

Earth and Planetary Science Letters 165 (1999) 197-211

EPSL

Long-term fluxes and budget of ferric iron: implication for the redox states of the Earth's mantle and atmosphere

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Received 8 June 1998; revised version received 15 October 1998; accepted 11 November 1998

Abstract

Net flux of ferric iron from the subducted oceanic crust to the mantle has been estimated to constrain the evolution of the redox state of the Earth's mantle. The main mechanism responsible for the transfer of ferric iron towards the mantle is the production of magnetite during the hydrothermal alteration of the oceanic crust. Both modeling and compilation of chemical data lead to a flux of 21×10^3 kg s⁻¹ of ferric iron transported by the subducted oceanic crust. The net flux of ferric iron towards the deep mantle is estimated to be 12×10^3 kg s⁻¹ when corrected from the production rates of basic magmas at oceanic ridges, island arcs, and hot spots. We discuss several hypotheses. Ferric iron could react at depth with reduced species that buffer the redox state of the mantle to its present-day value. One possible mechanism could be the reaction of this ferric iron accumulates in the deep mantle, being possibly accepted by the structure of spinel, garnet, and perovskite. The transfer of ferric iron from subducted slabs to the mantle contributes from 10 to 25% in the global budget of the ferric iron component of the mantle. The long-term loss of ferric iron from the Earth's surface may be considered as a plausible mechanism to regulate the photosynthetic production of molecular oxygen. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: ferric iron; hydrothermal alteration; Eh; mantle; atmosphere

1. Introduction

The redox state of Earth's mantle is a critical parameter required to model volatile speciation, physical properties of mantle rocks, core–mantle interactions, and the atmosphere chemistry through time (e.g., [1,2]). The redox state of the upper mantle is commonly estimated through values of oxygen fugacity calculated on the basis of Fe^{2+}/Fe^{3+} equilib-

rium distribution among mineral assemblages such as olivine–orthopyroxene–spinel [3–5]. Virgo et al. [6], Wood and Virgo [7] and Wood et al. [8] have shown that direct measurements of the ferric iron content by Mössbauer spectroscopy are more reliable than estimates from microprobe analysis [3]. Oxygen fugacities of co-existing minerals from peridotite and eclogite nodules are also measured with electrochemical cells (e.g., [9,10]) but reduction of the ferric iron during experiments with carbon-bearing samples provides spurious low f_{O_2} values [6]. Thermobarometric measurements lead to conclude

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that the redox state of the mantle is heterogeneous from highly reduced to moderately oxidized peridotites above metal saturation [5,10]. A chemically stratified mantle could also have generated a zonation with depth of the redox state of mineral assemblages. Based on the ability of mantle minerals to accept Fe^{3+} in their structure, O'Neill et al. [4] proposed that the transition zone may form "a shell of reducing conditions" between the upper and lower mantle that are characterized by oxygen fugacities below but close to the quartz-fayalite-magnetite oxygen buffer ($\Delta QFM = -1.5$ to +0.5). Two major oxidizing volatile phases in the mantle, carbon dioxide and water, are able to increase the ratio between ferric and ferrous iron. However, the fluxes and abundances of these volatiles in Earth's reservoirs as well as their chemical reactivity with mantle minerals at high pressure and temperature are not well constrained. This kind of mass balance calculation requires an inventory of net outgassing fluxes of the reduced volatiles H₂, CH₄, and CO. Such fluxes remain difficult to establish since we know, for example, that the dominant part of CH₄ and H₂ fluxes at oceanic ridges results from chemical reactions between peridotites and seawater, thermal breakdown of sedimentary organic matter, and bacterial production [11,12]. It is thus very delicate to model the evolution of the mantle redox state through time despite the attempts made by Kasting et al. [2] and Kadik [10]. These authors conclude that the upper mantle progressively became more oxidized through time as the result of crustal recycling.

To investigate the relative importance of the fluxes in ferric iron on the redox evolution of the mantle, mass balance calculations have been applied to the relative abundances of ferric and ferrous iron in rocks created at oceanic ridges and islands, and subducted along the active margins. Therefore, we propose an inventory of $Fe^{3+}/\Sigma Fe$ ratios and iron abundance in the main reservoirs of the Earth along with their related fluxes for establishing the transfer of ferric iron between the surface reservoirs (oceanic crust and sediments, continents) and the mantle. Mass balance budgets for iron may be established independently of the knowledge of mineralogical reactions that occur within the mantle. Integration over lithosphere subduction history should lead to an estimation of the amount of Fe³⁺ that entered the mantle. Before 2 Ga, however, the presence of banded iron formations (BIF) deposited on the seafloor [13] indicates more reducing conditions in the Precambrian oceans than at present. Therefore, fluxes of ferric iron that are calculated on the basis of modern or Phanerozoic hydrothermally altered oceanic rocks have been only extrapolated over 2 Ga.

