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The Redox Budget of Subduction Zones

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Abstract

Elements that can occur in more than one valence state, such as Fe, C and S, play an important role in Earth's systems at all levels, and can drive planetary evolution as they cycle through the various geochemical reservoirs. Subduction introduces oxidised Fe, C and S in sediments, altered ocean crust, and partially serpentinised mantle lithosphere to the relatively reduced mantle, with short- and long-term consequences for the redox state of the mantle. This then controls the redox state of mantle material added to the lithosphere and atmosphere, such as arc volcanic gases and the magmas that form arc-related ore deposits.

The extent of mantle oxidation induced by subduction zone cycling can be assessed, albeit with large uncertainties, with redox budget calculations that quantify the inputs and outputs to subduction zones. Literature data are augmented by new measurements of the chemical composition of partially serpentinised mantle lithosphere from New Caledonia and ODP 209. Results indicate that there is a net addition of Fe ($55 \pm 13 \times 10^{12}$ moles year⁻¹), C ($4.6 \pm 4.0 \times 10^{12}$ moles year⁻¹), S ($2.4 \pm 0.9 \times 10^{12}$ moles year⁻¹), and redox budget ($5 - 89 \times 10^{12}$ moles year⁻¹) at subduction zones. Monte Carlo calculations of redox budget fluxes indicate that fluxes are $46 \pm 12 \times 10^{12}$ moles year⁻¹ entering subduction zones, if input and output parameters are assumed to be normally distributed, and $46 - 58 \times 10^{12}$ moles year⁻¹ if input and output parameters are assumed to be log-normally distributed.

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Thus, inputs into subduction zones for Fe, C, S and redox budget are in excess of subduction zone outputs. If MORB and plume-related fluxes are taken into account then Fe, C and S fluxes balance, within error. However, the redox budget does not balance, unless the very lowest estimates for the extent of slab oxidation are taken. Thus it is likely that subduction continuously increases the redox budget of the mantle, that is, there is addition of Fe, C and S that are oxidised relative to the Fe, C and S in the mantle.

The fate of this redox budget can be constrained by consideration of element mobility under mantle conditions. If slab fluids are assumed to be dominantly aqueous and relatively low salinity then fluxes of Fe^{3+} , C^{4+} , and S^{6+} are limited to less than 10^9 , 2.3×10^{12} moles year^{-1} and 2×10^{12} moles year^{-1} respectively by the low solubility of these elements in slab-derived fluids. Nevertheless, such fluxes can produce the increased f_{O_2} inferred for sub-arc mantle from arc lavas after around 10 Ma subduction.

The rest of the redox budget added by the subduction process is likely to be carried to the deep mantle by the slab, and mix slowly with the whole mantle reservoir, depending on the timescale of reincorporation of subducted lithosphere into the mantle. Simple mixing calculations indicate that these fluxes will only cause a measurable difference to mantle redox on a 1Ga timescale, which is longer than the 550 Ma during which redox budget fluxes are likely to have been at present day levels. However, measurable effects, with potential consequences for the the Earth's evolution may be expected in the future.

Keywords: redox, subduction, iron, carbon, sulfur, cycling

1. INTRODUCTION

Subduction zones connect the Earth's interior to the lithosphere and exosphere (atmosphere/oceans) and thus play a central role in the geochemical cycles of many of the major, minor and trace elements. Much attention has been devoted to geochemical fluxes at subduction zones (e.g. Kerrick, 2001; Kerrick and Connolly, 2001; Lecuyer and Ricard, 1999; Plank and Langmuir, 1998; Hayes and Waldbauer, 2006; Kerrick and Caldeira, 1998; Staudigel et al., 1998; Morner and Etiope, 2002) because quantification of these fluxes is necessary if we are to understand the evolution of the atmosphere and oceans with geological time (e.g. Berner, 2001), plate margin volcanism (e.g. Alt et al., 1993), and the formation of ore deposits at convergent margins (e.g. Sun et al., 2004).

Particular attention has been paid to elements that are redox-sensitive, that is, elements that occur in more than one valence state. Examples include Fe (e.g. Lecuyer and Ricard, 1996), C (e.g. Kerrick, 2001; Morner and Etiope, 2002) and S (e.g. Alt et al., 1993). These elements are present in different concentrations and oxidation states in the different lithologies introduced to subduction zones, and are released, commonly after a change in oxidation state, by the processes associated with subduction. For example, carbon is carried into subduction zones as organic carbon (C^0) in sediments, as secondary carbonates (C^{4+}) in carbonated basaltic ocean crust and serpentinised mantle, and as primary carbonate in carbonaceous oozes. Carbon is released from subduction zones as dissolved carbonate e.g. Mottl et al., (2004), devolatilised CO_2 and CH_4 (C^{4-}) (e.g. Connolly, 2005), and carbonate in silicate melts (e.g. Dasgupta et al., 2006). Release may result in return of the carbon to the atmosphere by reflux up the slab to the trench (e.g. Mottl et al., 2004), or volcanism (e.g. Kerrick, 2001), or by devolatilisation/melting and transfer into the mantle wedge (e.g. Dasgupta et al., 2004). The released carbon may be gaseous species such as methane or carbon dioxide, ionic species in solution, e.g. HCO_3^- or CO_3^{2-} , or melt species. Alternatively, carbon may be transported into the deep man-

31 tle (e.g. Kerrick and Connolly, 2001; Yaxley and Brey, 2004), where it may
32 transform to high density carbonate phases, or occur as graphite or diamond.
33 A similarly complex range of alternatives exist for the other redox elements of
34 interest.

35 Redox-sensitive elements are of interest because they are of importance to
36 life, the Earth's evolution (e.g. Kump and Holland, 1992), and the formation
37 of ore deposits (e.g. Mungall, 2002) . Bacteria have harvested the energy that
38 could be obtained by catalysis of redox reactions since the dawn of life (e.g. Rus-
39 sell et al., 2005). Carbon dioxide is an essential nutrient for plants, and plays
40 a role in the regulation of the atmosphere. Iron, nitrogen and phosphorous
41 availability determine the productivity of the oceans (e.g. Petsch and Berner,
42 1998). Microbial sulphate reduction fixes sulphur in sediments and is one of
43 the major fluxes that controls the level of atmospheric oxygen (e.g. Petsch and
44 Berner, 1998). Interactions between redox-sensitive elements are also critical.
45 Oxidation (the loss of electrons) cannot occur without reduction (gain of elec-
46 trons) somewhere within the system considered, because the vast majority of
47 natural systems are uncharged, that is, they cannot carry a net positive or neg-
48 ative charge. Thus, coupled oxidation and reduction in open systems, where
49 a reactant or product may be lost, can drive massive changes in redox state.
50 Examples include the development of the Earth's core (e.g. Wood et al., 2008)
51 and the formation of the atmosphere (e.g. Kump and Holland, 1992).

52 The oxidising/reducing capacity of a rock is determined by the product of
53 the *quantity* of each of the redox-sensitive elements present and the *oxidation*
54 *state* of those elements (Evans, 2006), and cannot be described conveniently
55 by commonly used intensive variables such as f_{O_2} , because such variables, by
56 definition, are independent of the quantity of the elements present and are thus
57 unsuited to the measurement of fluxes (Giggenbach, 1992; Evans, 2006). For
58 this reason, we use the term redox budget to quantify the oxidising or reducing
59 capacity of the rock, where oxidising capacity increases with redox budget. The
60 formal definition of redox budget is given by Evans, (2006) and is summarised
61 in section 2.1.

62 A number of studies have addressed the coupled fluxes of redox-sensitive
63 elements in exospheric systems on a global scale (e.g. Petsch and Berner, 1998;
64 Berner, 2001; Hayes and Waldbauer, 2006). Such studies have been used to draw
65 conclusions on the rise of atmospheric oxygen, and the variation of oxygen with
66 geological time (e.g. Berner, 2001). However, these works have been forced,
67 for want of robust measurements, to assume that crust/mantle - exosphere ex-
68 changes of the redox-sensitive elements are at steady state.

69 Such a situation seems unlikely. Seafloor alteration of oceanic crust involves
70 significant oxidation of primary basalt-hosted iron (Johnson and Semyan, 1996;
71 Zhou et al., 2001), and serpentinisation results in the formation of magnetite
72 coupled with the release of hydrogen and methane into the ocean (e.g. Charlou
73 et al., 1991). Seafloor sediments can contain oxidised carbon in the form of cal-
74 careous oozes (e.g. Plank and Langmuir, 1998). The increase in redox budget
75 caused by the addition of this material to the mantle during subduction must
76 either oxidise the mantle, or be coupled with, on some time-scale, an equiva-
77 lent but opposite change in mantle redox budget as the result of processes at
78 mid-ocean ridges, arcs or in reflux zones at trenches. Secular variation in the
79 systematics of sedimentation (e.g. Canfield, 2004), MORB production rates and
80 subduction geodynamics are difficult to reconcile with the notion of steady state
81 mantle and exospheric redox budgets.

82 A limited number of studies have addressed global-scale redox fluxes. Lecuyer
83 and Ricard (1999) document an excess of oxidised iron in subduction zone in-
84 puts relative to outputs, and conclude that the Earth's core may be gradually
85 oxidising to compensate. Hayes and Waldbauer (2006) conclude that CO₂ from
86 the mantle continually adds to the redox budget of the exosphere, which implies
87 that the mantle redox budget is decreasing i.e. the mantle is becoming more
88 reduced. A number of studies (e.g. Kelley and Cottrell, 2009; Parkinson and
89 Arculus, 1999) propose that sub-arc mantle is more oxidised than that at BAB
90 (Back Arc Basin) or MOR (Mid Ocean Ridge) settings as a result of subduc-
91 tion zone processes. The significance of such such oxidation was assessed by
92 Hirschmann (2009) who calculated that 40% of the Earth's mantle has cycled

93 through these oxidised mantle wedge environments over geological time. In spite
94 of these conclusions, there is little conclusive evidence that the oxidation state of
95 the mantle as a whole has changed significantly over geologic time (e.g. Delano,
96 2001; Lee and Li, 2004).

97 The motivation to understand the evolution of the redox budgets of the dif-
98 ferent reservoirs is strong. The control on redox state that is exerted by fluxes
99 of redox-sensitive elements is responsible for the secular evolution of the man-
100 tle and atmosphere, the potential oxidation of arc-magma source zones, with
101 implications for the development of ore deposits (Mungall, 2002), the release
102 of sulphur aerosols from arc volcanism (e.g. de Hoog et al., 2004), and, po-
103 tentially, for climate extremes such as the Paleocene-Eocene thermal maximum
104 (e.g. Svensen et al., 2004).

105 However, there are a number of factors that prevent reliable quantification of
106 subduction-related fluxes of redox-sensitive elements. Subduction input fluxes
107 are heterogeneous along the 44,450 km (Jarrard, 2003) of active subduction zone,
108 and the inaccessible nature of these regions complicates acquisition of reliable
109 data. Nevertheless, the composition of sediments and cooling-related hydrother-
110 mal alteration of the ocean crust have been constrained from measurements on
111 a large number of ocean cores (e.g. Plank and Langmuir, 1998; Jarrard, 2003).
112 The redox budget contribution from partially serpentinised mantle lithosphere,
113 on the other hand, is poorly constrained but potentially significant (e.g. Skel-
114 ton et al., 2005; Ranero and Sallares, 2004) because serpentinisation reactions
115 create magnetite (e.g. Frost and Beard, 2006).

116 Outputs from subduction zones are even more difficult to quantify. Volcan-
117 ism is spatially and temporally heterogeneous, and access to degassing magma
118 chambers is limited, so quantification of volcanic outputs is necessarily sub-
119 ject to large uncertainties. Non-volcanic fluid outputs are thought to be very
120 large (e.g. Mottl et al., 2004; Bebout, 1995) but are diffuse and commonly
121 sub-aqueous, so that measurement is challenging. Additionally, processes such
122 as mineral precipitation, the entrainment of seawater, and microbial processes
123 such as sulphate reduction, alter the chemistry of fluids in the sub-surface envi-

124 ronment. Subduction zone outputs into non-exospheric reservoirs, such as the
125 mantle wedge and the deep mantle, can only be estimated by difference or from
126 exhumed material, and in the latter case, the possibility of modification of the
127 subduction signature by the exhumation process has to be accounted for.

128 Here, redox budget fluxes into, and out of, subduction zones are estimated.
129 Data used to estimate fluxes are mostly taken from the literature, but new data
130 are presented that constrain the fluxes related to partially serpentinised mantle
131 lithosphere. The extent to which these fluxes are offset by MORB and plume-
132 related magmatism is discussed, and the consequences of subduction zone redox
133 budget fluxes for the spatial and temporal evolution of mantle redox state are
134 evaluated.

