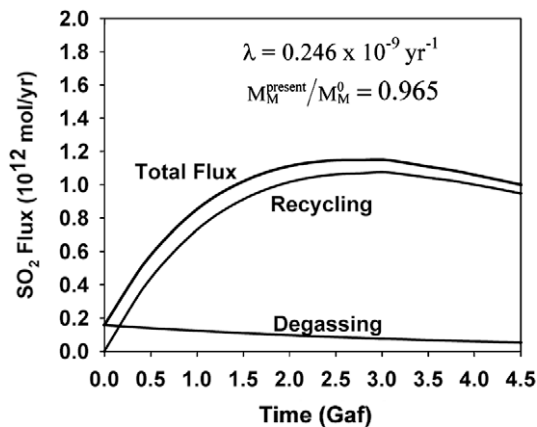


Fig. 7. The evolution of the degassing, recycling, and total SO_2 fluxes for the indicated values of the parameters.

creased markedly with time. Early in Earth history it was between ca. 4×10^{12} and 10×10^{12} mol/yr. It disappeared at the crossover of the H_2 supply curves with the H_2 demand curves. The excess H_2 was lost to interplanetary space. It is difficult to define the total quantity of atmospheric hydrogen in all H-containing species at the base of the exosphere that is needed to support the estimated rates of hydrogen loss, because it is not known whether the hydrogen escape rate was limited by diffusion through the homopause or by energy considerations at the exobase. Fortunately, it is easy to estimate an upper limit for the hydrogen escape flux, ϕ , because hydrogen cannot escape faster than the diffusion limit (Hunten, 1973; Walker, 1977). Hence

$$\phi \leq 2.5 \times 10^{13} f_T(\text{H}) \text{ atoms cm}^{-2} \text{ s}^{-1} \quad (10)$$

where

$$F_T(\text{H}) = f_{\text{H}} + 2f_{\text{H}_2} + 2f_{\text{H}_2\text{O}} + 4f_{\text{CH}_4} + \dots \quad (11)$$

is the sum of all H atoms in H-containing species at the base of the exosphere. In most geochemists' nomenclature the maximum rate of escape is

$$\phi \leq 6.67 \times 10^{15} P_{\text{H}_2} \text{ mols/yr} \quad (12)$$

where P_{H_2} is the atmospheric hydrogen pressure in atm. This implies that for a hydrogen escape rate of 3×10^{12} mol/yr the pressure of hydrogen gases would have been equal to or greater than 4.5×10^{-4} atm. If a good deal of the hydrogen was present as a constituent of CH_4 and other hydrocarbons, their warming effect together with that of CO_2 probably accounted for the apparent absence of glaciers during most of the Archean, a time of low solar luminosity (Kasting et al., 2001; Kasting, 2005; Haqq-Misra et al., 2008).

The excess hydrogen flux during the Archean may well have been greater than suggested by Figs. 3 and 4. Kump and Barley (2007) have pointed out that volcanic gases from submarine volcanoes are somewhat more reducing than those from subaerial volcanoes, and have proposed that a shift to more subaerial volcanic gases occurred at

the Archean–Proterozoic boundary. The proposed drop in the H_2 supply rate at that time may have triggered the rise of O_2 . The magnitude of the proposed offset is not known; it was probably not major.

The presence of larger quantities of ultramafics in Archean igneous rocks supplies a second reason for believing that the H_2 supply rates during the Archean were somewhat higher than the calculated values in Figs. 3 and 4 (Sleep et al., 2004). Serpentinization of ultramafic rocks below the seafloor generates fluids that are significantly more reducing than those generated during the alteration of basalts. Serpentinites also contain much more water than the hydrothermal alteration products of basalts. The amount of water and the accompanying H_2 that are released from subducted oceanic crust therefore increases with their serpentine content. The proportion of ultramafic rocks decreased rapidly toward the end of the Archean; their effect on the H_2 supply curve was therefore largely restricted to the Archean.

Claire et al. (2006) have proposed a third reason for an enhanced H_2 supply rate in the Archean: a decline in the flux of reducing gases from the crust that was driven by its irreversible secular oxidation due to hydrogen escape to space from the preoxic atmosphere. Their model assumes that the oxidation state of the mantle has been strongly buffered, but that the continental crust has become progressively more oxidized due to hydrogen escape. They suggest that the f_{O_2} of the bulk crust may have increased by ca. 1.5 log units from its initial to its present configuration, and that a resultant decrease in the flux of reducing gases is a plausible cause of the oxic transition. There is no direct evidence to support this suggestion, and there is some evidence to the contrary. The average FeO content of pre-2.3 Ga shales is ca. 5.6%; their Fe_2O_3 content is ca. 1.3% (Bekker et al., 2003a,b). This places their Fe_2O_3/FeO ratio well below that of average igneous rocks, an observation that is not consistent with an oxidized crustal source for these shales as proposed by Claire et al (2006).