In this paper, we discuss how ferric iron from subducted plates may accumulate in the mantle or react with reducing species. Ferric iron may also react with the core that could act as an ultimate buffer of the redox state of the mantle. Finally, we evaluate how the long-term storage of ferric iron in the mantle could be a feedback process controlling the partial pressure of molecular oxygen in the atmosphere.

2. Compilation of chemical data

A compilation of 837 chemical analyses of total iron and Fe^{3+}/Fe^{2+} ratios has been made for basalts and gabbros from oceanic ridges, ophiolites, island arcs, and oceanic islands. Only samples for which the amount of total iron and ferrous iron have been determined by wet chemistry have been selected for the purpose of this study. This may overestimate the amount of Fe³⁺ compared to Mössbauer determinations on minerals [4,14]. The database along with the reference sources are available upon request to the authors. The data have been presented as frequency histograms (Figs. 1–3), and statistics for $Fe^{3+}/\Sigma Fe$ ratios and Fe concentrations in basalts and gabbros from each reservoir have been summarized in Table 1. Fluxes of total and ferric iron have been calculated for the oceanic crust (Table 2) assuming one third of basalts for two thirds of gabbros, an average expansion rate of 5 cm a^{-1} , a crustal depth of 6 km, 65,000 km of oceanic ridges, and a density of 2800 kg m^{-3} . We estimated production rates of magmas close to 1.1×10^{12} kg a⁻¹ and 1.4×10^{12} kg a⁻¹ at island arcs and oceanic islands, respectively. Intra-plate volcanism activity has been estimated using production rates of magmas for the Ontong Java and other oceanic plateaus [15]. Fluxes of ferric iron for island arc (IAT) and oceanic island (OIB) volcanism are about one order of magnitude lower than those calculated for ridge volcanism (Table 2). Based on



Fig. 1. Fe³⁺/ Σ Fe ratios of oceanic island, island arc, ophiolite, and mid-ocean ridge basalts and gabbros.

the rate of oceanic sediments subducted each year [16] and their high content in ferric iron [17], the flux of ferric iron carried by sediments towards the mantle is balanced by the opposite flux of ferric

iron brought by OIB towards the surface (Table 2). Based on various calculations (Table 3), the continental crust constitutes a huge reservoir of ferric iron $(3.8 \times 10^{20} \text{ to } 5.9 \times 10^{20} \text{ kg})$ when compared to the



Fig. 2. Total iron abundance in wt% of oceanic island, island arc, ophiolite, and mid-ocean ridge basalts and gabbros.

present-day mass of oceanic sediments (5.6 \times 10¹⁸ kg).

From the compilations of the Fe³⁺/ Σ Fe ratios in the various magmatic reservoirs, several important observations must be underlined. The hydrothermally altered oceanic crust has a Fe³⁺/ Σ Fe ratio of 0.22 ± 0.08 about three times higher than the average ratio (0.073 ± 0.017) measured in fresh mid-ocean ridge basalts [18]. Note that our estimate (Table 2) is slightly lower than the earlier estimate of 0.24 given by Ronov and Yaroshevsky [19] who did not take into account the gabbro component of



Fig. 3. Comparison of $Fe^{3+}/\Sigma Fe$ ratios between fresh basalts from oceanic islands and mid-ocean ridges.

the oceanic crust. Arc volcanism is characterized by a high Fe³⁺/ Σ Fe ratio of 0.38 ± 0.17 (Table 1; Fig. 1) that mainly results from the partial melting of the most oxidized parts of the oceanic crust and its sedimentary cover (e.g., [20–22]). Ophiolites and modern oceanic crust have similar Fe³⁺/ Σ Fe ratios (Tables 1 and 2; Fig. 1) that suggest stable conditions of oxidation of the oceanic crust exposed to hot seawater over the Phanerozoic (Ordovician to Miocene). The significant scattering of Fe³⁺/ Σ Fe ratios and the average value of 0.25 for ophiolites compared to the clustered Fe³⁺/ Σ Fe ratios for the modern altered oceanic crust may be partly explained by the back-arc or intra-arc environment of some ophiolites [23–25]. In the case of OIB, we selected samples whose water contents do not exceed 0.6% to minimize alteration by surface waters. Their average Fe³⁺/ Σ Fe ratio of 0.29 ± 0.13 is much higher (Fig. 3) than the ratio of 0.07 ± 0.03 computed for fresh MORB [18].