135 **2. Material and Methods**

136 *2.1. Conceptual Model*

137 For the purposes of this study, the subduction zone is assumed to com-
138 prise (Figure 1) a downgoing slab of altered ocean crust (AOC), that is over-
139 lain by sediment, and supported by partially serpentinised mantle lithosphere.
140 The overriding lithosphere, of unspecified composition, supports a volcanic arc,
141 which occurs above a wedge of sub-arc mantle. There may be partially serpen-
142 tinised mantle wedge overlying the subducting slab (e.g. Hattori and Guillot,
143 2007) but this is not considered separately in the model. Inputs into the sub-
144 duction zone are the sediments, the AOC, and partially serpentinised mantle
145 lithosphere. AOC is assumed to consist of ocean crust 6 km thick, which in-
146 cludes 4 km of gabbro and 2 km of basalt, after Lecuyer and Ricard (1999).
147 Outputs are volcanic rocks and gases from the arc, and non-volcanic fluid re-
148 lease up the surface of the subducting slab. Any difference between the inputs
149 and outputs is assumed to be added to either the sub-arc mantle, or the deep
150 mantle after slab incorporation into the mantle, but the proportion added to
151 each reservoir can only be assessed qualitatively.

152 **Figure 1 near here**

153 Tectonic accretion and erosion at the subduction interface are not considered
154 explicitly, as it is assumed that they balance on some geological timescale. The
155 model does not consider the effects of subduction of ore deposits, the formation
156 of ore deposits, or the subduction of continental crust. The main reason for
157 these omissions is that quantification of compositions and fluxes on a global scale
158 is difficult for these sources, due to their chemically, spatially and temporally
159 heterogenous nature. However, ore deposits, although containing locally high
160 concentrations of certain elements, particularly sulfur, are unlikely to provide
161 a significant contributor to global elemental or redox budgets because of their
162 relative rarity. Continental crust is much more common but it's buoyancy means
163 that subduction is mostly ineffective. Return to the Earth's surface of partially
164 subducted continental crust is well documented (e.g. Zhang et al., 2008) in
165 high pressure and ultra-high pressure metamorphic terrains. The volume of such
166 partially-subducted continental material is known to be small, but the volume
167 of fully-subducted material is unknown.

168 Each component flux is made up of contributions from all the redox-sensitive
169 elements, Fe, C, S, O, H, N, P, U, and so on. Here, we focus on Fe, C, S, O and
170 H in detail; the other elements are neglected because they do not contribute
171 significantly to redox budget on the global scale, even though they may be
172 significant locally, and can provide a useful record of intensive redox variables
173 such as fO_2 . The object of the exercise is to review evidence from the literature
174 for the magnitude of the subduction-related fluxes, and to make a best estimate,
175 with uncertainties, for the fluxes of each component.

176 The overall effect of the fluxes on the oxidising capacity of the reservoirs is
177 assessed by calculation of the redox budget (Evans, 2006). The redox budget of
178 a rock is defined as the number of moles of electrons that need to be added to
179 the rock to reach a given reference state:

$$RB = \sum_i n_i \nu_i, \quad (1)$$

180 where RB is the redox budget, n_i is the number of moles of redox state i

181 present in the sample of interest, and ν_i is the number of electrons required to
 182 take one mole of redox state i to the reference redox state. For example, the
 183 redox budget of two moles of FeO with respect to a reference state of Fe as Fe³⁺
 184 and O as O²⁻ is -2, because 2 moles of electrons would need to be removed
 185 to oxidize the Fe²⁺ to Fe³⁺. It should be noted that some reference states for
 186 redox budget are hypothetical, because a reservoir in which all elements were
 187 present at the reference valence state might be charged. However, this does not
 188 affect the validity or usefulness of the concept. For the purposes of this study,
 189 two different reference states are considered. The first is mantle-like; that is, Fe
 190 is considered to be present as Fe²⁺, C as C⁰, O as O²⁻, H as H¹⁺ and S as S²⁻.
 191 Redox budgets relative to this reference state are shown with the subscript M .
 192 The second is crust-like; that is, Fe is considered to be present as Fe³⁺, C as
 193 C⁴⁺, O as O²⁻, H as H¹⁺ and S as S⁶⁺. Redox budgets relative to this reference
 194 state are shown with the subscript C .

195 Redox budget is an extensive variable, that is, it is independent of the quan-
 196 tity of material considered. However, it is also useful to be able to define redox
 197 budget for a unit mass or quantity, for which the term specific redox budget
 198 (\overline{RB}) can be used. For example, in section 4, we use a specific redox budget
 199 (\overline{RB}) with the units of moles kg⁻¹. It is also useful to define a symbol for redox
 200 budget fluxes, that is, the rate of change of redox budget with respect to time,
 201 and for this the notation \dot{RB} is used.

202 Redox budget is the most appropriate variable for use in studies of this
 203 type because it allows: quantification of fluxes, unlike intensive redox variables
 204 such as f_{O_2} , which are independent of the quantity of material considered;
 205 consideration of the combined effect of fluxes of redox sensitive elements, without
 206 the need to consider interchanges in valence between those elements explicitly;
 207 and, by specification of different appropriate reference states, consideration of
 208 the effect of subduction on mantle and exospheric geochemical reservoirs.

209 *2.2. Input Fluxes*

210 *2.2.1. Sediments*

211 Most of the information on sediment inputs into subduction zones are taken
212 from the Plank and Langmuir (1998) comprehensive study of the material de-
213 livered to the world's subduction zones, updated to reflect new estimates of
214 convergence rates recorded by Jarrard (2003). Other estimates integrated into
215 the assessment are those of Rea and Ruff (1996), Lecuyer and Ricard (1999),
216 and Von Huene and Scholl (1991).

217 Estimates of the total mass of sediments subducted each year range from
218 1.0 (Hay et al., 1988) to 4.0×10^{12} kg year⁻¹ (Von Huene and Scholl, 1991).
219 The preferred estimate here is that of Plank and Langmuir (1998), updated
220 in line with the suggestions of Jarrard (2003), to reflect updated convergence
221 rates and subduction zones not sampled by Plank and Langmuir (1998). The
222 assumed value for the total subducted sediment flux is 1.73×10^{12} kg year⁻¹,
223 which includes 8 weight % water. A somewhat arbitrary uncertainty of 20% of
224 the total is assigned to this value.

225 *Carbon* Holser et al (1988) estimated the rate of subduction of organic carbon
226 to be 0.2×10^{12} moles year⁻¹. Wallman (2001) estimates that the sediment-
227 hosted flux of organic carbon into subduction zones is 0.54×10^{12} moles year⁻¹,
228 based on the input flux of terrigenous and biogenic sediments, at 1×10^{12} kg
229 year⁻¹ and 2×10^{11} kg year⁻¹ respectively (Plank and Langmuir, 1998), and
230 the organic content of these sediments, which are 0.6 wt % and 0.25 wt%.
231 Bebout (1995) based on a 1 wt% average organic carbon content, estimates an
232 annual flux of 1.1 to 2.9×10^{12} moles year⁻¹, but this is based on a possibly
233 unrealistically high proportion of subducted pelitic material.

234 Rea and Ruff (1996) estimated that 1.8×10^{13} moles of carbonate-hosted
235 carbon are subducted each year. Plank and Langmuir (1998) estimated that
236 0.9×10^{12} moles of carbonate carbon are subducted each year. A significantly
237 higher estimate is provided by the compilation of Jarrard (2003), who estimates
238 that total global subduction of sediment-hosted CO₂ is 4.25×10^{12} moles year⁻¹.

239 Here, we assume that the average subducted sediment is 3 ± 1.4 weight %
240 carbon as CO_2 in carbonate, after Plank and Langmuir (1998), which gives a
241 carbonate carbon flux of $1.18 \pm 0.60 \times 10^{12}$ moles year $^{-1}$. The uncertainty on
242 the flux is calculated by standard error propagation from the uncertainties of
243 the initial carbonate content and the sediment flux value, assuming that the
244 two parameters are uncorrelated. For zero valent carbon, we take the Wallman
245 estimate of 0.54×10^{12} moles year $^{-1}$, and increase it by one third, to account for
246 the subduction zones not investigated by Plank and Langmuir (Jarrard, 2003),
247 to give $0.72 \pm 0.39 \times 10^{12}$ moles year $^{-1}$, equivalent to an average organic carbon
248 content of 0.5 ± 0.25 wt% in subducted sediments. The 50 % uncertainty on
249 the latter figure is arbitrary and reflects the wide range of literature estimates.

250 *Iron* Chester (1990) estimates that ocean sediments have an average total
251 iron content of 4.17 wt%, and that the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of this material is 0.82. The
252 concentration is consistent with the analysis of Plank and Langmuir (1998),
253 who give a value of 5.41 ± 0.42 wt % FeO. Here we assume a Fe^{2+} content of
254 0.72 wt% and an Fe^{3+} content of 3.28 wt%, with uncertainties of 8% relative on
255 each. The total iron is equal to 5.14 wt% as FeO or 5.72 wt% as Fe_2O_3 . The
256 sediment-hosted flux of Fe^{2+} and Fe^{3+} into subduction zones is therefore 0.22
257 ± 0.05 and $1.02 \pm 0.22 \times 10^{12}$ moles year $^{-1}$ respectively.

258 *Sulphur* Pyrite is relatively rare in deep sea sediments (Canfield, 2004), and
259 estimates of the sulphur content of subducting sediments were not presented in
260 the Plank and Langmuir (1998) compilation. Here we follow the approach of
261 Canfield (2004) and assume that approximately 1 wt % Fe in deep sea sediments
262 is available for pyrite formation (Raiswell and Canfield, 1998), which gives a S
263 content for these sediments of 1.15 wt%. This value is a maximum for the case
264 where all subducting sediments have undergone pyrite formation in the sulphide
265 stability field, and is given a 50% relative uncertainty. The calculated sediment
266 flux of S^- into subduction zones is therefore $0.62 \pm 0.33 \times 10^{12}$ moles year $^{-1}$.

267 *2.2.2. Ocean Crust*

268 Previous estimates of the mass of ocean crust subducted have been presented
269 by Ito et al. (1983) who estimated a subduction flux of 58.9×10^{15} grams
270 year^{-1} , and by Peacock (1990) who give a value of 60×10^{15} grams year^{-1} .
271 Jarrard (2003) estimates that 2.45 km^2 of ocean crust is subducted each year.
272 This value is about 1/3 less than that from previous works, mainly because
273 of reductions in estimated plate spreading rates. If this estimate is combined
274 with the assumptions regarding the thickness and composition of AOC given
275 in the conceptual model and an assumed average density of 3100 kg m^{-3} , then
276 a subduction flux of 45.6×10^{15} grams year^{-1} is calculated. A comparable
277 estimate is provided by Lecuyer and Ricard (1999), who state that the average
278 ocean crust is produced at $65,000 \text{ km}$ of ridge, spreading at 5 cm year^{-1} , to give
279 a volume of $15.6 \text{ km}^3 \text{ year}^{-1}$, implying a subduction flux of 48.4×10^{15} grams
280 year^{-1} . Crisp (1984) estimates that ocean crust creation proceeds at 21 km^3
281 year^{-1} , which implies a subduction flux of 65.1×10^{15} grams year^{-1} if rates of
282 crust creation and destruction are taken to be equal. Here, we take the most
283 up to date estimate of Jarrard (2003), with the proviso that this represents a
284 minimum flux. The uncertainty is taken to be 20% of the total, to reflect the
285 spread of estimates.

286 *Carbon* The erupted CO_2 content of MORB is about 200ppm (Hayes and
287 Waldbauer, 2006). Carbonate is also added, post-eruption, to ocean floor basalts
288 by hydrothermal circulation at the mid-ocean ridge (Staudigel et al. 1989; Alt
289 and Teagle 1999, 2003). Staudigel et al. (1989) undertook a detailed study of
290 material from holes 417A, 417D, and 418A. A weighted average CO_2 concen-
291 tration for these holes gives 2.95 wt%, indicating substantial CO_2 addition. Alt
292 and Teagle (1999) calculated a weighted average for the CO_2 content of AOC
293 of 0.21 wt%, and estimated that addition of carbon to ocean crust in the form
294 of carbonate occurs at a rate of $1.5 - 3.4 \times 10^{12}$ moles year^{-1} . Kerrick (2001)
295 estimated that carbonate formation in MOR hydrothermal systems produces
296 3.5×10^{12} moles year^{-1} of carbonate. A lower estimate is provided by Paul et

297 al. (2006), who used measurements from ODP Site 1224, which is less altered
298 than most ocean crust segments. Paul et al. (2006) calculated that, if site 1224
299 were representative then carbonation of ocean crust would add 0.21×10^{12} moles
300 year^{-1} of carbonate to the AOC. This estimate is an order of magnitude smaller
301 than estimates (e.g. Alt and Teagle, 1999) derived from more altered crustal
302 sections. The compilation of Jarrard (2003) indicates that CO_2 enrichment is
303 progressive over at least 10 Ma, and that the CO_2 subduction fluxes depend on
304 the age of subducted crust.