The suggested adjustments to the excess H_2 flux computed above affected the H_2 supply curve. The H_2 demand curve is also subject to adjustment. As far back in time as the record of the $\delta^{13}C$ value of organic and carbonate carbon extends, the fractionation of the carbon isotopes seems to have been such that 16–20% of the carbon introduced into the atmosphere has been removed as elemental carbon. The conclusion has been challenged by Bjerrum and Canfield (2004) and Canfield (2005), who proposed that the burial rate of organic carbon early in Earth history was much smaller than suggested by the isotopic record of carbon in sedimentary rocks. This proposition is based on the supposed presence of a $\delta^{13}C$ depleted reservoir of carbonates in the oceanic crust. This is not, however, consistent with Nakamura and Kato's (2004) measurements of the $\delta^{13}C$ value of 3.46 Ga carbonatized basalts from the Marble Bar area in Australia. It therefore seems best to retain the standard interpretation of the $\delta^{13}C$ record.

The reasons for the reduction of 16–20% of the volcanic input of CO_2 during the Archean are not well understood. 3.5 Ga ago, the estimated volcanic H_2 flux was roughly 6.0×10^{12} mol/yr (see Fig. 3). Of this quantity ca.

2.0×10^{12} mol were needed to reduce the volcanic flux of SO_2 to H_2S , and to remove the H_2S as a constituent of FeS_2 (see Fig. 7). The remaining 4.0×10^{12} mol/yr was used in part to reduce CO_2 to CH_2O ; the rest must have escaped into interplanetary space as described above.

At an atmospheric H_2 pressure of 450×10^{-6} atm the concentration of H_2 in seawater at the air–water interface at 25 °C would have been 3.2×10^{-7} mol/kg (i.e. 320 nmol/kg seawater) (Seiler and Schmidt, 1974). If the area of the oceans was the same as today, the quantity of H_2 in the upper 100 m of the oceans would have been ca. 1.1×10^{12} mol. As pointed out by Broecker and Peng (1982), the piston velocity of most gases in seawater is large enough to replace them once a month in the upper 100 m of the oceanic water column. An annual H_2 flux of ca. 13×10^{12} mol could therefore have been supplied to the photic zone of the oceans at a constant atmospheric H_2 pressure of 450×10^{-6} atm. This is so much larger than the flux of ca. 1.8×10^{12} mol/yr that was probably required to reduce 20% of the volcanic CO_2 flux 3.5 Ga ago, that the rate of H_2 supply to the photic zone was almost certainly not the factor that limited the fraction of volcanic CO_2 which was reduced to CH_2O at that time.

The most likely candidate for the role of limiting factor was the availability of phosphorus. The geochemistry of this element during the early Archean was probably not as complex as today (Compton et al., 2000), because the complexities related to the Fe^{2+} – Fe^{3+} and other redox couples (Colman and Holland, 2000) were not nearly as important as today. Apatite, the major phosphate mineral in most igneous rocks, is decomposed during weathering in all but alkaline soils. Today, most of the released phosphorus is reprecipitated as a constituent of Fe^{3+} and Al^{3+} phosphates. In the absence of atmospheric O_2 , the Fe^{3+} phosphates were absent or of minor importance. Wavellite, $Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$, and variscite, $AlPO_4 \cdot 2H_2O$, are the most common Al-phosphates in soils today (Stevenson, 1986), and were probably equally important repositories of phosphorus in Archean soils.