Table 1

Statistics for total and ferric iron abundances in basalts and gabbros from modeled and sampled oceanic crust, Phanerozoic ophiolites, oceanic islands and island arcs

Reservoir	Variable	Minimum	Maximum	Points	Mean	Standard deviation
Crust model basalts	$Fe^{3+}/\Sigma Fe$	0.16-0.20	0.44-0.68	201	0.27-0.39	_
Crust model gabbros	$Fe^{3+}/\Sigma Fe$	0.07	0.16-0.20	400	0.10-0.11	-
Oceanic crust basalts	$Fe^{3+}/\Sigma Fe$	0.03	0.57	221	0.26	0.08
Oceanic crust basalts	Fe (wt%)	1.90	14.68	221	7.35	1.45
Oceanic crust gabbros	$Fe^{3+}/\Sigma Fe$	0.04	0.45	130	0.20	0.08
Oceanic crust gabbros	Fe (wt%)	1.51	22.36	130	5.80	3.60
Ophiolite basalts	$Fe^{3+}/\Sigma Fe$	0.02	0.74	104	0.30	0.15
Ophiolite basalts	Fe (wt%)	4.78	11.58	104	7.48	1.62
Ophiolite gabbros	$Fe^{3+}/\Sigma Fe$	0.06	0.50	51	0.22	0.10
Ophiolite gabbros	Fe (wt%)	1.24	14.82	50	5.23	2.67
Ocean island basalts	$Fe^{3+}/\Sigma Fe$	0.07	0.96	187	0.29	0.13
Ocean island basalts	Fe (wt%)	4.46	11.14	187	8.86	0.89
Island-arc basalts	$Fe^{3+}/\Sigma Fe$	0.13	0.92	99	0.41	0.17
Island-arc basalts	Fe (wt%)	1.86	11.20	99	7.53	1.30

Table 2

Estimated magma productions and fluxes of ferric iron associated with rates of oceanic sedimentation, hydrothermal alteration of the oceanic crust, and volcanism at ridges, oceanic islands and island arcs

Reservoirs	Oceanic crust Ronov and Yaroshevsky [19]	Oceanic crust compilation, this study	Oceanic crust model, this study	Ophiolitic sequences compilation, this study	Oceanic sediments Chester [17]	Intra-plate volcanism compilation, this study	Arc volcanism compilation, this study	Ridge volcanism compilation, this study
$3+\Sigma Fe$	0.24	0.22	0.19	0.25	0.82	0.29	0.38	0.07
Fe^{3+} (wt%)	1.89	1.38	1.20	1.49	3.42	2.53	2.42	0.44
ΣFe (wt%)	7.88	6.31	6.31	5.98	4.17	8.86	6.36	6.31
Production (kg a^{-1})	5.46×10^{13}	5.46×10^{13}	5.46×10^{13}	5.46×10^{13}	1.40×10^{12}	1.37×10^{12}	1.12×10^{12}	5.46×10^{13}
Fe^{3+} flux (kg a^{-1}) ^a	-1.03×10^{12}	-7.55×10^{11}	-6.55×10^{11}	-8.16×10^{11}	-4.79×10^{10}	$+4.10 \times 10^{10}$	$+2.71 \times 10^{10}$	$+2.41 \times 10^{11}$

^a A negative sign for ferric iron fluxes indicates a mass transfer from surface to mantle.

Table 3		
Various estimates of the abundance of total	and ferric iron in oceanic sediments,	continental crust, and lower mantle

Reservoirs	Oceanic sediments McLennan and Taylor [61]	Continental crust Clarke and Washington [62]	Continental crust Clarke and Washington [62]	Continental crust Goldschmidt [63]	Continental crust Daly [64]	Continental crust Poldervaart [65]	Continental crust Ronov and Yaroshevsky [19]	Lower mantle
Fe ₂ O ₃ (wt%)	4.89	3.08	3.10	3.41	3.55	2.30	2.40	_
FeO (wt%)	0.94	3.80	3.71	3.58	4.06	5.00	5.60	_
Fe ³⁺ (wt%)	3.42	2.15	2.17	2.39	2.48	1.61	1.68	_
Fe ²⁺ (wt%)	0.73	2.95	2.88	2.78	3.16	3.89	4.35	_
$\mathrm{Fe}^{3+}/\Sigma\mathrm{Fe}$	0.82	0.42	0.43	0.46	0.44	0.29	0.28	_
ΣFe (wt%)	4.15	5.11	5.05	5.17	5.64	5.50	6.03	5.8
Unit mass (kg)	1.63×10^{20}	2.36×10^{22}	2.36×10^{22}	2.36×10^{22}	2.36×10^{22}	2.36×10^{22}	2.36×10^{22}	2.94×10^{24}
ΣFe (kg)	6.77×10^{18}	1.21×10^{21}	1.19×10^{21}	1.22×10^{21}	1.33×10^{21}	1.30×10^{21}	1.42×10^{21}	1.71×10^{23}
ΣFe^{3+} (kg)	5.58×10^{18}	5.08×10^{20}	5.12×10^{20}	5.63×10^{20}	5.86×10^{20}	3.80×10^{20}	3.96×10^{20}	-