305 Jarrard incorporates the effect of increasing CO_2 with crustal age into cal-
306 culations to produce an estimate of the subduction flux of CO_2 as carbonate in
307 AOC of 2.3×10^{12} moles year^{-1} . Here, we multiply the average CO_2 content of
308 ocean crust obtained by Alt and Teagle (1999) by the Jarrod (2003) estimate
309 of AOC mass flux to obtain an estimate of C^{4+} subduction rate of $2.2 \pm 0.6 \times$
310 10^{12} moles year^{-1} . The uncertainty is based on an assumed 20% uncertainty
311 on both the CO_2 content and the AOC mass flux.

312 *Iron* Lecuyer and Ricard (1999) estimate that ocean basalt has an average
313 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.26 ± 0.08 and a total Fe content (wt %) of 7.35 ± 1.45 ($n=221$,
314 where n is the number of samples in their study), and that gabbro has an
315 average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.2 ± 0.08 and a total Fe content (wt %) of 5.8 ± 3.6
316 ($n=130$). This gives an average value for the hydrothermally altered ocean
317 crust for $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.22 ± 0.08 . This value is slightly lower than a previous
318 estimate of 0.24, made by Ronov and Yaroshevsky (1976), but these workers
319 did not take the lesser extent of oxidation in the gabbro section of the ocean
320 crust into account. The value is also comparable to that measured by Lecuyer
321 and Ricard (1999) for ophiolites and back-arc basin basalts, of 0.25. Johnson
322 and Semyan (1994) examined the top 50 metres of basaltic ocean crust using
323 data from all available Deep Sea Drilling and Ocean Drilling Program holes
324 available at that time. They measured an average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.14 in basalt
325 younger than 5 Ma, with an increase to 0.29 at 5 Ma, and a further increase
326 to 0.36 between 5 and 20 Ma. Further age increases did not result in further
327 statistically significant changes in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$.

328 A weighted average of the values given by Lecuyer and Ricard (1999), using
329 the ocean crust structure summarised in the conceptual model, gives an Fe^{2+}
330 content of AOC of 4.9 ± 0.59 wt%, and an Fe^{3+} content of 1.4 ± 0.62 wt%. The
331 flux of Fe^{2+} is therefore $40 \pm 9.3 \times 10^{12}$ moles year⁻¹, while the flux of Fe^{3+} is
332 $11.4 \pm 5.6 \times 10^{12}$ moles year⁻¹. Uncertainties on iron contents and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$
333 ratios are propagated from those reported by Lecuyer and Ricard (1999).

334 *Sulfur* Measurements of sulfur contents of AOC are relatively sparse in the
335 literature. However, detailed measurements (Alt, 1995) have been made for sam-
336 ples from Ocean Drilling Program hole 504B, near the Costa Rica rift, which
337 penetrates 1700m of oceanic basement, and hole 735B, which penetrates gab-
338 broic ocean crust. The primary magmatic sulfur content at hole 504B is 0.096
339 wt% sulfur, consistent with measured primary sulfur contents in MORB of be-
340 tween 0.064 and 0.18 wt%. Subsequent seawater alteration is highly spatially
341 heterogeneous. Honnorez (2003) records sporadic anhydrite and common pyrite
342 as secondary minerals throughout the volcanic and sheeted dykes section of
343 hole 504B. There is a continuum between the bulk of ocean crust, which is
344 less altered, the 'ocean floor metamorphism' of Honnorez (2003), with the 504B
345 and 735B cores taken as the type example, to the extreme hydrothermal alter-
346 ation induced by intense hydrothermal circulation in locations such as the TAG
347 mound, where basalts are almost completely replaced by quartz-paragonite-
348 pyrite assemblages.

349 Alt (1995) present sufficient data to allow a post-alteration weighted average
350 S content of 0.0716 wt% to be calculated for hole 504B. 1% of this sulfur was
351 held in anhydrite, and 99% in pyrite. This distribution is incompatible with the
352 large proportion of sulfur lost during hydrothermal circulation of seawater at
353 mid-ocean ridges (Alt, 2003), which is assumed to be precipitated as anhydrite.
354 This apparent contradiction can be explained by the retrograde solubility of
355 anhydrite. The solubility of this mineral increases as temperature decreases,
356 so it has been proposed (Alt, 1995; Alt, 2003) that anhydrite precipitated in
357 MOR hydrothermal circulation cells redissolves on cooling. Alternatively, hole
358 504B may be unrepresentative - the sheeted dyke complex exposed within the

359 Macquarie Island ophiolite contains intense gypsum veining, where gypsum is
360 after anhydrite, though exposures are insufficient to quantify sulfur addition
361 satisfactorily.

362 Here, we take the Alt (1995) weighted average value of 0.07 wt% for the
363 S^- content of AOC. The S^{6+} content, is taken to be half way between the Alt
364 (1995) value of 0.0007 wt% from 504B and the maximum value of 0.072 wt%,
365 which is consistent with the observed sulfate losses from seawater at mid-ocean
366 ridges documented by Alt (2003). Uncertainties are taken to be 20% on the S^-
367 content, and 50% on the S^{6+} content. These assumptions result in calculated
368 sulfur subduction fluxes of $1.01 \pm 0.28 \times 10^{12}$ moles year $^{-1}$ for S^- and $0.51 \pm$
369 0.28×10^{12} moles year $^{-1}$ for S^{6+} .

370 *2.2.3. Mantle Lithosphere*

371 Subduction of un-serpentinised mantle lithosphere has no net effect on the
372 redox budget of the exosphere or the mantle, so only fluxes that relate to ser-
373 pentinised material need to be estimated. However, it is very difficult to con-
374 strain the rate of subduction of serpentinised mantle lithosphere, because of
375 the heterogeneous nature of serpentinisation. Serpentinisation is known to oc-
376 cur at transform faults (e.g. Mevel, 2001), fracture zones, along slow-spreading
377 mid-ocean ridges (e.g. Cannat, 1996), and at passive margins (e.g. Skelton et
378 al. 2005). Estimates of the volume percentage of serpentinised lithosphere vary
379 substantially. Carlson (2001) examine seismic evidence from the Atlantic Ocean
380 crust and state that serpentinised material cannot make up more than 5% of
381 the lower ocean crust, though higher values in the lower velocity zone could
382 bring the average to around 6%. Mevel (2003) discuss serpentinisation at slow-
383 spreading and ultra-slow spreading ridges. These workers summarise evidence
384 consistent with highly serpentinised peridotite ($> 70\%$) in regions of ridge with
385 low magma production. Hacker et al. (2003) show that seismic velocities in the
386 low velocity zone are consistent with around 20% serpentinisation, while exam-
387 ination of the results of Skelton et al. (2005) reveals that the seismic profile of
388 the Iberian Margin is consistent with 28% serpentinisation of an 8km section of

389 initially peridotitic crust.

390 Serpentinisation is also thought to occur as a result of lithosphere bending
391 and subsequent fluid infiltration as the lithosphere enters subduction zones.
392 Ranero and Salleres (2004) use seismic evidence to estimate that the lithosphere
393 entering the North Chile trench is 17 % serpentinised to a depth of 20 km. A
394 more conservative estimate is provided by Rupke et al. (2004), who assume
395 that a 10 km thick layer of the mantle lithosphere is 5 % serpentinised; this
396 estimate is broadly consistent with that of Carlson (2001). An even higher
397 estimate is provided by Gorman et al. (2006), who model subduction zone
398 processes assuming 20km of 20% serpentinised mantle. If the two most extreme
399 estimates are treated as brackets, and the thickness is taken to be the product
400 of the percentage serpentinisation and the total thickness, then the average
401 thickness of serpentinised peridotite entering the Earth's subduction zone is
402 between 0.5 and 3.4 km. The volume of subducted serpentinised peridotite,
403 calculated assuming a subducted area of $2.45 \text{ km}^2 \text{ year}^{-1}$, after Jarrard (2003),
404 is then 1.23 to $8.33 \text{ km}^3 \text{ year}^{-1}$, equivalent to a mass flux of 3.4 to 23.3×10^{15}
405 grams year^{-1} for a density of 2800 kg m^{-3} . Here we take the average of the two
406 estimates of $13 \times 10^{15} \text{ grams year}^{-1}$, with an uncertainty of $10 \times 10^{15} \text{ grams}$
407 year^{-1} .

408 Estimates of Fe, C and S contents of serpentinised peridotite are relatively
409 rare, though estimates for one or more of these parameters are presented by
410 Alt and Shanks (2003); Paulick et al. (2006); Hattori and Guillot (2007) and
411 Vils et al. (2008). Additionally, it is difficult to obtain good constraints on
412 the spatial heterogeneity of data because of the limited diameter of drill core.
413 Ideally, it would be possible to use partially serpentinised ophiolites as analogues
414 for partially serpentinised mantle lithosphere, because easy access is possible
415 to large areal extent of outcrop. However, it is not necessarily the case that
416 ophiolite-hosted serpentinised peridotites are a satisfactory analogue for those
417 found in subducting slabs. For this reason we present here new measurements
418 of Fe, C and S contents for serpentinised peridotite material from the New
419 Caledonia ophiolite and from ODP leg 209, holes 1268 and 1274. The data allows

420 us to (1) compare the characteristics of the two different types of ultramafic
421 material and (2) to gain additional estimates of the carbon, iron, and sulfur
422 contents of serpentinised peridotite.

423 *Geological Settings New Caledonia* Samples were collected from the ophiolite
424 that forms the Massif du Sud in New Caledonia (Prinzhofer et al. 1980; Marchesi
425 et al. 2009). The Massif du Sud is constructed from supra-arc mantle (DuPuy
426 et al., 1981) that was thrust onto pre-existing continental basement of New
427 Caledonia during the Eocene (Aitchison et al. 1995). The ophiolite consists of
428 mostly harzburgitic peridotite with rare gabbro pods; structurally higher units
429 such as pillow basalts and sheeted dykes are absent. Much of the ophiolite
430 is heavily lateritised, but unweathered material has been exposed by human
431 activities in some areas.

432 Samples were collected from three localities with varying degrees of serpen-
433 tinisation from the relatively unweathered exposures in the spillway of the Yate
434 Dam. Samples NC07-01 to 04 were collected from outcrop that was heavily
435 veined and serpentinised, and located within metres of a highly altered thrust
436 fault at 166°40.051' E, 022°08.593' S. Samples NC07-05 to 07 and NC07-10 were
437 taken from an outcrop with an intermediate extent of alteration at 166°53.072'
438 E, 022°08.863' S. Samples NC07-08 and 09 were taken from the margin of an
439 orthopyroxene vein in harzburgite at this intermediate outcrop. Samples NC07-
440 11 to 14 were taken from relatively fresh outcrop at 166°52.985' E, 022°08.933'
441 S. At this outcrop, olivine and orthopyroxene grains could still be distinguished
442 in some areas.

443 *ODP Leg 209* ODP Leg 209 drilled abyssal peridotite from the 15°20'N
444 area of the Mid-Atlantic ridge. These peridotites are sections of the upper
445 mantle, which are exposed on the seafloor by tectonic faulting associated with
446 crustal thinning and extension. In this area, peridotite and gabbroic rocks are
447 exposed on both sides of the slow-spreading Mid-Atlantic Ridge in the vicinity
448 of the 15°20'N fracture zones. Evidence for seawater-peridotite interactions are
449 provided by the high temperature hydrothermal discharges of the Logatchev
450 black smoker field (e.g. Charlou et al., 1998). Full details of lithologies and the

451 geochemistry of the rocks are provided by Paulick et al. (2006) and Vils et al.
452 (2008).

453 For the purposes of this study, we obtained samples from two drillholes. Hole
454 1268A (samples 69321-69332) samples talc- and serpentine-altered harzburgite
455 and dunite, with pyrite, which is relatively rare in samples from the other ODP
456 209 drillholes. Material from this hole is highly altered and alteration minerals
457 form over 90% of the mineral assemblage in most samples. Hole 1274A (samples
458 69427-69499) samples the least altered material found, and alteration minerals
459 comprise between 60 to 95 % of the mineral assemblage. A detailed description
460 of the mineralogy and geochemistry of samples from these holes is provided by
461 Paulick et al. (2006).