The concentration of phosphorus in surface waters saturated with variscite at 25 °C and at pH values between 6 and 7 is ca. 1×10^{-6} mol/l, i.e. ca. 30 $\mu g/l$, (Stumm and Morgan, 1996). This is greater than the estimated concentration of P in average unpolluted modern streams, 10 $\mu g/l$ (Meybeck, 1998). Gaillardet et al. (2004) did not give a value for the average P concentration in unpolluted streams. The range of P concentrations in the rivers which they cite ranges from 1.8 to 14.4 $\mu g/l$. If the flux of river water during the early Archean was comparable to the present day flux, the flux of P was probably ca.

$$\frac{10 \times 10^{-6} \text{ mol}}{31 \text{ kg}} \times 4 \times 10^{16} \frac{\text{kg}}{\text{yr}} = 1.3 \times 10^{10} \frac{\text{mol}}{\text{yr}}$$

This figure is obviously quite uncertain, but it is at least a starting point for estimating the availability of P as a nutrient for Archean organisms. The C/P ratio of organic matter buried in sedimentary rocks is highly variable. It is not equal to the Redfield ratio, but is frequently on the order of 250 mol/mol (Mach et al., 1987). On this basis a river flux of 1.3×10^{10} mol/yr P would have been able

to accompany a burial flux of ca. 3.2×10^{12} mol C/yr. This is significantly greater than the estimated organic carbon burial rate of ca. 0.9×10^{12} mol/yr. The result suggests that P was added to the oceans in excess of the amount that was buried with organic carbon, and that the excess P was removed by inorganic processes, probably as a constituent of marine apatite. This result should not, of course, be taken seriously, but it does suggest that enough P was added to the Archean oceans to supply the P requirements of the Archean biosphere. The precipitation of marine apatite may have been important in limiting the burial rate of P with organic carbon and hence in limiting the fraction of Archean volcanic CO_2 that was reduced to CH_2O .

Toward the end of the Archean, the flux of excess H_2 probably decreased rapidly. The most likely curves in Fig. 3 suggest that 3.0 Ga ago the excess H_2 flux had dropped to ca. 1.0×10^{12} mol/yr. By ca. 2.5 Ga ago, the excess had disappeared. Hydrogen levels in the atmosphere decreased concomitantly, as did the concentration of H_2 in surface waters. The biologic use of H_2 as an electron donor in photosynthesis became progressively less attractive, and the use of H_2O with the excretion of molecular oxygen became progressively more so. The isotopic composition of carbon in some organic matter became very negative ca. 2.76 Ga indicating the presence of methanotrophs in the biosphere (Hayes, 1994; Rye and Holland, 2000; Hayes and Waldbauer, 2006; Rasmussen et al., 2009). These organisms metabolize CH_4 and O_2 . Their presence is probably the best evidence among several (Buick, 2008) for the existence of late Archean oxygenic photosynthesis. It seems likely that the methanotrophs thrived in near-surface aqueous environments where CH_4 and nutrients were plentiful and where H_2 was scarce. These environments probably became O_2 oases. However, the presence of strong signals of the mass independent fractionation of sulfur (Farquhar and Johnston, 2008) in 2.5–2.7 Ga sulfides and sulfates shows that O_2 levels in the atmosphere were still less than ca. 10 ppm at that time. The end of the MIF signal of sulfur at ca. 2.5 Ga indicates that by then the rate of H_2 use and O_2 production in the generation of CH_2O had begun to exceed the input of H_2 required to reduce ca. 20% of the input of volcanic CO_2 and all of the input of volcanic SO_2 . If this account is correct, one does not have to invoke a nitrogen crisis (Falkowski and Godfrey, 2008) to account for the delay between the invention of oxygenic photosynthesis and the Great Oxidation Event.

3.4. The timing of the crossover

One of the most significant successes of the proposed model is its ability to explain the timing of the transition from a reducing to an oxidizing atmosphere. Geologically preferred values of the parameters in the controlling equations suggest that the H_2 supply and H_2 demand curves should have intersected ca. 2.5 Ga ago. But, as shown in Figs. 3 and 4, the time of the intersection is not seriously constrained, in part because there is considerable latitude in the choice of the several model parameters, in part due to the uncertainties described above, and in part because

some potential sources of uncertainty have been neglected altogether (see for instance Korenaga, 2008).

The availability of H_2 , CH_4 , and other reduced gases for use in photosynthesis via photosystem-I decreased with time as the intersection of the H_2 supply curve with the H_2 demand curve was approached. This is consistent with the use of photosystem-I early in Earth history and with the development of photosystem-II during the later part of the Archean. After the transition to an H_2 -deficient system, photosystem-I was of limited use, since reductants must have been scarce in the marine photic zone below an oxygenated atmosphere.