In the frame of this compilation of iron data, a first question arises: how is the oceanic crust progressively oxidized with depth and time before being subducted and recycled through the deep mantle? Therefore, we propose to model the oxidation of the oceanic crust that occurs during the hydrothermal alteration of basic rocks by seawater. The comparison of measured and modeled $Fe^{3+}/\Sigma Fe$ ratios should avoid an over-estimation of the Fe³⁺ flux from the surface towards the mantle. We can remark, indeed, that the shallow layers of the oceanic crust have been oversampled at the expense of the deep gabbroic layers as the consequence of the drilling techniques that restrict the sampling of the oceanic crust to the first thousand meters. A few sections of oceanic gabbros have been sampled at the Hess Deep close to the East Pacific Rise (Hole 894G) and along the Indian Ridge (Hole 735B) but do not represent the whole deep oceanic crust.

3. Iron oxidation during hydrothermal activity at oceanic ridges

Experimental approaches of basalt–seawater interactions at high temperatures (200–350°C) have shown that the oxidation of basaltic Fe^{2+} into Fe^{3+} proceeds through seawater sulfate reduction whose extent is controlled by water–rock ratios [26]. The normative fayalite component of basaltic rocks is oxidized to pyrite and magnetite according to the following reaction:

$$11\text{Fe}_2\text{SiO}_4 + 2\text{SO}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{FeS}_2 + 7\text{Fe}_3\text{O}_4$$
$$+11\text{SiO}_2 + 2\text{H}_2\text{O} \tag{1}$$

If water–rock ratios are large enough, after complete oxidation of the fayalite component, magnetite is further oxidized into hematite. According to the common occurrence of magnetite instead of hematite in oceanic rocks, oxidation is considered to be restricted to the production of magnetite, thus only two thirds (more exactly 7/11 taking into account the pyrite component) of the ferrous iron can be oxidized [26]. Knowing that sulfate concentration in seawater is 0.265 wt%, the above reaction indicates that 2.65 g of SO_4^{2-} will convert 6.9 g of Fe²⁺ into Fe³⁺ for a mass water–rock ratio of 1. Kinetics

of such chemical reactions are fast at hydrothermal temperatures [27]. Reactions are achieved for hydrothermal systems whose life expectancies are higher than twenty thousand years, which is the case for oceanic hydrothermal systems. Consequently, the limiting factor for the progress of chemical reaction (1) is the amount of available reacting seawater (water-rock ratio) that varies with depth as a function of the permeability of the oceanic crust. Theoretical and experimental studies show that the water-rock ratio decreases exponentially with depth [28,29]. The smooth profiles of porosity and permeability observed in both modern oceanic crust [30] and ophiolites [31] suggest that an exponential decay law is valid to simulate permeability variations with depth in the oceanic crust:

$$\frac{W}{R} = \left(\frac{W}{R}\right)_0 \left[\frac{\exp(-ah) - \exp(-az)}{\exp(-ah) - 1}\right]$$
(2)

where $(W/R)_0$ is the water–rock ratio at z = 0. The porosity closes at the depth h = 6 km, the parameter a is chosen to obtain an integrated water-rock ratio between 1 and 1.5 in agreement with those deduced from strontium isotope studies along various segments of mid-ocean ridges [32,33]. The initial $Fe^{3+}/\Sigma Fe$ ratio of oceanic rocks was set to 0.07 before water-rock interaction starts to oxidize the crust. The computed profiles of $Fe^{3+}/\Sigma Fe$ ratios in the oceanic crust are depicted in Fig. 4. The ratios decrease from 0.5 to 0.2 in the basaltic layer supposedly 2 km thick, down to 0.07 at the bottom of the oceanic crust where infiltration of water stops. Profiles of $Fe^{3+}/\Sigma Fe$ ratios progressively decreasing with depth have been observed in some ophiolite sequences. For example, Spooner et al. [34] have reported $Fe^{3+}/\Sigma Fe$ ratios of pillow lavas from Liguria (Italy) that regularly decrease from 0.47 at surface down to 0.22 at a few hundred of meters deeper in the crust. They also observed some scattering in the ratios at a same depth that results from the heterogeneous permeability of rocks, a property that is not accounted for by our model whose main goal is to reproduce the amplitude and zonation of oxidation in the oceanic crust at first order level. Similarly, the Trinity ophiolite (northern California) shows a 1-km-deep sequence of basalts and gabbros having $Fe^{3+}/\Sigma Fe$ ratios decreasing from 0.52 at the top



Fig. 4. Modeled profiles of variations of the Fe³⁺/ Σ Fe ratio with depth in the oceanic crust for integrated mass water–rock ratios of 1 and 1.5.

down to 0.11 near the boundary between crustal gabbros and mantle peridotites [35].