462 *Methods* Polished thin sections were made from selected samples from both
463 sample suites and subjected to petrological examination. Major element com-
464 position, plus selected trace elements of the rocks was determined by fusion with
465 lithium tetraborate and X-ray Fluorescence (XRF) analysis. Carbon and sulfur
466 contents were determined by LECO analysis. Total iron was determined by
467 XRF, and the FeO content was determined by titration against ceric sulfate. It
468 should be noted that this titration will also oxidise reduced sulfur, so values are
469 overestimated for sulfur-bearing samples. The overestimation was calculated to
470 be less than 1% for the New Caledonia samples, and less than 5% for all but
471 four of the ODP 209 samples, but reaches 30% for sample 69332, which has the
472 highest sulfur content. All analysis was performed by the commercial Genalysis
473 laboratory in Perth, Australia.

474 **Tables 1, 2 and 3 near here**

475 **Figure 2 near here**

476 *Results* The primary assemblage at the ODP 209 site and in the New Cale-
477 donia ultramafics is that of harzburgite, with clinopyroxene generally absent.
478 Chromite is present in most of the New Caledonia samples, but is less common
479 in the ODP 209 samples.

480 Samples from both localities are heavily serpentised with primary min-
481 erals forming less than 40% of the assemblage in all cases. Olivine is almost

482 completely destroyed in all of the ODP 209 samples, whereas orthopyroxene
483 is more resistant and is present in variously altered states in most samples.
484 The New Caledonia samples are slightly less altered, with some primary olivine
485 remaining in some cases. The most common alteration mineral is serpentine.
486 It is present as an hour-glass textured replacement of olivine, and in multiple
487 generations of veins that cross-cut all the samples. Magnetite is also present
488 in most samples, but is volumetrically more abundant in the New Caledonia
489 samples where it forms rims on serpentine, and forms part of the vein mineral
490 assemblage. Talc and carbonate veins are sporadically present in the ODP 209
491 samples but are rare in the New Caledonia samples. Where talc and carbonate
492 are found together, the carbonate veins and alteration postdate the talc veins.
493 Pyrite is present in a small number of samples from both localities, anhydrite
494 and pyrrhotite were not observed, but preparation techniques would probably
495 have resulted in anhydrite dissolution if it were present.

496 The major element geochemistry of both sample suites (Table 1) is consis-
497 tent with a depleted mantle origin for the harzburgites. The New Caledonia
498 samples are slightly more depleted than the ODP 209 samples, as shown by the
499 lower Al_2O_3 and TiO_2 and higher MgO contents for the New Caledonia samples
500 (Figure 2a). The New Caledonia samples also show higher Cr and Ni and lower
501 Ti (Table 2), consistent with a greater degree of depletion. The LOI (Loss on
502 Ignition) is a proxy for serpentinisation, as the primary assemblage is assumed
503 to be effectively anhydrous; inspection of the results for this parameter (Figure
504 2b) show that the New Caledonia samples are generally less altered than the
505 ODP 209 samples, consistent with the petrological observations. Pure magne-
506 sian serpentine of the formula $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ has a H_2O content of 13.04 wt%,
507 so the more water-rich values obtained for some samples from both sample sites
508 indicates the presence of other hydrated minerals. Brucite ($\text{Mg}(\text{OH})_2$) is 31 wt%
509 water and is common as an alteration product of olivine (Paulick et al., 2006;
510 Frost and Beard, 2007) so it is likely that fine-grained brucite not recognised by
511 optical microscopy is also present.

512 The ODP 209 rocks, in addition to the higher degree of alteration, also

513 exhibit higher sulfur contents (Figure 2b), $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios (Figure 2c), and
514 higher concentrations of carbon (Figure 2d), than the New Caledonia samples.
515 There is broad continuity between the two sample sets, although the most sulfur-
516 and carbon-rich samples from ODP 209 ($\text{S} > 0.2 \text{ wt}\%$, $\text{C} > 0.5 \text{ wt}\%$) are outliers
517 to the broad trend defined by the remaining samples. Redox budgets for the
518 two sample suites are also broadly similar, with apparent continuity between
519 the New Caledonia and the majority of the ODP 209 samples (Figure 2e,f).
520 The difference between the two data sets is small because slightly lower iron
521 contents in the ODP 209 sample suite offsets the slightly higher $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ for
522 this suite.

523 To conclude, the ODP and New Caledonia samples are different with respect
524 to the degree of serpentinisation, but petrological and geochemical evidence sug-
525 gests that the serpentinisation process itself has proceeded in a similar way and
526 with similar chemical consequences. It is therefore viable to use the New Caledo-
527 nia rocks, with caution, as an analogue for the earlier stages of serpentinisation
528 undergone by abyssal peridotites.

529 *Carbon* Measurements of the carbon content of serpentinised peridotite are
530 provided by Paulick et al. (2006) for 5 samples from four different drillholes
531 sampled by ODP 209. The value obtained for carbon as CO_2 , by a similar
532 method to that used here, is $0.05 \pm 0.03 \text{ wt}\%$. This is comparable to values
533 obtained for the New Caledonia samples of $0.13 \pm 0.08 \text{ wt}\%$ ($n=13$) and some-
534 what lower than values obtained for ODP 209 samples by this study, of 0.45
535 $\pm 0.56 \text{ wt}\%$ ($n=18$), which reflects the inclusion of a small number of samples
536 that contain a large proportion of carbonate veins. A weighted combination
537 of all analyses gives a value of $0.28 \pm 0.8 \text{ wt}\%$ C, and this value is used here.
538 Carbon is assumed to be present as carbonate, as other forms of carbon were
539 not observed. The mass flux of C^{4+} in serpentinised peridotite is therefore 3.03
540 $\pm 3.83 \times 10^{12} \text{ moles year}^{-1}$.

541 *Iron* Measurements of FeO and Fe_2O_3 contents of 13 serpentinised peri-
542 dotite samples from ODP 209 are provided by Paulick et al. (2006). Values
543 of $6.88 \pm 0.95 \text{ wt}\%$ for total Fe as FeO, and 0.63 ± 0.07 for $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ were

544 obtained. These values are comparable to values for the New Caledonia sam-
545 ple suite ($n=13$) of 7.14 ± 0.34 wt% for total Fe as FeO, and 0.5 ± 0.13 for
546 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, and values for the ODP sample suite of 6.46 ± 0.37 wt% for total Fe
547 as FeO, and 0.52 ± 0.08 for $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. These values are within uncertainty of
548 each other so the weighted average was taken, which gives a Fe^{2+} content of 2.39
549 ± 0.4 wt% and a Fe^{3+} content of 2.88 ± 0.4 wt%. The mass flux of Fe^{2+} and
550 Fe^{3+} in serpentinised peridotite are therefore $5.56 \pm 4.38 \times 10^{12}$ moles year⁻¹
551 and $6.70 \pm 5.24 \times 10^{12}$ moles year⁻¹ respectively. The large uncertainties on
552 the fluxes are mainly derived from the uncertainties on the volume of subducted
553 serpentinised mantle lithosphere.

554 *Sulfur* Unaltered peridotite contains, on average, 0.025 wt% sulfur. Alt et
555 al. (2007) present measured sulfur contents for peridotites and gabbros from
556 ODP site 209, at the 15°20'N fracture zone on the Mid-Atlantic Ridge. Average
557 acid volatile sulfur contents, which is taken to reflect the contribution from
558 S^{2-} -bearing minerals such as pyrrhotite was 0.041 ± 0.055 wt% S ($n=27$), with
559 a range of 0 to 0.21 wt% S. The average chromium-reduced sulfide, which is
560 taken to represent pyrite (S^-) was 0.048 ± 0.14 wt% S ($n=28$), with a range
561 of 0 to 0.73 wt% S. The average sulfate sulfur content was 0.078 ± 0.073 wt%
562 S ($n=36$), with a range of 0.011 to 0.420 wt% S. The large ranges indicate the
563 spatially heterogeneous nature of serpentinising reactions. Sulfur was assumed
564 to be derived from either the primary magmatic source or microbial reduction
565 of seawater. Additional sulfur analyses, from ODP leg 209 (Paulick et al., 2006;
566 Vils et al., 2008; this study), serpentinised peridotites from mud volcanoes in
567 the Izu-Bonin Forearc (Alt and Shanks, 2006), serpentinised peridotites from
568 the MARK fracture zone sampled on ODP leg 125 (Alt and Shanks, 2003), and
569 from New Caledonia (this study), are summarised in Table 3. Values are highly
570 heterogeneous. Values for the New Caledonia and Izu-Bonin forearc sites are
571 lower than those from the MAR fracture zone sites, which may reflect that the
572 former are mantle wedge serpentinites that may have experienced less direct
573 seawater interaction than the MAR fracture zone samples. The values from
574 Alt et al. (2007) are preferred for this study, because of the detail provided

575 on speciation, and because they are known to involve abyssal peridotites. The
576 mass flux of S^{2-} , S^{1-} and S^{6+} in serpentinised peridotite are therefore $0.16 \pm$
577 0.24×10^{12} moles year $^{-1}$, $0.2 \pm 0.59 \times 10^{12}$ moles year $^{-1}$ and $0.33 \pm 0.38 \times 10^{12}$
578 moles year $^{-1}$ respectively.

579 *2.3. Output Fluxes*

580 *2.3.1. Igneous rocks*

581 The flux of igneous rocks from subduction-related magmatism is taken from
582 the work of DePaolo (1983) on the growth of continents, and includes plutonic
583 material. DePaolo's estimate is of 2.5 ± 0.4 km 3 year $^{-1}$, which for a density of
584 3000 kg m $^{-3}$, gives a mass flux of $7.5 \pm 1.2 \times 10^{15}$ grams year $^{-1}$.

585 *Carbon* Wysoczanski et al. (2006) measured volatile contents of quenched
586 glasses from pillow-lava rims in the Kermadec Arc. Carbon contents are gen-
587 erally low, at 0.0007 ± 0.0003 wt% ($n=11$), and always less than 0.0016 wt%
588 in glasses, although a content of 0.018 wt% was measured in a single melt in-
589 clusion. Wallace (2005) presents a summary of CO $_2$ contents from a range of
590 arc and back-arc magmas, and concentrations are generally less than 0.1 wt %,
591 though maximum concentrations of 0.1 and 0.21 wt% are recorded in melt inclu-
592 sions from Cerro Negro, Nicaragua, and Central Mexico, respectively. Carbon
593 dioxide is quite insoluble in silicate melts (e.g. Dixon and Stolper, 1995) so it is
594 reasonable to assume that most of the carbon degases, and that this degassed
595 carbon is included in the arc volcanic gases contribution to the budget. Here,
596 we take the average of the Wysoczanski et al. (2006) measurements of 0.0007
597 ± 0.0003 wt%. The redox state of the arc lavas is consistent with carbon in the
598 $+4$ valence state so this estimate implies a C $^{4+}$ flux of $0.0044 \pm 0.002 \times 10^{12}$
599 moles year $^{-1}$.

600 *Iron* Lecuyer and Ricard (1999) measured the average Fe^{3+}/Fe_{tot} in arc lavas
601 to be 0.41 ± 0.17 , with an average iron content of 7.53 wt% ($n=99$). Note that
602 this estimate excludes the effects of degassing-related oxidation. Kelley and
603 Cottrell (2009) measure Fe^{3+}/Fe_{tot} in a selection of arc-lava hosted olivine melt
604 inclusions, and obtain a value for Fe^{3+}/Fe_{tot} of 0.21 ± 0.05 , with an average total

605 FeO+Fe₂O₃ of 10.34 ± 2.39 wt %. However, their values may be skewed to high
606 iron values by the use of olivine-hosted melt inclusions. There is no published
607 data, to the author's knowledge, on Fe³⁺/Fe_{tot} ratios of intrusive igneous rocks
608 associated with arc magmatism, so the composition is assumed to be the same as
609 those for the arc extrusive rocks. A weighted average of the Kelley and Cottrell
610 (2009) and Lecuyer and Ricard (1996) data gives concentrations of 4.6 ± 1.4
611 and 3.1 ± 1.4 wt % and fluxes of 6.2 ± 2.1 and $4.2 \pm 2 \times 10^{12}$ moles year⁻¹
612 Fe²⁺ and Fe³⁺ respectively.