3.5. The Great Oxidation Event

The intense mass independent fractionation of the sulfur isotopes in sedimentary sulfide and sulfate minerals older than 2.5 Ga is strong evidence that Archean atmospheric O_2 levels were less than a few ppm. The absence of this fractionation in sediments younger than ca. 2.4 Ga indicates that O_2 levels had risen beyond a few ppm by that time (see for instance Mojzsis, 2007). The intersection of the H_2 supply curve with the H_2 demand curve is therefore well dated. The appearance of molecular O_2 had a profound effect on the geochemistry of iron, sulfur, and carbon in near-surface environments. Many shales deposited between 2.3 and 2.1 Ga are highly oxidized. Their average Fe_2O_3 content is ca. 1.5% greater and their FeO content ca. 1.5% smaller than in pre-2.3 Ga shales (Bekker et al., 2003a,b).

It could be argued that the difference between the Fe_2O_3 and FeO content of the pre-2.3 Ga and the 2.3–2.1 Ga shales in Bekker et al.'s (2003a,b) compilation is simply due to the oxidation of the younger shales during and since their diagenesis. However, the likelihood of diagenetic overprinting increases with the time that has elapsed since the deposition of sediments; yet it is the older, pre-2.3 Ga shales that are less oxidized than the younger shales. It is also possible that the sets of pre-2.3 Ga shales somehow escaped diagenetic oxidation, whereas the younger sets of shales did not; but the number of analyses in both data sets is sufficiently large, that this explanation is unattractive. Finally, the average Fe_2O_3 and FeO content of shales that are younger than 2.1 Ga is quite similar to that of shales deposited between 2.3 and 2.1 Ga (Ronov et al., 1990; Bekker et al., 2003a,b). This suggests that the difference between the Fe_2O_3 and FeO content of the pre-2.3 Ga and the 2.3–2.1 Ga shales is largely due to compositional differences at the time of deposition rather than due to differences imposed by postdepositional processes.

The isotopic composition of sulfur in Paleoproterozoic shales is variable and generally not close to 0‰ (Cameron and Garrels, 1980). Their $\delta^{34}\text{S}$ values are consistent with a post-Archean rise in the sulfate content of seawater and with the deposition of 2.1–2.2 Ga marine evaporites that contain gypsum and/or anhydrite (Schröder et al., 2008).

The disturbance of the carbon cycle during the Great Oxidation Event is evident in the large positive values and in the scatter of the $\delta^{13}\text{C}$ values of marine carbonates

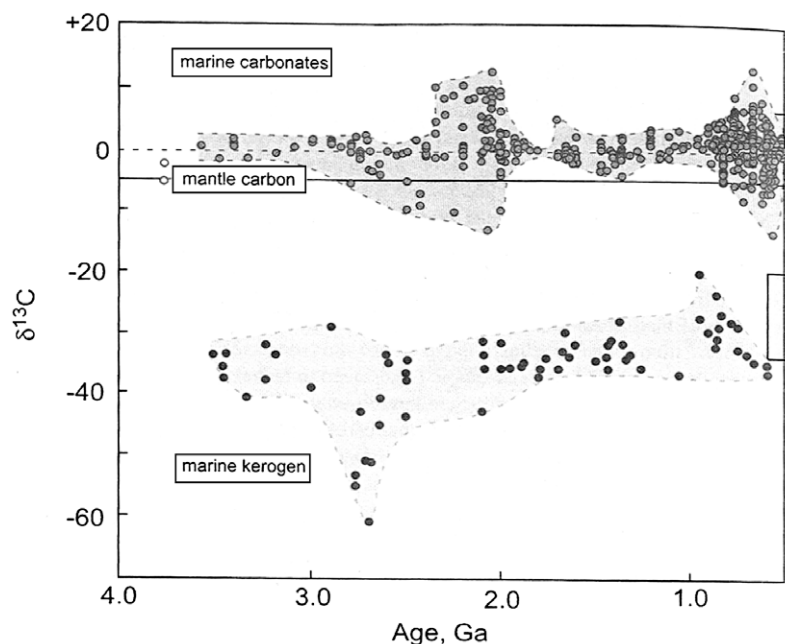


Fig. 8. The $\delta^{13}\text{C}$ evolution of marine carbonates and marine kerogen (Shields, 2007).

deposited between 2.3 and 2.0 Ga (Hayes and Waldbauer, 2006; see Fig. 8). Schidlowski et al. (1975) discovered the first evidence for this disturbance in the carbonates of the Lomagundi formation in Africa. Karhu found that the signal of the disturbance extended throughout the Fennoscandian shield (Karhu and Holland, 1996). Melezhik et al. (1999) pointed out that the high $\delta^{13}\text{C}$ values during the Great Oxidation Event are probably the product of a world wide marine signal that was enhanced in local environments, and have reexamined the length of the Lomagundi event (Melezhik et al., 2007). Bekker et al. (2008) have interpreted the wide range of the $\delta^{13}\text{C}$ values in these marine carbonates in terms of heterotrophic and chemotrophic productivity in a redox-stratified ocean during what is now generally called the Lomagundi event.