The average $Fe^{3+}/\Sigma Fe$ ratio for the modelled basalts is calculated to be in the range 0.27-0.39, somewhat higher than those deduced from the compilation of data from oceanic and ophiolitic basalts (Table 1). This slight discrepancy may result from the choice of parameter a in Eq. 2 but also from a sampling bias; the most altered samples are commonly discarded for petrological and geochemical studies. The uppermost gabbros have computed $Fe^{3+}/\Sigma Fe$ ratios close to 0.2 in agreement with the data obtained from oceanic and ophiolitic gabbros. However, the average $Fe^{3+}/\Sigma Fe$ ratio for the whole gabbro section (4 km thick in our model) is 0.1, about two times less than the average ratio deduced from oceanic data (Table 1). The model predicts the existence of a large section of deep oceanic gabbros only slightly oxidized by the low amounts of circulating hydrothermal waters. The calculated $Fe^{3+}/\Sigma Fe$ ratio for the whole crust is thus estimated to be between 0.16 and 0.20 instead of 0.22, a difference that could reflect a substantial sampling bias of the oceanic crust (Table 2).

4. Discussion

4.1. Long-term fluxes and the fate of ferric iron

The similarity of $Fe^{3+}/\Sigma Fe$ ratios between ophiolites and modern oceanic crust suggests that the oxidation mechanism at the surface remained the same at least through the Phanerozoic. We do not know on the contrary if the oxidation state of the basalts has changed through time. If the $Fe^{3+}/\Sigma Fe$ ratio of MORB has increased through time, mass balance calculations that assume steady-state ferric iron fluxes between reservoirs will provide only an upper limit for the flux of Fe³⁺ towards the mantle. However, according to Canil [36], the oxidation state of the upper mantle has not evolved significantly. Both modeling and compilation of chemical data lead to calculate a net flux of 12×10^3 kg s⁻¹ of ferric iron transported towards the mantle when corrected from opposite fluxes at oceanic ridges, island arcs, and oceanic islands (Table 2; Fig. 5):

$$\Phi_{\text{crust-mantle}} = \Phi_{\text{subduction}} + \Phi_{\text{sediments}} - \Phi_{\text{ridges}}$$
$$- \Phi_{\text{islands}} - \Phi_{\text{arcs}} \qquad (3)$$

The flux of ferric iron transported by altered subducted plates is mainly counterbalanced by the flux of ferric iron at ridges whereas contributions from other reservoirs are at least five times lower (Table 2). We estimate that the uncertainty on this calculated flux is mainly related to those associated with the Fe³⁺/ Σ Fe ratios of the two largest mass fluxes ($\Phi_{subduction}$ and Φ_{ridges}), i.e. about 50%.

We may question whether or not the integral amount of Fe³⁺ produced during hydrothermal activity is really transferred to the deep mantle. The flux of ferric iron extracted by arc volcanism is negligible, but the fact that this material is highly oxidized argues for a near conservative transfer of ferric iron from the trenches to the volcanism sources [37]. Wood et al. [8] also observed that highly oxidized xenoliths (f_{O_2} greater than FMQ) come from subduction-related areas. However, we may consider that a fraction of the ferric iron may react with reduced species such as carbon or sulfur that are



Fig. 5. Sketch summarizing the fluxes and amounts of Fe^{3+} for the main terrestrial reservoirs. A net flux of 12.5×10^3 kg s⁻¹ of Fe^{3+} towards the mantle has been deduced using a mass balance equation (Eq. 3).

themselves contained in the subducted lithosphere. If this process operates, the net flux of ferric iron towards the mantle may be over-estimated in our calculations. We also emphasize that the subducted slabs behave as a closed system regarding the oxygen budget among the various chemical species. One way to test in what extent the Fe³⁺/ Σ Fe ratio could be preserved during subduction would consist in a comparison between measurements made on eclogites of oceanic origin and hydrothermally altered oceanic rocks (D. Canil, pers. commun.). However, we note that this comparison requires the identification of the eclogite protoliths (basalts, gabbros and peridotites). Unfortunately, such a set of data is not available in the literature.