613 *Sulfur* Arc lavas commonly have low sulfur contents. Alt et al. (1993) record
614 a range of 0.002 to 0.029 wt %, with an average of 0.01 wt% in glasses from the
615 Marianas Island Arc. Similarly, Wysoczanski et al. (2007) record concentrations
616 of 0.03 to 0.07 wt% from the Kermadec arc. The low sulfur contents have been
617 attributed to a low sulfur content in the arc magma source (Alt et al., 1993),
618 which is consistent with the low sulfur contents of wedge-derived serpentinite
619 from seamounts in the Izu-Bonin arc (Alt and Shanks, 2006). Alternative, or
620 complementary, reasons for the low sulfur contents are degassing (Wysoczanski
621 et al., 2007) and the relatively low solubility of sulfur in silicate melts
622 that originate from slightly oxidised mantle (e.g. Alt et al., 1993). Higher sulfur
623 contents are recorded in the review of arc and back-arc basaltic magma volatile
624 contents by Wallace (2005), who assumes a global average of 0.13 wt% for arc
625 basalt S content. Here, we take an intermediate value of 0.05 ± 0.04 wt% sulfur
626 for arc-related igneous rocks. Observed sulfur-bearing phases in arc-related
627 igneous rocks are pyrite, pyrrhotite, and chalcopyrite (e.g. Wysoczanski et al.
628 2007). Primary sulfides occur in small quantities as inclusions in phenocrysts.
629 Sulfides also occur in vesicles, so these grains are likely to be secondary, although
630 the sulfur is probably derived from the magma. Here it is assumed that S⁻ is
631 the dominant valence. This estimate implies a S⁻ flux of $0.12 \pm 0.1 \times 10^{12}$
632 moles year⁻¹.

633 *2.3.2. Volcanic Gases*

634 Fluxes of volcanic gases are heterogeneous and difficult to quantify, but their
635 importance in exospheric element budgets and influence on the environment
636 has motivated many studies of this topic. Estimates of fluxes tend to be made
637 by measurement of gases at individual volcanoes, followed by extrapolation to
638 global values with power law distribution expressions, and removal of mantle
639 contributions via measurements of ^3He (e.g. Hilton et al. 2002).

640 *Carbon* Hilton et al. (2002) made an extensive compilation of the outputs
641 of volatiles from arcs, which included outputs from 11 arc segments worldwide.
642 The total flux of CO_2 from arc volcanism is 1.62×10^{12} moles year $^{-1}$ (Hilton
643 et al., 2002). ^3He measurements have been used to estimate that about 13%
644 of this carbon is from the mantle (Shaw et al., 2003) and the rest is recycled
645 carbon from the subducting slab. This is consistent with estimates by previous
646 authors that range between 0.3 and 3.1×10^{12} moles year $^{-1}$ (Marty et al., 1989
647 and Sano and Williams, 1996, respectively).

648 A theoretical estimate for CO_2 release from subducted ocean crust sections
649 that includes serpentinised upper mantle, altered ocean crust, and sediments
650 as a function of geothermal gradient is provided by Gorman et al. (2006).
651 A combination of their model with the subduction zone data compilation of
652 Jarrard (2003) gives a flux of CO_2 into the sub-arc region of 0.3 to 9×10^{12}
653 moles year $^{-1}$, with the higher end of the range preferred by the authors.

654 Here we take the estimate of Hilton et al. (2002), corrected to remove
655 the 13% mantle contribution, to give a flux of 1.41×10^{12} moles year $^{-1}$. The
656 uncertainty of 20% is taken to be the same as the correction between global and
657 observed fluxes.

658 *Iron* The iron content of volcanic gases is assumed to be negligible.

659 *Sulphur* Estimates of SO_2 fluxes from arcs range from 0.16- 0.32×10^{12} moles
660 year $^{-1}$ (Hilton et al., 2002; Wallace, 2005). Reduced sulphur species are much
661 less abundant than SO_2 . Here, we use the estimate of Hilton et al. (2002),
662 which is based on a compilation of measurements of gases from 11 arc segments.

663 These authors calculate a global SO₂ volcanic flux of 0.32 x 10¹² moles year⁻¹.
664 An uncertainty is not provided by these authors, so a value of 20% of the total
665 is assumed.

666 *Hydrogen* Hydrogen may contribute to the redox budget of subduction zones
667 by its presence in volcanic gases. Here, we follow the approach of Waldbauer
668 and Hayes, (2006), who assume that the ratio of hydrogen to water in volcanic
669 gases is 0.01 (Giggenbach, 1992). This assumption permits calculation of the
670 hydrogen flux from the arc magmatic water flux, which is estimated to be 17 x
671 10¹² moles year⁻¹ (Wallace, 2005). Thus, the hydrogen flux is 0.17 x 10¹² moles
672 year⁻¹. No uncertainty is provided so a value of 20% of the total is assumed.

673 2.3.3. *Non volcanic fluid release*

674 Non volcanic fluid release occurs via fluids that escape through the accre-
675 tionary wedge, and possibly, in the back-arc region, although this issue is contro-
676 versial (e.g. Sano et al., 2001, discussion in Hilton et al., 2002). The magnitude
677 of non-volcanic fluid release is difficult to constrain, because of the wide range
678 of wedge geometries and characteristics, and the diffuse, sub-aerial nature of
679 fluid release. However, the mass homogenisation of δ¹⁸O in accretionary wedge
680 material (Bebout, 1995) suggests that the fluids are likely to be voluminous
681 and H₂O-rich. The total flux of H₂O into subduction zones is of the order of
682 1-2 x 10¹⁵ grams year⁻¹ (Rea and Ruff, 1996, and references therein; Jarrard,
683 2003). 60 - 70% of this water is structural water in low temperature diagenetic
684 minerals, or pore-water in sediments or altered ocean crust (Jarrard, 2003), and
685 is likely to be released at relatively shallow depths and to flux either up the
686 slab/mantle interface (Jarrard, 2003) or upwards through the mantle and ac-
687 cretionary wedge (Mottl et al. 2004). The mass of water released in this way
688 is likely to be around 1 x 10¹⁵ grams year⁻¹, and the fluxes of solutes can be
689 calculated if sufficient estimates of their concentrations are known. A separate
690 contribution may be made by methane-rich fluids from mud volcanoes and seeps
691 (e.g. Kopf, 2002).

692 *Carbon* The extent of to which CO₂ and other C-bearing gases are emitted in

693 non-volcanic settings is very poorly constrained and a wide range of estimates
694 have been presented. Carbon is present as dissolved carbonate in seep fluids
695 (e.g. Mottl et al. 2004), and as methane in mud volcanoes and seeps (e.g.
696 Kopf, 2002; 2003; Milkov et al., 2003).

697 Hilton et al. (2002) use a mass balance approach, based on the assumption of
698 steady state mantle carbon concentrations, to calculate a total fore-arc carbon
699 flux of 0.4×10^{12} moles year⁻¹. Wallman (2001) gives a conservative estimate
700 of the return of carbon to the exosphere via fluid venting in fore-arcs of $0.04 \times$
701 10^{12} moles year⁻¹, but the oxidation state of this carbon is not specified, and
702 the contribution of back-arc degassing is omitted.

703 Jarrard (2003) combines the inferred flux of fore-arc fluids (around $1.4 \times$
704 10^{15} grams year⁻¹) with the calculated solubility of CO₂ in fore-arc fluids (0.02
705 wt%) to calculate a CO₂ flux of about 0.2 % of subducted CO₂, or 6.6×10^9
706 moles year⁻¹. Mottl et al. (2004) measure alkalinity in fluids from springs in the
707 Marianas forearc region. Measured CO₂ concentrations, which were corrected
708 for carbonate precipitation were 20 - 60 mmol kg⁻¹. These values, coupled
709 with a total reflux fluid volume of 1.4×10^{12} kg year⁻¹, imply a carbonate
710 flux of $2.8 - 8.4 \times 10^{10}$ moles year⁻¹, an order of magnitude higher than the
711 Jarrard (2003) estimate. The higher estimate is preferred, because it is based
712 on actual rather than theoretical calculated CO₂ concentrations. Even higher
713 estimates are provided by Gorman et al. (2006) who model CO₂ release from
714 subducted ocean crust sections that includes serpentinised upper mantle, altered
715 ocean crust, and sediments as a function of geothermal gradient. A combination
716 of their model with the subduction zone data compilation of Jarrard (2003)
717 gives a flux of CO₂ into the fore-arc region of $0.3 - 2.1 \times 10^{12}$ moles year⁻¹,
718 dependent on the geometry of fluid flow. These high values are not consistent
719 with the restricted solubility of CO₂ in fluids at the low temperatures and
720 pressures found in fore-arc regions (Jarrard, 2003), unless phase separation and
721 subsequent emission of gas-phase CO₂ operate to increase the CO₂ flux.

722 Estimates of carbon emitted as methane from mud-volcanoes and seeps vary
723 widely, from 7×10^9 to 1×10^{13} moles of methane year⁻¹ (Kopf, 2002; 2003;

724 Milkov et al., 2003). The earlier estimates are lower and may be discarded, as
725 newly discovered mud volcanoes have augmented the fluxes, but the range of
726 possible values is still large, at around 10^{11} - 10^{13} moles year⁻¹. Uncertainties
727 are increased by the likely incomplete nature of the current data compilations,
728 and the fact that the tectonic environment is not specified in many literature
729 sources. However, it is suggested that the bulk of mud volcanism is caused
730 by plate convergence, and the dewatering of fluid-saturated sediment (Kopf,
731 2003). The likely under-reporting of seeps cancels somewhat against the likely
732 inclusion of non-subduction zone sources in some studies, although the extent of
733 the compensation is unclear. Isotope evidence from Bebout (1995) suggest that
734 less than 25% of subducted organic carbon devolatilises in the sub-arc region,
735 which would provide a flux of less than 0.18×10^{12} moles year⁻¹ if the value for
736 organic carbon fluxes in Table 2 is correct.

737 Here, the estimate for CO₂ flux based on the Mottl (2004) measurements,
738 of 5.6×10^{10} moles year⁻¹ is used, with an uncertainty of 70% of the absolute
739 value. A value of 10×10^{12} moles year⁻¹ for methane fluxes is used, again with
740 with an uncertainty of 70% of the absolute value.

741 *Iron* The iron content of non-volcanic fluids is assumed to be negligible. This
742 is valid so long as the fluids are relatively poor in chlorine, and is consistent with
743 measured fore-arc fluid compositions (e.g. Mottl et al., 2004).

744 *Sulphur* Mottl et al. (2004) measure sulphate concentrations in fluids from
745 springs in the Marianas forearc region. Values increase as the depth to the slab
746 increases. Values, corrected for anhydrite/gypsum precipitation and microbial
747 sulphate reduction, of 12 - 46 mmol kg⁻¹, coupled with a total reflux fluid
748 volume of 1.4×10^{12} kg year⁻¹, imply a sulphate flux of 1.7 - 6.4×10^{10} moles
749 year⁻¹. These values are much lower than the sulphur inputs to the subduction
750 zone, and are likely to be controlled by anhydrite solubility in the mantle wedge,
751 so the use of concentrations from a single subduction zone, while sub-optimal,
752 is likely to provide a reasonable estimate of sulphur fluxes in these fluids. Here
753 we take the mean value of 4.1×10^{10} moles year⁻¹ from the Mottl et al. (2004)
754 estimates, and use an arbitrary uncertainty of 70% of the absolute value.

755 *2.3.4. Sub-arc and deep mantle*

756 Evidence of redistribution of redox-sensitive elements between the sub-arc
757 and deep mantle is mostly qualitative, and uncertainties on quantitative esti-
758 mates are so large as to make the estimates largely meaningless. For this reason
759 we combine the sub-arc and deep mantle, and calculate element fluxes by dif-
760 ference. Nevertheless, it is useful to discuss possible differences between these
761 two reservoirs.

762 *Carbon* The carbon content of non-arc related mantle is estimated at between
763 50 – 120 ppm (McDonough and Sun, 1995; Salters and Stracke, 2004). Estimates
764 of carbon contents of sub-arc mantle are higher. Carbon contents presented here
765 for the New Caledonia supra-subduction zone mantle are around 1,000 ppm,
766 although the possibility of contributions from obduction and post-obduction
767 processes for these samples cannot be excluded. Higher carbon contents in the
768 sub-arc mantle are also supported by the results of Fischer and Marty (2005)
769 who used CO₂:noble gas ratios to infer elevated C contents in sub-arc mantle,
770 and the observations of Ducea et al. (2005), who noted primary calcite globules
771 and veins in peridotite xenoliths from sub-Sierra Nevada mantle.