It is difficult to establish a convincing redox balance for the Lomagundi event, but the effects of the observed redox changes can be balanced (see Table 5). The average loss of FeO in shales during this period was ca. 1.5%, i.e. 0.21 mol/kg shale. The oxidation of this quantity of FeO to Fe_2O_3 generates 0.10 mol H_2 /kg shale. If the rate of weathering during the Paleoproterozoic was equal to the present rate, $(16 \pm 2) \times 10^{12}$ kg/yr, and if the products of weathering involved the oxidation of 50% of the weathered mass, the H_2 generated was ca.

$$(16 \pm 2) \times 10^{12} \times 0.50 \times 0.10 = (0.8 \pm 0.1) \times 10^{12} \text{ mol/yr}$$

After the crossover a small fraction of the sulfur in volcanic SO_2 was removed from the atmosphere-ocean system as a constituent of gypsum and/or anhydrite. If we take this fraction to be 0.10, the conversion of 90% of the flux of volcanic SO_2 to FeS_2 required $(2.5 \pm 0.4) \times 10^{12}$ mol H_2 /yr,

Table 5

An approximate redox balance before, during and after the Great Oxidation Event.

	Estimated Fluxes in 10^{12} mol/yr		
	2.7 Ga	2.2 Ga	1.7 Ga
<i>H₂ supply</i>			
Volcanic H_2 input	4.9	4.4	3.7
Oxidation of 10% of volcanic SO_2 to SO_3	0	0.1	0.1
Oxidation of FeO in shales	0	0.8	0.2
Conversion of weathered FeS_2 to CaSO_4	0	1.2	0.2
Total	4.9	6.5	4.2
<i>H₂ demand</i>			
Reduction of volcanic CO_2 to CH_2O	1.8	2.6	1.6
Reduction of volcanic SO_2 to FeS_2	2.7 (all)	2.5 (90%)	2.6 (90%)
H_2 escape into interplanetary space	0.4	0	0
Reduction of river HCO_3^- to CH_2O	0	1.4	0
Total	4.9	6.5	4.2

The C, S and H_2 fluxes are the same as those used to construct the curves marked "b" in Fig. 3.

and the oxidation of the remaining 10% of SO_2 to SO_3 released $(0.1 \pm 0.04) \times 10^{12}$ H_2 mol/yr.

Until the crossover, essentially all the sulfur in sedimentary rocks was present as a constituent of FeS_2 . If we adopt Cameron and Garrels' (1980) figure of 0.65% for the sulfur content of late Archean shales and again assume an early Proterozoic weathering rate equal to the present rate, the

conversion of 10% of the volcanic sulfur to CaSO_4 released ca.

$$\frac{6.5 \text{ mols}}{3.2 \text{ kg}} \times (16 \pm 2) \times 10^{12} \frac{\text{kg}}{\text{yr}} \times \frac{11}{3} \times 0.1$$

$$= (1.2 \pm 0.1) \times 10^{12} \frac{\text{mol}}{\text{yr}}$$

The distribution of carbon between carbonates and organic carbon during the Lomagundi event is rather uncertain, largely because of the wide spread in the $\delta^{13}\text{C}$ value of marine carbonates deposited during this period. $+4.7\text{‰}$ is a reasonable value for the average $\delta^{13}\text{C}$ of the marine carbonates (Shields and Veizer, 2002). The average $\delta^{13}\text{C}$ value of the contemporary organic matter was ca. -30‰ (Hayes and Waldbauer, 2006). The combination implies that ca. 28% of the volcanic carbon flux was buried with organic matter, the remainder with carbonates. The volcanic CO_2 flux was ca. $(4.5 \pm 1.0) \times 10^{12}$ mol/yr. The conversion of 28% of this flux to CH_2O required $(2.6 \pm 0.5) \times 10^{12}$ mol/yr H_2 .