If arc volcanism recycles large amounts of altered oceanic crust, we question the size of recycled altered crust into hot spot volcanism that is considered to sample the lower mantle. For comparison with MOR volcanism, $Fe^{3+}/\Sigma Fe$ ratios of OIB must be corrected from partial melting rates that are different from those affecting the upwelling asthenosphere beneath ocean ridges [30]. $Fe^{3+}/\Sigma Fe$ ratios may be normalized to another incompatible chemical species such as H₂O assuming similar incompatible behaviors relatively to silicate melts. Canil et al. [14] proposed a partition coefficient of about 0.1 for Fe³⁺ between solid and melt during partial melting of mantle rocks. Water is three to four times more

abundant in OIB than in MORB in agreement with different rates of source melting [38]. Using the following mass balance equation:

$$\left(\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}\right)_{\text{OIB}} \times \frac{[\text{H}_2\text{O}]_{\text{MORB}}}{[\text{H}_2\text{O}]_{\text{OIB}}} = f \times \left(\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}\right)_{\text{subducted}} + (1 - f) \times \left(\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}\right)_{\text{fresh MORB}}$$
(4)

we deduce that the amount of subducted oceanic crust recycled in hot spot volcanism ranges from 2 to 20 wt%, an estimate that brackets the 9 wt% of contamination quantified by Woodhead et al. [39] on the basis of correlations between radiogenic and stable oxygen isotope compositions of various ocean island basalts. This contribution of recycled oceanic crust must be considered as an upper limit since we do not know whether or not contamination occurs when hot spot volcanism is ascending through a pre-existing altered oceanic lithosphere like in Hawaii or Iceland.

Continental crust also accumulated ferric iron during its growth through time (Table 3; Fig. 5). Oxidation of the continental crust results from lateral accretion of oxidized marine sediments and island arc-related components, but also from a progressive alteration of the eroded surfaces in contact with the atmosphere and fresh waters. Depending on methods of calculation, its Fe³⁺/ Σ Fe ratio is estimated in the range 0.28–0.46. Assuming that the mass of the

continental crust is 2.36×10^{22} kg [40,41], the total amount of Fe³⁺ stored in this reservoir may be estimated from 4×10^{20} kg to 5.9×10^{20} kg (Table 3). This amount is about the half of the total amount of Fe³⁺ (8 × 10²⁰ kg) transferred towards the mantle over a period of 2 Ga.

4.2. Implication for the redox state of the deep mantle

Several hypotheses concerning the fate of ferric iron in the deep mantle may be considered. They are highly speculative although we think they are worth to be discussed. Two main behaviors can be envisioned: either the mantle oxidation increases through time or the introduction of oxidized species is buffered at depth.

(1) Ferric iron may have progressively accumulated in the mantle, being possibly accepted by the structure of garnet [8] and perovskite [42,43]. Mc-Cammon [43] found that perovskites that accept Al^{3+} may accommodate large amounts of ferric iron and be in equilibrium with iron metal. If true, it means that ferric iron from subducted plates does not react with the core but is simply continuously added to the deep mantle. Adding Fe³⁺ in the deep mantle means that some species is reduced accordingly; for example, oxidized carbon from carbonates could react to produce diamonds.

This hypothesis of a secular increase of the mantle Fe³⁺/ Σ Fe ratio is actively debated. For example, Ballhaus [44] and Canil et al. [14] proposed that the upper mantle beneath cratons was likely progressively oxidized since the early Archean. However, more recently, Canil [36] reached an opposite conclusion that was inferred from a study of vanadium partitioning between komatiitic liquid and olivine from Archean lava flows. Komatiite lavas may have been as oxidized or even more oxidized than present-day mid-oceanic ridge basalts. From our study, we can estimate what is the amount of ferric iron introduced by subduction relatively to the presentday $Fe^{3+}/\Sigma Fe$ ratio of the mantle estimated between 0.023 and 0.06 [4]. In the framework of our model, the Fe³⁺/ Σ Fe ratio of the mantle is at least 0.005 when only taking into account the long-term recycling of subducted plates over 2 Ga. Therefore, lithospheric recycling only contributes from one tenth to

one quarter of the mantle ferric iron abundance. This process, although non negligible, cannot explain by itself the present-day oxidation state of the Earth's mantle. If the mantle was more reduced than now. other redox processes must be involved to explain the present-day mantle oxidation state. Inward fluxes of CO_2 (10¹⁰ to 10¹¹ kg a⁻¹; [45]) and H₂O (10¹¹ to 10^{12} kg a⁻¹; [45]) may be responsible for the oxidation of ferrous iron into ferric iron as was proposed by Kasting et al. [2]. In mol s^{-1} , these different fluxes are from 1.7×10^5 to 1.7×10^6 for H₂O, about 2 \times 10⁵ for Fe³⁺, and from 6.8 \times 10³ to 6.8 \times 10⁴ for CO₂. This suggests that water is the major oxidizing agent followed by Fe³⁺, while carbonates would be the least important. These fluxes altogether may explain the present-day $Fe^{3+}/\Sigma Fe$ ratio of the whole mantle.

It is also possible that the primitive mantle was already as oxidized as now [36], for example, subsequently to a late accretion of an oxidized veneer [46]. In that case, introduced oxidized species are buffered at depth.