772 Connolly (2005) applies thermodynamic modelling techniques to investigate
773 the release of carbon from subducting slabs, and concludes that the bulk of
774 CO₂ (> 73%) is not released until below sub-arc depths. This value is broadly
775 consistent (Fig. 3) with results of calculations made by those who study arc
776 volcano gas outputs (e.g. Hilton et al. 2002), where isotope mass balance
777 evidence has been used to propose constrain the proportion of emitted CO₂ with
778 a crustal source. The results are also consistent with the results of Dasgupta et
779 al. (2004) who demonstrate experimentally that carbonate minerals are stable
780 in carbonated eclogite down to pressures of 5 - 9 GPa, and the petrological
781 observations of Bebout (1995) who find little evidence for significant removal of
782 reduced carbon, at least in the upper parts of a subduction zone. If carbon is
783 indeed retained, then much of the carbon in the slab is likely to proceed directly
784 to the deep mantle.

785 *Iron* There is little evidence of a systematic difference in iron concentrations
786 between the sub-arc and non sub-arc mantle; compare McInnes (2001) with
787 Salters and Stracke (2004). However, a number of studies suggest that the
788 oxidation fugacity of iron is higher by one or two log units in sub-arc mantle
789 relative to MOR-mantle (Balhaus et al., 1990; Wood et al., 1990; Brandon
790 and Draper, 1996; Parkinson and Arculus, 1999; Kelley and Cottrell, 2009).
791 Parkinson and Arculus (1999) calculate that the observed difference is consistent
792 with the presence of 0.6 to 1 wt% Fe₂O₃ in sub-arc mantle, whereas normal
793 mantle has maybe 0.1 – 0.3 wt% Fe₂O₃. Iron is unlikely to move directly from
794 the slab to the sub-arc mantle because it is relatively insoluble (Eggler and
795 Schneider, 1986) and see discussion below.

796 *Sulphur* The sulphur content of primitive and depleted mantle are given as
797 250 and 119 ± 30 ppm respectively (McDonough and Sun, 1995; Salters and
798 Stracke, 2004). There is little evidence that sulfur concentrations in sub-arc
799 mantle is higher than this. Serpentinised mantle material from seamounts has
800 been metasomatised, with addition of sulphur by reduction of aqueous sulphate
801 from slab sediments, but even after this metasomatism the sulphur content is
802 generally less than 164 ppm (Alt and Shanks, 2006). McInnes et al. (2001)
803 report S contents from harzburgites at the Lihir subduction zone, and these
804 vary between 10 and 60 ppm. Similarly, S contents from the New Caledonia
805 peridotites, which are thought to represent supra-subduction zone mantle, are
806 no higher than the depleted mantle values (Table 1). It is therefore likely that
807 sulfur is either recycled to the exosphere by reflux or melting processes, or is
808 subducted to the deep mantle.

809 **Table 4, 5 near here**

810 *2.4. Flux estimates and uncertainties*

811 Element fluxes were calculated by multiplying reservoir fluxes by the con-
812 centration of the appropriate compositional variable (Table 5) for the different
813 elemental redox states considered. Uncertainties were taken to be those dis-
814 cussed in the text, and were used to calculate a minimum and maximum flux of

815 each redox state of each element (Table 5). If uncertainties were greater than
816 100%, that is, the minimum flux would have been negative, then the minimum
817 flux was set to zero. Where two parameters with uncertainties were combined,
818 the uncertainty of the product was calculated assuming that the two parameters
819 were uncorrelated. Such an approach is likely to be valid where one parameter
820 is a mass flux, such as the rate of subduction of ocean crust, and the other is a
821 compositional variable, such as the carbonate content of ocean crust sediments.
822 Uncertainties can be considered as approximately 2σ in that they cover most
823 of the range of values measured or estimated, although too many of the uncer-
824 tainties are defined arbitrarily for the value to be statistically meaningful. The
825 fluxes of the individual redox states were then combined to give total element
826 budgets for the subduction zones, with uncertainties propagated as before (Fig.
827 3, Table 6).

828 Redox budget fluxes (Table 7) were then calculated using equation 1 for a
829 mantle redox state and a crustal reference state. So, for example, the redox
830 budget flux of 1×10^{12} moles year^{-1} of S^{6+} relative to the S^{2-} mantle reference
831 state is 8×10^{12} moles year^{-1} , because 8 moles of electrons are needed to reduce
832 each mole of S^{6+} to S^{2-} . The redox budget flux of 1×10^{12} moles year^{-1} of S^{6+}
833 relative to the S^{6+} crustal reference state is, on the other hand, zero, because
834 the sulphur is already in the reference state. The mantle reference state is used
835 to assess the effect of subduction on the mantle, and the crustal reference state
836 is used to assess the effect of subduction on the exosphere.

837 The uncertainties were used in two different ways. First, the possible ranges
838 of redox budgets were calculated, so the maximum effect of subduction on the
839 mantle was estimated by combining the highest (most oxidising) redox budget
840 fluxes for subduction input with the lowest redox budget fluxes (least oxidising)
841 for the subduction outputs. The minimum effect on the mantle, the maximum
842 effect on the crust and the minimum effect on the crust were calculated in similar
843 ways. Element and redox budgets were used to calculate the net addition to the
844 mantle, and the percentage recycled, for both the individual elements (Table 6)
845 and for the overall redox budget (Table 8).

846 Second, Monte Carlo calculations were undertaken, assuming (i) that uncer-
847 tainties were normally distributed and (ii) that values were log-normally dis-
848 tributed. Monte Carlo calculations involve numerous repetitions of the redox
849 budget calculation, with, in each repetition, values for each of the inputs and
850 outputs taken randomly from a normal, in the case of (i), or a log-normal, in
851 the case of (ii), distribution with the same mean and standard deviation as
852 that inferred for each of the element fluxes from each of the inputs and out-
853 puts (Table 5). The mean and standard deviation redox budget flux was then
854 calculated from the array of values created. These calculations were performed
855 using Mathematica, and the results given are for 100 000 iterations. Effectively
856 identical answers were obtained for 1000 and 10000 iterations.

857 **3. Results**

858 *3.1. Element Budgets*

859 Element fluxes (Table 5, Table 6) indicate net addition of Fe ($55 \pm 13 \times 10^{12}$
860 moles year⁻¹), C ($4.6 \pm 4.0 \times 10^{12}$ moles year⁻¹) and S ($2.4 \pm 0.9 \times 10^{12}$ moles
861 year⁻¹) to the crust at subduction zones, even given the large uncertainties.
862 The percentage of the elements recycled is 16 ± 6 % for Fe, 35 ± 22 % for C,
863 and 17 ± 7 % for S. The extent to which these fluxes are balanced by known
864 fluxes at MOR and ocean islands is discussed below.

865 AOC dominates the supply of Fe to subduction zones ($51 \pm 11 \times 10^{12}$ moles
866 year⁻¹), with about 20% supplied by the serpentinitised lithosphere ($12 \pm 7 \times 10^{12}$
867 moles year⁻¹) and around 2 % ($1.2 \pm 0.2 \times 10^{12}$ moles year⁻¹) by sediments.
868 Arc rocks dominate the return of Fe, because the Fe content of arc gases and
869 non-volcanic fluid sources are assumed to be zero.

870 Serpentinitised lithosphere is calculated to be biggest contributor of carbon
871 to subduction zones ($3.0 \pm 3.8 \times 10^{12}$ moles year⁻¹), although the contribution
872 of AOC ($2.2 \pm 0.6 \times 10^{12}$ moles year⁻¹) is within the rather large uncertainty
873 of the serpentinitised lithosphere value. The sediment contribution ($1.9 \pm 0.7 \times$
874 10^{12} moles year⁻¹) is also of the same order of magnitude. Return of carbon

875 is controlled by the contribution of arc gases ($1.4 \pm 0.3 \times 10^{12}$ moles year⁻¹),
876 although the contribution of non-volcanic fluid sources is within the uncertainty
877 of the arc gas contribution ($1.1 \pm 0.7 \times 10^{12}$ moles year⁻¹).

878 AOC is the main contributor to the sulphur input budget of subduction
879 zones ($1.5 \pm 0.4 \times 10^{12}$ moles year⁻¹), though contributions from serpentinised
880 lithosphere ($0.7 \pm 0.8 \times 10^{12}$ moles year⁻¹) and sediments ($0.6 \pm 0.3 \times 10^{12}$
881 moles year⁻¹) are of the same order of magnitude. It is thus likely that different
882 sulphur sources, and therefore different sulphur oxidation states, dominate the
883 sulphur input at different subduction zones. Arc gases control the output of S
884 from subduction zones ($0.3 \pm 0.06 \times 10^{12}$ moles year⁻¹), with outputs about
885 three times higher than that from the arc rocks ($0.12 \pm 0.10 \times 10^{12}$ moles year⁻¹)
886 , and eight times higher than the best estimate of the non-volcanic flux ($0.04 \pm$
887 0.03×10^{12} moles year⁻¹).

888 **Tables 6,7,8 near here Figure 3,4 near here**

889 3.2. Redox Budget Fluxes

890 3.2.1. Relative to mantle reference state

891 Both maximum and minimum oxidation redox budget fluxes (Table 8) for
892 the mantle indicate that subduction increases the redox budget of the mantle
893 over geological time, that is, a net increase in oxidising capacity results from
894 subduction. The maximum value is 89×10^{12} moles year⁻¹, and the minimum
895 is 4.6×10^{12} moles year⁻¹. The wide range of estimates reflects the large un-
896 certainties on many of the potentially important contributors to these redox
897 budget fluxes. Monte-Carlo calculations for the mantle (Table 8) give a value of
898 $46 \pm 12 \times 10^{12}$ moles year⁻¹ for the assumption of a normal distribution, and
899 $10^{13.5} \pm 0.3$ moles year⁻¹ for the assumed log normal distribution. The range
900 for the latter calculation is $46 - 59 \times 10^{12}$ moles year⁻¹, which is consistent with
901 the value of $46 \pm 12 \times 10^{12}$ moles year⁻¹ for the normal distribution.

902 In the maximum mantle oxidation model, the largest contribution to the
903 mantle oxidation is made by the subduction of serpentinised lithosphere ($46 \times$
904 10^{12} moles year⁻¹), in which carbon as carbonate is the main contributor (27

905 $\times 10^{12}$ moles year⁻¹) with subsidiary contributions from Fe³⁺ (12×10^{12} moles
 906 year⁻¹) and S in pyrite and sulphate minerals (6×10^{12} moles year⁻¹). A slightly
 907 smaller contribution is made by AOC (36×10^{12} moles year⁻¹), within which
 908 Fe³⁺ dominates (17×10^{12} moles year⁻¹), with smaller contributions from C⁴⁺
 909 (11×10^{12} moles year⁻¹) and sulphate and sulphide minerals (7×10^{12} moles
 910 year⁻¹). Sediments contribute about 10% of the input redox budget flux, in
 911 which C⁴⁺ dominates (7×10^{12} moles year⁻¹) with smaller contributions from
 912 Fe³⁺ (1.2×10^{12} moles year⁻¹) and S⁻ (1×10^{12} moles year⁻¹). The largest
 913 output contribution to the redox budget is made by non-volcanic fluids (-6.6
 914 $\times 10^{12}$ moles year⁻¹). This number is negative i.e. it causes a net increase
 915 of the mantle redox budget, because the carbon in methane is more reduced
 916 than the mantle reference state. The redox budget of the methane component
 917 is the largest contributor (-6.8×10^{12} moles year⁻¹) to the redox budget flux
 918 attributable to non-volcanic fluid release. The non-volcanic fluid contribution is
 919 offset by the release of volcanic gases (5.9×10^{12} moles year⁻¹) and arc igneous
 920 rocks (2.2×10^{12} moles year⁻¹). In the arc volcanic gases C⁴⁺ is the major
 921 contributor (4.5×10^{12} moles year⁻¹), with a smaller contribution from S in
 922 SO₂ (1.5×10^{12} moles year⁻¹) and a small decrease in the mantle redox budget
 923 due to the release of hydrogen (-0.2×10^{12} moles year⁻¹). In the arc rocks,
 924 Fe³⁺ provides the only significant contribution (2.2×10^{12} moles year⁻¹) with
 925 much smaller components provided by C⁴⁺ (0.01×10^{12} moles year⁻¹) and S⁻
 926 in pyrite (0.02×10^{12} moles year⁻¹).