Finally, the carbon in weathered Archean sediments consisted of ca. $18 \pm 2\%$ organic carbon and 82% carbonate carbon. During the Lomagundi event, the weathered sediments were reburied containing ca. 28% organic carbon and 72% carbonate carbon. At present, average river water contains ca. 0.38 meq/kg HCO_3^- . Of this ca. 0.31 meq/kg are derived from carbonates and 0.07 meq/kg from organic matter (Holland, 1978). The proportions would have been similar during the weathering of Archean rocks. At the same bicarbonate flux 0.035 meq/kg HCO_3^- would have to have been reduced to CH_2O during the Lomagundi event to generate a CH_2O -carbonate mixture containing 28% organic carbon. At the present river flow rate of 4×10^{16} kg/yr, the required H_2 flux rate would have been

$$(0.035 \pm 0.01) \times 10^{-3} \text{ mol/kg} \times 4 \times 10^{16} \text{ kg/yr}$$

$$= (1.4 \pm 0.4) \times 10^{12} \text{ mol/yr.}$$

The H_2 balance of the atmosphere–ocean system in Table 5 is based on very uncertain numbers. Yet it is surprisingly satisfactory. It implies that after the crossover of the

H_2 supply with the H_2 demand curve, when photosynthetically produced O_2 began to accumulate in the atmosphere, an abnormally large percentage of the CO_2 input from volcanism and weathering left the system as organic matter. The resulting O_2 flux oxidized a considerable fraction of the Fe^{2+} released during rock weathering and raised the SO_4^{2-} concentration of seawater sufficiently to generate marine evaporites containing CaSO_4 (Schröder et al., 2008). At the end of the Great Oxidation Event the near-surface geochemical cycle of iron had become modern.

Estimates of the oxygen content of the atmosphere during the G.O.E. are still uncertain. The chemistry of the well-studied, very extensive ca. 2.25 Ga Hekpoort paleosol in South Africa (Holland and Beukes, 1990) indicates that during its formation the O_2 content of the atmosphere was between ca.

2.5×10^{-4} and 9×10^{-3} atm (Yang and Holland, 2003). Equating this paleosol with modern laterites (Beukes et al., 2002) is not reasonable. The formation of modern laterites requires the presence of an abundant terrestrial biosphere or of extensive lakes or swamps. 2.25 Ga ago there was no terrestrial biosphere comparable to today's, and there is no evidence for the existence of sufficiently extensive lakes or swamps at the top of the very widespread Hekpoort paleosol.

The paleosols developed in Griqualand on the Ongeluk basalt at Wolhaarkop and at Drakenstein (Wiggering and Beukes, 1990) are highly oxidized, suggesting that the atmospheric P_{O_2} was greater than or equal to 0.03 atm during their formation. They and the Hekpoort paleosol all formed during the Great Oxidation Event. The Ongeluk paleosols may be slightly younger. We have suggested (Yang and Holland, 2003) that the oxygen content of the atmosphere rose dramatically between the formation of the two sets of paleosols. However, the average isotopic composition of sulfur in sedimentary pyrite at the end of the Great Oxidation Event was still close to 0‰ (Fig. 9), indicating that atmospheric P_{O_2} was not high enough to lead to the oxidation of a significant fraction of volcanic SO_2 to SO_3 and the burial of this SO_3 as a constituent of gypsum and anhydrite.

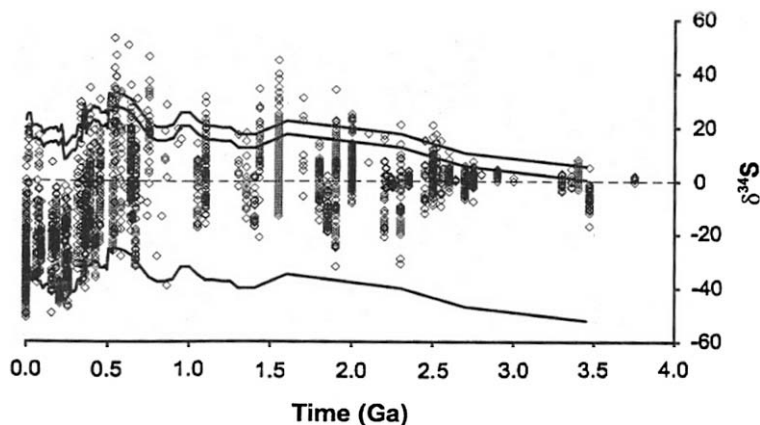


Fig. 9. Compilation of the isotopic composition of sedimentary sulfides (diamonds) through time. Also shown is a reconstruction of the isotopic composition of sulphate (upper line) and, as a guide, the isotopic composition of sulphate offset by 55‰ (lower line) (Canfield, 2005).