(2) If the subducted plates or their derived-components collide with the Earth's core, this latter may act as a buffer of the mantle redox state by converting its iron metal into ferrous iron according to the following equation:

$$Fe^0 + 2Fe^{3+} \leftrightarrow 3Fe^{2+}$$
 (5)

Such a reaction will decrease the core radius by only 500 m over a period of 2 Ga. Following this hypothesis, the redox state of Earth's mantle would have been maintained nearly constant throughout most of the Earth's history.

(3) Other buffering processes could occur in the mantle. Ferric iron brought by the subducted lithosphere could react with 'metal droplets' that would have remained trapped in the deep mantle as a consequence of an incomplete segregation from the silicate matrix during core differentiation. According to Ballhaus [5], starting from the transition zone, the deep mantle could be indeed metal-saturated.

(4) The mantle abundances of reduced species such as C and S are large enough [8,14] to potentially convert all the subducted ferric iron into ferrous iron according to the following reactions:

$$2Fe_2O_3 + C \leftrightarrow 4FeO + CO_2 \tag{6}$$

$$2Fe_2O_3 + S \leftrightarrow 4FeO + SO_2 \tag{7}$$

If such reactions occur in the mantle, the lithospheric recycling progressively consumes the mantle reservoirs of reduced carbon and sulfur. We cannot determine what are the respective contributions of C and S in a possible buffering of the mantle redox state. However, we can estimate, independently for each species, the maximum amount of C or S that are necessary to buffer the Fe^{3+} brought by subducted plates.

According to Blundy et al. [47], carbon should be the major element that buffers the Fe^{3+}/Fe^{2+} ratio of mantle-derived rocks. Therefore, assuming that only reaction (6) occurs, 4.3×10^{19} kg of diamond has been consumed in the last 2 Ga. Although such a quantity of diamonds is certainly impressive, the mantle is known to contain about 400–500 ppm of carbon (2 × 10²¹ kg; [48]). The buffering of mantle oxidation state by carbon would mean that an initial 3 wt% of this carbon was in its reduced form. This process can explain why most diamonds are probably of Precambrian age [49,50]: the remaining ones are too deep to be exhumed.

(5) Reduced volatiles may have been more abundant during the early Earth than now (e.g., [51]) and may have maintained the mantle redox state constant through two major reactions:

$$4Fe_2O_3 + CH_4 \leftrightarrow 8FeO + CO_2 + 2H_2O \tag{8}$$

$$Fe_2O_3 + H_2 \leftrightarrow 2FeO + H_2O$$
 (9)

The products of reaction, water and carbon dioxide, will be consequently released at oceanic ridges as observed by Javoy and Pineau [52].

In any case, we conclude that ferric iron is subtracted from the surface towards the mantle and the continental crust (Fig. 5). Oxidation of sulfide in sulfate is required to maintain sulfate concentration in seawater at steady state [51] in response to its consumption during hydrothermal alteration at ridges. It means that a stoichiometric amount of molecular oxygen is trapped into rock-forming minerals at the expense of the Earth's atmosphere, whereas oxygen that escapes Earth's mantle is bounded in carbon dioxide and water molecules. Kasting et al. [2] previously emphasized that "the questions of atmospheric oxidation state and mantle redox evolution are inextricably interlinked" and likely had a critical influence on life development during the Precambrian.

4.3. A mechanism to regulate the atmospheric oxygen partial pressure?

The accumulation of ferric iron in both mantle and continental crust may be examined as a plausible feedback mechanism regulating the atmospheric oxygen partial pressure. One way to test this hypothesis is to combine the equations of photosynthesis and oxidation of ferrous iron as follows:

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2$$
 (10)

$$2\text{FeO} + 1/2\text{O}_2 \leftrightarrow \text{Fe}_2\text{O}_3 \tag{11}$$

For two consumed moles of ferrous iron, one half mole of organic matter is produced. Knowing that the total amount of ferric iron accumulated in both continental crust and deep mantle is about 1.3 $\times 10^{21}$ kg, a corresponding mass of 10^{20} kg of buried organic carbon is required to balance oxygen consumption during iron oxidation at ridges over a period of 2 Ga. We do not know how much organic carbon is subducted each year but it is interesting to note that this mass of organic carbon is about 5 times the estimated total biomass (including kerogen) of 2 $\times 10^{19}$ kg [53,54]. This calculation suggests that a large amount of reduced carbon has been stored in crustal rocks or in the mantle.

The evolution of the atmospheric oxygen content is classically approached by the competing between the burial rate of organic carbon (reaction 10) and its oxidation rate (reverse of reaction 10). Excess of organic matter burial has been proposed for the Cretaceous and the Cenozoic [55-58] and the classical two box model predicted large increases of oxygen atmospheric contents from 20% up to 80% relatively to present atmospheric level (PAL) even when integrating the phosphorus cycle [51,58]. Time scales of such fluctuations occur at a 10 Ma scale as the consequence of flux sizes of 10¹¹ kg a⁻¹ compared to reservoir sizes that are 10^{18} kg of oxygen in the atmosphere and about 10¹⁹ kg of reduced carbon in sediments. Ferric iron fluxes towards the mantle are of the same order of magnitude as carbon burial fluxes. Consequently they are able to compete for

regulating the amount of molecular oxygen in the atmosphere.