927 In the minimum mantle oxidation model, AOC provided by far the largest
 928 input contribution to the redox budget flux (15×10^{12} moles year⁻¹). Ser-
 929 pentinised lithosphere provides only around 10% of this value (1.5×10^{12} moles
 930 year⁻¹), and the difference between this and the previous model reflects the wide
 931 range of uncertainties associated with the flux and composition of serpentinised
 932 lithosphere. The sediment contribution is around 20% of the AOC contribution
 933 (3×10^{12} moles year⁻¹). In terms of element contributions, the redox budget
 934 for AOC contains subequal contributions from C⁴⁺ (6×10^{12} moles year⁻¹) and
 935 Fe³⁺ (6×10^{12} moles year⁻¹), with a factor of two smaller contribution from

936 S in sulphide and sulphate (3×10^{12} moles year⁻¹). In the serpentinised litho-
937 sphere, Fe³⁺ is the only contributor (1.5×10^{12} moles year⁻¹), because the S
938 and C contributions are within uncertainty of zero. In the sediments, the C⁴⁺
939 component dominates (7×10^{12} moles year⁻¹), with smaller contributions from
940 Fe³⁺ (1×10^{12} moles year⁻¹) and S⁻ (0.3×10^{12} moles year⁻¹). In the output, a
941 small degree of increase in the mantle oxidation budget is provided by methane
942 in non-volcanic fluids (-1.2×10^{12} moles year⁻¹), but this is almost completely
943 offset by carbonate C⁴⁺ and sulphate S⁶⁺ dissolved in the fluids with fluxes
944 of (0.4×10^{12} moles year⁻¹) and (0.6×10^{12} moles year⁻¹) respectively. Net
945 decreases in the mantle redox budget are also due to the emission of arc gases
946 (9×10^{12} moles year⁻¹) and arc rocks (6×10^{12} moles year⁻¹). C⁴⁺ dominates
947 the arc gas contribution (7×10^{12} moles year⁻¹), with a smaller contribution
948 from SO₂ (2×10^{12} moles year⁻¹) and a slight negative effect from H₂ release
949 (-0.1×10^{12} moles year⁻¹). In arc rocks, the greatest contribution comes from
950 Fe³⁺ (6×10^{12} moles year⁻¹) with a smaller addition from S⁻ (0.2×10^{12} moles
951 year⁻¹).

952 3.2.2. *Relative to crustal reference state*

953 Calculated changes in the redox budget of the exosphere due to subduction
954 are positive, that is, subduction increases the oxidising capacity of the exosphere
955 relative to the specified crustal reference state. This may seem counterintuitive,
956 given that subduction also increases the redox budget of the mantle, but can
957 be understood in the terms that much of the subducted material, such as the
958 Fe²⁺ in the AOC for example, is reduced relative to the crustal reference state,
959 so subduction of this material increases the redox budget of the exosphere. The
960 heterogeneous nature of the exosphere means that large scale crustal reference
961 states will never represent the individual reservoirs accurately, and that the
962 figures presented cannot represent the true effect of subduction on the exosphere.
963 However, the values can be used to gain an idea of the relative effects of the
964 fluxes of the different components. For both maximum and minimum crustal
965 oxidation models, the largest contributor to crustal oxidation is the AOC, with

966 fluxes of -58×10^{12} moles year⁻¹ and -36×10^{12} moles year⁻¹ respectively. The
967 AOC budget is dominated by the contribution of Fe²⁺ of -49×10^{12} moles year⁻¹
968 and -31×10^{12} moles year⁻¹ for the maximum and minimum crustal oxidation
969 respectively, with a smaller contribution from S⁻ of 0.02×10^{12} moles year⁻¹
970 and $(0.21 \times 10^{12}$ moles year⁻¹ for maximum and minimum crustal oxidation
971 respectively.

972 In the maximum crustal oxidation model, serpentinised lithosphere provides
973 the next largest contribution (-19×10^{12} moles year⁻¹), within which the largest
974 component is Fe²⁺ (-10×10^{12} moles year⁻¹), followed by S⁻ and S²⁻ (-9×10^{12}
975 moles year⁻¹). Sediments provide the smallest contribution (-11×10^{12} moles
976 year⁻¹), in which S⁻ in pyrite provides the largest component (-6.7×10^{12} moles
977 year⁻¹), followed by C⁰ (-4.4×10^{12} moles year⁻¹), and a small Fe²⁺ component
978 (-0.3×10^{12} moles year⁻¹). The largest output contributor in the maximum
979 crustal oxidation model is the arc rocks (-4.2×10^{12} moles year⁻¹), within which
980 Fe²⁺ (-4.1×10^{12} moles year⁻¹) makes the largest contribution, decreasing the
981 exospheric redox budget relative to the crustal reference state. There is also
982 a small S⁻ contribution (-0.1×10^{12} moles year⁻¹). Small reductions to the
983 exospheric redox budget relative to the crustal reference state are also made
984 by the non-volanic fluid flux (-2.4×10^{12} moles year⁻¹) and arc gases ($-0.7 \times$
985 10^{12} moles year⁻¹). In the non-volcanic fluids, the only contributor is C⁴⁻ in
986 methane. In the arc gases, S⁴⁺ in SO₂ (-0.5×10^{12} moles year⁻¹) and H⁰ (-0.2
987 $\times 10^{12}$ moles year⁻¹) in H₂ both make small contributions.

988 In the minimum crustal oxidation model, sediments provide the second
989 largest contribution next to AOC (-3.5×10^{12} moles year⁻¹), with contribu-
990 tions from S⁻ in pyrite (-2×10^{12} moles year⁻¹), C⁰ (-1.3×10^{12} moles year⁻¹),
991 and Fe²⁺ (-0.2×10^{12} moles year⁻¹). Serpentinised lithosphere provides only
992 a small component (-1.2×10^{12} moles year⁻¹), in which the only contribution
993 comes from Fe²⁺, because C and S are present in zero concentrations due to
994 the large uncertainties. The largest output is, again, C⁴⁻ in methane in non-
995 volcanic fluids (-13.6×10^{12} moles year⁻¹). Smaller outputs come from arc rocks
996 (-9.8×10^{12} moles year⁻¹) and arc gases (-1×10^{12} moles year⁻¹). The arc rock

997 redox budget flux comprises a large contribution from Fe^{2+} (-8.3×10^{12} moles
998 year^{-1}) and a much smaller one from S^- (-1.5×10^{12} moles year^{-1}). The arc
999 gas redox budget is made up of contributions from S^{4+} in SO_2 (-0.8×10^{12} moles
1000 year^{-1}) and H^0 (-0.2×10^{12} moles year^{-1}).

1001 To summarise, subduction increases the mantle redox budget. Major input
1002 contributions are made by AOC, and, potentially, by serpentinised lithosphere,
1003 although the latter flux is poorly constrained. Sediments provide a smaller (11-
1004 16%) but significant contribution. Fe and C are large contributors to all fluxes,
1005 with S in a variety of redox states providing a small but significant component.
1006 Individual output fluxes are generally smaller than input fluxes, and the total
1007 is significantly less (Table 8).

1008 The largest effect on the exospheric redox budget relative to the crustal
1009 reference state is made by subduction of Fe^{2+} in AOC, with smaller but similar
1010 order of magnitude contributions made by subduction of reduced material in
1011 sediments and serpentinised lithosphere. This effect is offset by the release of
1012 non-volcanic fluids, arc gases and arc rocks, all of which are reduced relative to
1013 the crustal reference state.

1014 4. Discussion

1015 4.1. Comparison with previous work

1016 The results indicate large imbalances in elemental and redox budgets, with
1017 fluxes from the exosphere to the subduction zone, sub-arc and deep mantle of
1018 Fe, C, S, and redox budget. These values can be compared with those obtained
1019 by previous work.

1020 Lecuyer and Ricard (1999) estimated that 11.2×10^{12} moles year^{-1} of Fe^{3+}
1021 are transported into the mantle by subduction. This compares with a value for
1022 our study of $19.1 \pm 7.6 \times 10^{12}$ moles year^{-1} . The main reason that the value
1023 for this study is higher is that ferric iron in serpentinised lithosphere was not
1024 considered in the Lecuyer and Ricard study.

1025 Hayes and Waldbauer (2006) present a study that focusses on the exospheric
1026 redox budget, and do not present a full redox budget for subduction zones.
1027 However, they do present some estimates relevant to the study of subduction
1028 zone redox fluxes. They suggest that redox budget changes associated with
1029 organic carbon flux into the mantle are similar to redox budget changes induced
1030 by the emission of reduced gases at subduction zones. The implicit reference
1031 state for their calculations is C as C^{4+} and S as S^{2-} . Using this reference state,
1032 the redox budget of the organic carbon that is added to subduction zones is -2.9
1033 $\pm 1.6 \times 10^{12}$ moles $year^{-1}$, and the redox budget of the reduced arc gases is -1.9
1034 $\pm 0.4 \times 10^{12}$ moles $year^{-1}$. These figures are within error of each other, so the
1035 values presented in Table 6 are consistent with those of Hayes and Waldbauer
1036 (2006).

1037 4.2. Balances against MOR and OIB

1038 The net addition of Fe, C, S and redox budget must be balanced, to some
1039 extent, by outputs from plume and mid-ocean ridge (MOR) magmatism. Esti-
1040 mates for these fluxes were therefore made (Table 9). Iron contents for MOR
1041 rocks were taken from Lecuyer and Ricard (1999), assuming the Fe^{3+}/Fe_{tot}
1042 measured for undegassed basaltic lavas by Christie et al. (1986). MOR CO_2
1043 contents were taken from the work of Saal et al. (2002), and carbon is assumed
1044 to be all C^{4+} . S contents for MOR presented by Edmond et al. (1979), Wallace
1045 and Carmichael (1992) and Saal et al. (2002) are all similar, so a value of 0.09
1046 ± 0.01 wt% S was taken for MOR rocks. Wallace and Carmichael (1992) mea-
1047 sured sulphur valence in MOR basalts, and their value for $S^{6+}/S(tot)$ of 0.07 ,
1048 with a large uncertainty of 0.07 , was taken here. The large uncertainty reflects
1049 the difficulty in the measurement of sulphur valence states by electron micro-
1050 probe methods, as well as the inherent variability and relatively small sample
1051 set. The overall flux is set to be equal to the AOC subduction flux, since there is
1052 no good evidence that there is non-steady state with respect to the quantity of
1053 ocean crust, at least on long timescales. Iron contents and Fe^{3+}/Fe_{tot} for plume
1054 rocks were taken from the compilation of Lecuyer and Ricard (1999). The CO_2

1055 content of plume-related igneous rocks was obtained by extrapolation from the
1056 estimate of a global CO₂ flux from this source of 3×10^{12} moles year⁻¹ (Marty
1057 and Tolstikhin, 1998), and the estimate of the global flux of plume-related ig-
1058 neous rocks, which was taken to be 10% of the MOR flux, after Marty and
1059 Tolstikhin (1998). The S content of the OIB lavas was taken from the mea-
1060 surements of Gurenko and Schminke (2000), with information on valence states
1061 from Wallace and Carmichael (1992).

1062 Fe, C, and S fluxes balance, within error, once the MOR and OIB fluxes are
1063 added to the subduction and arc outputs. The total MORB plus OIB output of
1064 Fe is $57 \pm 21 \times 10^{12}$ moles year⁻¹, which balances against the net subduction
1065 addition of $55 \pm 13 \times 10^{12}$ moles year⁻¹. Similarly, the MORB plus OIB output
1066 of C is $3.2 \pm 1.3 \times 10^{12}$ moles year⁻¹, which balances against the net subduction
1067 addition of $4.6 \pm 4 \times 10^{12}$ moles year⁻¹, and the MORB plus OIB output of
1068 S is $1.8 \pm 0.3 \times 10^{12}$ moles year⁻¹, which balances against the net subduction
1069 addition of $2.4 \pm 0.9 \times 10^{12}$ moles year⁻¹. The MORB plus OIB budgets
1070 are systematically slightly smaller, though within error, of the net subduction
1071 budget.