3.6. The Boring Billion, Snowball Earths, and the Phanerozoic

The Great Oxidation Event was followed by a long period of redox stasis, which is commonly called the Boring Billion. The average FeO and Fe₂O₃ content of shales changed very little during this period (Bekker et al., 2003a,b). The δ¹³C of marine carbonates returned to values close to 0‰, indicating that the gap between the H₂ demand for and the H₂ supply of volcanic gases was nearly constant. This differs from predictions based on the curves in Fig. 3. These indicate that the gap between the H₂ demand and H₂ supply should have increased significantly during the Boring Billion. A progressively larger fraction of volcanic SO₂ should therefore have been removed as a constituent of gypsum/anhydrite, and a progressively smaller fraction as a constituent of pyrite. At redox steady state after the Great Oxidation Event

$$0.4F_C + 2.5yF_S - (1 - y)F_S = F_{H_2} \quad (13)$$

where y = fraction of SO₂ that is removed as a constituent of FeS₂. It follows that

$$y = \frac{1}{3.5} \left[\frac{F_{H_2} - 0.4F_C}{F_S} + 1 \right] \quad (14)$$

The values of F_{H_2} , F_C , and F_S all depend on the value of λ and on the value of the parameters “ a ” and “ b ”. It is difficult to determine which of these parameters varied during the Boring Billion so as to give rise to the unexpectedly large values of y . The only changes that can be ruled out are periods of speeding up or slowing down of the entire system during which F_{H_2} , F_C , and F_S all changed by the same factor. One, somewhat attractive but quite speculative explanation for the large values of y during the Boring Billion, is a progressive increase in the storage of limestones and dolomites on carbonate platforms. This process could have decreased the subduction rate of carbonates. The CO₂ flux, F_C , would then have been reduced, and the value of y would have increased.

The last 300 Ma of the Proterozoic might be called the “Roaring 300”. It was the time of the Snowball Earths (Hoffman and Schrag, 2002), and the breakup of Rodinia.

The sulfur cycle had become modern by the end of this period. The δ³⁴S value of marine gypsum/anhydrite reached all-time highs close to +40‰, and the sulfate concentration of seawater had become comparable to that of present day seawater (Horita et al., 2002). Oxygen levels must have risen significantly during this period (see Fig. 1). The increase was probably a major factor in the evolution of animals with high metabolic rates.

The rapid change in the disposition of volcanic SO₂ into the sedimentary record during this period is not predicted by the model in which the values of λ and the “ a ” and “ b ” parameters are constant. Determining which of these parameters varied during the last 300 Ma of the Proterozoic is as difficult as doing so for the Boring Billion. A reasonable, but unproven, guess is that the increase in the SO₄²⁻ concentration of seawater altered the interaction of seawater with MOR basalts, that the rate of sulfur subduction may then have increased, and that the volcanic flux of SO₂ may have increased. As shown in Eq. (14), the effect of such an increase would have been to decrease y , the fraction of SO₂ which was incorporated in sedimentary pyrite.

The curves in Fig. 3 suggest that the gap between the H₂ supply and the H₂ demand changed very little during the Phanerozoic. This has, indeed, been the case. The average Fe₂O₃/FeO ratio of shales has increased very little since the Proterozoic (Ronov et al., 1990). The δ¹³C values of carbonates and the δ³⁴S values of gypsum and anhydrite have varied significantly, but in a compensatory manner as shown in Figs. 10 and 11. The inverse relationship between the changes of δ¹³C and those of δ³⁴S was documented in 1980 by Veizer et al. (1980) and was explored by me a few years later (Holland, 1984). Oxygen seems to have been traded rather efficiently between the crustal carbon and the crustal sulfur cycle. There seem to have been only minor changes in the overall redox state of the ocean–atmosphere–upper crust system. However, the O₂ content of the atmosphere and the sulfate concentration of seawater have fluctuated significantly (Bernier, 2004; Horita et al., 2002) (see Fig. 1). They have served as part of the control mechanism that has maintained the constancy or near-constancy of the overall redox state of the system during the Phanerozoic.