We propose to model the evolution of the oxygen atmospheric content by coupling the reaction of iron oxidation at ridges (reaction 11). We treat the atmospheric oxygen cycle with first-order kinetic exchange laws. For a system of three exchanging reservoirs A (atmosphere), B (sediments) and C (mantle), we have for the atmosphere [59,60]:

$$\frac{\mathrm{d}M_{\mathrm{A}}}{\mathrm{d}t} = k_{\mathrm{BA}}M_{\mathrm{B}} - k_{\mathrm{AB}}M_{\mathrm{A}} - k_{\mathrm{AC}}M_{\mathrm{A}} \tag{12}$$

 M_A is oxygen mass of the atmosphere, k_{BA} , k_{AB} and k_{AC} are the rate constants (a⁻¹) of oxygen transferred from B to A, A to B and A to C, respectively. The rate constant at which oxygen is transferred towards the mantle increases in proportion to the ridge spreading rate (Fig. 6). For expansion rates higher than 5 cm a⁻¹, iron oxidation acts as a feedback mechanism regulating the atmospheric pO_2 with response times equal to or less than 10 Ma. For example, if we consider a 50% excess of organic carbon burial flux, which is considered as an upper limit over the Phanerozoic [56], a model without mantle

oxidation predicts a new steady-state oxygen atmospheric content of 1.8×10^{18} kg with a response time of 20 Ma. By comparison, for a ridge activity of 10 cm a⁻¹, the initial perturbation, illustrated by a rapid oxygen increase, will be absorbed in 40 Ma (Fig. 6). The oxidation of ferrous iron in ferric iron during hydrothermal activity at oceanic ridges may be therefore considered as a plausible mechanism that stabilizes atmospheric pO_2 in addition to other surface mechanisms such as those associated with limiting nutrients controlling the biomass. The absence of rapid and large depletion or inflation of atmospheric O_2 are necessary to conciliate geochemical models with the biological evolutionary trends recorded in the Phanerozoic sediments.

5. Conclusions

Mass balance calculations reveal that the mantle and the continental crust are sinks for ferric iron. Both modeling and compilation of chemical data lead to calculate a net flux of 12×10^3 kg s⁻¹ of ferric iron transported towards the deep man-



Fig. 6. Variations of the atmospheric O_2 content as a function of the expansion rate of mid-ocean ridges. The curves have been calculated using first-order kinetic exchange laws for a system of three exchanging reservoirs that are the atmosphere, the sediments, and the mantle. Initial conditions: mass of atmospheric oxygen was taken at 1×10^{18} kg according to the present-day value, and mass of buried carbon in sediments was estimated around 2×10^{19} kg. Flux of oxygen equivalent to carbon burial in sediments was set at 4×10^{11} kg a^{-1} [66] and 50% higher than the reverse flux of organic matter degradation (see Eq. 10). Flux of oxygen equivalent to iron oxidation at the ridges equals 5.5×10^{10} kg a^{-1} for an expansion rate of 5 cm a^{-1} .

tle when corrected from opposite fluxes at oceanic ridges, island arcs, and oceanic islands. Subduction of hydrothermally oxidized oceanic lithosphere could have injected 8×10^{20} kg of Fe³⁺ towards the mantle over 2 Ga, i.e. about two times the amount of ferric iron stored in the present-day continental crust. The transfer of ferric iron from subducted slabs to the mantle contributes from 10% to 25% in the global budget of the Fe³⁺/ Σ Fe of the mantle.

By combining the equations of photosynthesis and oxidation of ferrous iron, a corresponding mass of 10^{20} kg of buried organic carbon is required to balance oxygen consumption during iron oxidation at ridges over a period of 2 Ga. A first-order kinetic model of oxygen transfer between the atmosphere, the sediments, and the mantle predicts maximal variations of $\pm 30\%$ of the oxygen atmospheric content at a 10-Ma scale.

The oxidation of ferrous iron in ferric iron during hydrothermal activity at oceanic ridges may be therefore considered as a plausible mechanism that participates in the regulation of atmospheric pO_2 . Such an inorganic chemical process may also have delayed the rising of free oxygen in the terrestrial atmosphere during the Early Precambrian.

Acknowledgements

The authors thank Ph. Gillet, F. Guyot and B. Reynard for their helpful comments on a first draft of this manuscript. Constructive reviews provided by D. Canil and B.J. Wood significantly helped to improve the overall scientific quality of this work. *[CL]*

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