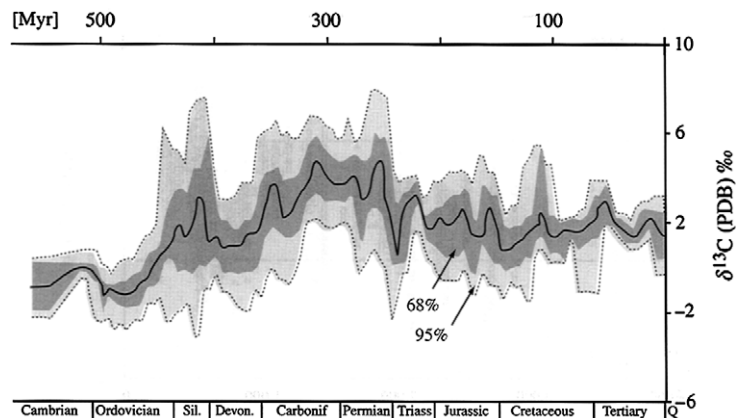


Fig. 10. The Phanerozoic δ¹³C trend for LMC shells. The running mean for ~4500 samples is based on a 20 Ma window and 4 Ma forward step. The shaded areas around the running mean include the 68% (±1σ) and 95% (±2σ) of all data (after Veizer and Mackenzie, 2004).

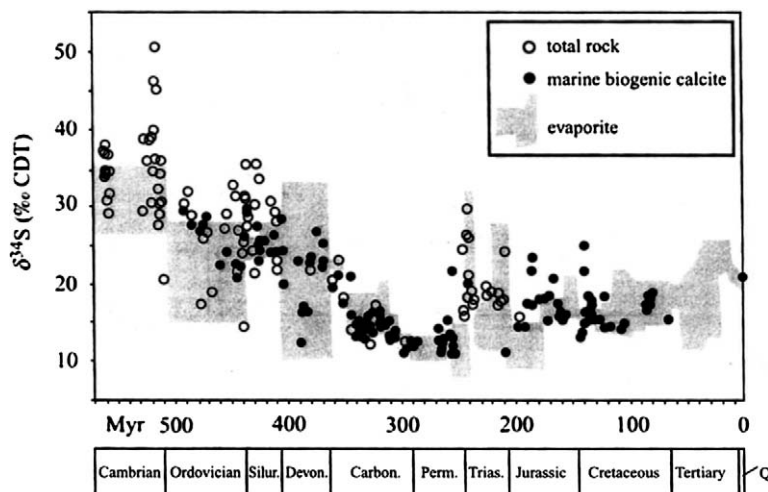


Fig. 11. Sulfur isotopic composition of Phanerozoic seawater based on measurements of sulfur structurally bound in calcitic shells as well as evaporites. Note that the shell samples are mostly the same as those of the Sr, O, and C isotopes in Veizer and Mackenzie (2004).

4. ASSESSMENT AND CONCLUSIONS

Since the H_2/H_2O ratio of volcanic gases has changed very little during the past 3.8 Ga, and the fraction of the volcanic CO_2 that has been reduced to elemental carbon has remained remarkably constant, we are driven to the conclusion that an increase in the CO_2/H_2O and/or the SO_2/H_2O ratio of volcanic gases has been responsible for much of the gradual increase in the oxidation state of the atmosphere. Several mechanisms have been proposed to explain this increase. The most important of these involves the difference between the recycling mechanism of carbon and sulfur, and the recycling mechanism of water in subduction zones. The rate at which carbon and sulfur are recycled through the mantle depends on the quantity of these elements that has accumulated on the continents and on the ocean floor. On the other hand, the recycling of water via subduction zones depends only weakly on the mass of the oceans.

A simple first-order model of the cycling of carbon, sulfur and water has been developed. The history of the CO_2/H_2O and the SO_2/H_2O ratio of volcanic gases that is predicted by this model agrees surprisingly well with the geologic record. The predicted values of the excess H_2 during the Archean agree with those that seem to be required to explain Archean climates, and the predicted CO_2 fluxes are consistent with the CO_2 demand for generating Archean sediments. The timing of the crossover from an H_2 -dominated to an O_2 -dominated atmosphere is consistent with the record of the mass independent fractionation of sulfur in sulfide and sulfate minerals. The changes in the geochemical cycle of Fe, C, and S during the early Proterozoic Great Oxidation Event are consistent with the predictions of the model, as is the modernization of the sulfur cycle by the end of the Proterozoic.

The model does, however, have its problems. It does not address the nature of the earliest atmosphere. The values of the necessary parameters are uncertain, and a host of geologic variables have been ignored in the model. The model

in its present form explains neither the stasis of the Boring Billion nor the furious events of the late Proterozoic. The trading of oxygen between the crustal carbon and the sulfur cycles during the Phanerozoic is permitted within but not required by the model. The successes of the model are surely encouraging; its deficiencies point to the need for improvement and refinement.

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