1072 **Table 9 near here Figure 5 near here**

1073 Comparison of the redox budget fluxes, on the other hand, suggests that
1074 an imbalance exists. If the net subduction redox budget flux is taken to be
1075 halfway between the maximum and minimum mantle oxidation value, with an
1076 uncertainty that covers the range of estimates then a mean value is obtained that
1077 is a factor of 2.5 higher than the best estimate of the MORB plus OIB outputs.
1078 If the results of the Monte Carlo calculations with the normally distributed
1079 subduction zone inputs and outputs are used, then the subduction input flux
1080 is significantly larger ($46 \pm 12 \times 10^{12}$ moles year⁻¹) than the MORB plus
1081 OIB output ($19 \pm 6 \times 10^{12}$ moles year⁻¹). If the results of the Monte Carlo
1082 calculations with the log normal distributed subduction zone inputs and outputs
1083 are taken then the ranges are again outside of uncertainty, with a value of 46 – 58
1084 $\times 10^{12}$ moles year⁻¹ for the subduction zone input. To conclude, even though the
1085 extremities of the estimates overlap because of the large uncertainties, results of

1086 the Monte Carlo calculations suggest that the subduction redox budget flux is
1087 not balanced by the MOR and plume-related outputs, and that a net increase
1088 in mantle redox budget over geological time on the order of $10^8 \times 10^{12}$ of moles
1089 year^{-1} is implied.

1090 *4.3. Spatial and temporal evolution of mantle redox budgets*

1091 Results indicate that the redox budget of the mantle has increased with time,
1092 unless the minimum estimates of redox budget fluxes are taken. It is interesting
1093 to consider (a) what effect this increase in redox budget could have had on
1094 mantle f_{O_2} over geological time and (b) how the added redox budget might be
1095 distributed throughout the mantle. Clearly, the two questions are related; if
1096 added redox budget is localised then the increase of f_{O_2} in that area will be
1097 much bigger than if it were well mixed throughout the whole mantle.

1098 An estimate of the relationship between upper mantle f_{O_2} and redox bud-
1099 get was made using pMELTS (Ghiorso et al., 2002). The bulk composition
1100 was assumed to be that of the depleted upper mantle presented by Salters and
1101 Stracke (2004), with an H_2O content of 116ppm and a CO_2 content of 50ppm.
1102 Calculations were made by setting f_{O_2} and equilibrating the model system at
1103 1200°C and 1 GPa. This provided a calculated value for the wt% Fe_2O_3 , which
1104 was then converted to a specific redox budget (moles kg^{-1}). Results were then
1105 fit to an arbitrary but appropriate function so that ΔQFM could be calculated
1106 as a function of specific redox budget. It was assumed that Fe_2O_3 is the prin-
1107 ciple contributor to unaltered mantle redox budget; there is little evidence that
1108 CO_2 or sulphate species are present in sufficient quantities to make a significant
1109 contribution. Values of Fe_2O_3 are sensitive to the assumed pressure and temper-
1110 ature, but the specified conditions were chosen because they are typical of the
1111 region of equilibration for melts for which redox conditions have been calculated
1112 (e.g. Parkinson and Arculus, 1999). f_{O_2} will vary as the mantle mixes through
1113 different pressure and temperature conditions, but redox budget will not, unless
1114 open system processes occur to change the composition of the system.

1115 f_{O_2} varies as a function of specific redox budget according to equation 2:

$$\Delta\text{QFM} = 4.77 + 1.61 \ln \overline{RB}, \quad (2)$$

1116 where ΔQFM is $\log f_{\text{O}_2} - \log f_{\text{O}_2\text{QFM}}$, where QFM refers to the quartz, fayalite,
1117 magnetite buffer and \overline{RB} is the specific redox budget in moles kg^{-1} . This
1118 relationship is shown in Fig. 6, and is similar to that illustrated by Parkinson
1119 and Arculus (1999) for similar input values.

1120 **Figure 6 near here**

1121 The effect that added redox budget has on the mantle specific redox budget,
1122 and thus on f_{O_2} depends on volume within which the added redox budget mixes
1123 according to

$$\overline{RB_M} = \overline{RB_{M,\text{init}}} + \int_t^{t=0} \frac{R\dot{B}_M \partial t}{FM} \quad (3)$$

1124 where $R\dot{B}_M$ is the redox budget flux relative to the mantle reference state, t is
1125 time, F is the fraction of mantle to which the redox budget is added, and M is
1126 the mass of the mantle, which is assumed here to be 3.64×10^{24} kg. If $R\dot{B}_M$ is
1127 constant then

$$\overline{RB_M} = \overline{RB_{M,\text{init}}} + \frac{R\dot{B}_M \Delta t}{FM} \quad (4)$$

1128 where Δt is the time period of interest over which the addition of redox budget
1129 occurred, in years.

1130 Existing constraints on F and temporal changes in f_{O_2} come from a variety of
1131 sources. Local highs in f_{O_2} in sub-arc mantle proposed by a number of workers
1132 (e.g. Wood et al., 1990; Parkinson and Arculus, 1999; Kelley and Cottrell,
1133 2009) suggest that redox budget increases are localised in the mantle wedge, at
1134 least to some extent, although the results of Lee et al. (2005), based on V/Sc
1135 measurements, contradict this suggestion.

1136 The results of work by Kump et al. (2001) and Holland (2002) call on changes
1137 in the oxidation state of the Earth's mantle during the Archean to explain the
1138 rise in atmospheric oxygen. However, Lee and Li (2004) present evidence based
1139 on V/Sc systematics, that the f_{O_2} of MORB is not more than 0.3 \log_{10} units

1140 greater than it was in the Archean. This work is consistent with that of Delano
1141 (2001), who used whole-rock Cr and V, and the Cr content of spinels, to obtain
1142 a similar result. If the mantle f_{O_2} is indeed relatively constant then increases
1143 in redox budget may be restricted to sub-arc mantle, which may then become
1144 cratonised and isolated, or to the deep parts of subduction zones which may
1145 also be isolated on long timescales. Alternatively, increases in redox budget may
1146 be simply too small to shift the mantle off its current f_{O_2} buffer once mixing
1147 has occurred. The timescale over which redox budget fluxes have been similar
1148 to those of the present day may be comparatively short. Subduction redox
1149 budget fluxes prior to 2.3 Ga, the time of the GOE (Great Oxidation Event),
1150 are likely to have been much lower, because seawater was most likely too reduced
1151 to create the carbonates, sulphates, and ferric iron that drive the increases in
1152 redox budgets proposed for the present day. However, serpentinisation reactions
1153 may still have created ferric iron in magnetite, so redox budget fluxes may still
1154 have been significant. Redox budget fluxes were probably also much reduced
1155 between the GOE and 550 Ma, when atmospheric oxygen levels are thought to
1156 have reached current values,

1157 It is beyond the scope of this paper to investigate these issues via modelling,
1158 but first order constraints can be obtained from four end-member scenarios.

1159 **Figure 7 near here**

1160 First, the case where all redox budget is added to the sub-arc mantle is
1161 considered. This can be visualised as addition of the subduction flux to the
1162 sub-arc mantle over the timescale of subduction, followed by immobilisation of
1163 the oxidised sub-arc mantle by incorporation into the lithosphere. The volume
1164 of subduction zones is calculated to be the volume of a prism, 44,450 km in
1165 length (Jarrard, 2003) by 80 km deep by 100 km wide, which gives a volume
1166 of $1.78 \times 10^{17} \text{ m}^3$. If the average density of this material is 3000 kg m^{-3} then
1167 the value of F for a mantle mass of $3.64 \times 10^{24} \text{ kg}$, is 0.00015. The results
1168 of redox budget fluxes of 70, 35, 1, 0.1 and $0.01 \times 10^{12} \text{ moles year}^{-1}$ are
1169 shown in Fig. 7a. Note the log scale on the x axis. The location of the grey
1170 box represents the range of f_{O_2} values calculated for the upper mantle by Lee

1171 and Li (2004), and its height indicates their estimate of the sensitivity of the
1172 technique. Mantle f_{O_2} that lie within the grey box are indistinguishable from
1173 unaltered material. It can be seen that redox budget changes on the order of
1174 those observed for subduction zones (e.g. Kelley and Cottrell, 2009), i.e. one
1175 to two log f_{O_2} units, occur on the 1 Ma to 10 Ma timescale, even for redox
1176 budget fluxes as low as 1×10^{12} moles year⁻¹. Subduction that continued
1177 for longer than 100 Ma, if fluxes were high and no mixing between sub-arc and
1178 other mantle occurred, would increase f_{O_2} to values much higher than those
1179 observed. This is reasonable, fluxes into the sub-arc mantle are likely to be only
1180 a small fraction of the total (see below), and the assumption that sub-arc mantle
1181 associated with a subduction zone could fail to mix effectively with surrounding
1182 mantle breaks down on the 100 Ma timescale. Further, only the most long-lived
1183 subduction zones operate on 100 Ma timescales (e.g. Chiarenzelli et al., 2010).

1184 The next case to be considered is addition of redox budget to the whole of
1185 the upper mantle, a scenario that would be physically represented by effective
1186 upper mantle mixing on the timescale of interest, but with restricted interchange
1187 between upper and lower mantle material. For an upper mantle with depth 660
1188 km, and density 3300 kg m^{-3} , the mass fraction of the upper mantle relative
1189 to the whole mantle, F , is calculated to be 0.25. The results of redox budget
1190 fluxes of 70, 35 and 1×10^{12} moles year⁻¹ are shown in Fig. 7b. It can be seen
1191 that if redox budget fluxes are of the order of 10×10^{12} moles year⁻¹ or higher,
1192 and if they are largely transferred to the upper mantle alone, then measurable
1193 differences in upper mantle redox state should occur on the 100 Ma to 1 Ga
1194 timescale.

1195 The third end-member scenario is that of effective whole-mantle mixing on
1196 the timescale of interest, i.e. F is equal to 1. The results of redox budget fluxes
1197 of 70, 35, and 1×10^{12} moles year⁻¹ are shown in Figs 7c. It can be seen that
1198 measurable differences in mantle redox state would occur only after timescales on
1199 the order of several 100 Ma to Ga. If redox budget fluxes increased significantly
1200 at 550 Ma, when atmospheric oxygen levels are thought to have reached current
1201 values, then the present day is likely to lie within the grey area of the plots. In

1202 this case changes in mantle redox state have not yet occurred, but would occur
1203 in the next Ga or so.

1204 Clearly, instantaneous effective mixing within the chosen reservoir is an un-
1205 realistic assumption, so in the fourth end-member scenario a crude attempt was
1206 made to incorporate the effects of gradual mixing. F was set to increase via

$$F = 0.00015 + 0.99985 \left(1 - \exp \left[\frac{-\Delta t}{e \cdot 10^8} \right] \right) \quad (5)$$

1207 which allows F to increase exponentially from the value for subduction zones
1208 (0.00015) to that for the whole mantle over about 1 Ga, a value based on
1209 the estimates of whole mantle mixing time in Hoffman and MacKenzie (1985).
1210 Results, for redox budget fluxes of 70, 35 and 1×10^{12} moles year⁻¹ are shown
1211 in Fig 7d. Mantle f_{O_2} increases to a level that might be recognisable only after
1212 over several hundred Ma, even for the highest redox budget fluxes. However
1213 significant changes would be expected in the future, on a Ga timescale.

1214 4.4. Mechanisms of redox budget transfer to the mantle wedge

1215 It is also necessary to consider the method by which redox budget might be
1216 transferred from the subducting slab to the sub-arc mantle. Fe^{3+} , S^{6+} , and C^{4+}
1217 are the potential transfer agents, but the potential of each is restricted by their
1218 solubility.

1219 The solubility of Fe^{3+} in subduction zone fluids is not well known, but Wykes
1220 et al. (2008) present some measurements of Fe concentrations for fluids with an
1221 $X(NaCl)$ of 0.1 in equilibrium with hematite at 800°C and 1 GPa. The molality
1222 of Fe in these fluids is less than 0.01, and this value is probably a maximum
1223 for subduction zone fluids, since solubility tends to decrease with decreasing
1224 temperature and salinity, and the values used for the experiments are at the
1225 upper limits of those applicable at subduction zones. If the solubility of Fe^{3+}
1226 is taken to be 0.01 molar, and the flux of water into the mantle wedge is taken
1227 to be 10^{11} kg year⁻¹ (c.f. Bebout, 1995), then the flux of Fe^{3+} is of the order
1228 of 10^9 moles year⁻¹, which is three to four orders of magnitude lower than the

1229 available redox budget flux. It has been proposed that high salinity fluids and
1230 silica-rich melt-like fluids may carry this element more effectively (e.g. Kessel et
1231 al., 2005) but such chemical characteristics are inconsistent with the relatively
1232 low salinities and concentrations proposed for subduction zone fluids (Hermann
1233 et al., 2006), and the existence of the silica-rich melt-like fluids is still not proven.
1234 It is therefore likely that the Fe remains in the slab during subduction, although
1235 Fe^{3+} could oxidise other fluid components so that the redox budget of the slab
1236 is effectively fractionated into slab fluids which may enter the sub-arc mantle,
1237 and the possibility of its movement cannot be excluded.

1238 The solubility of CO_2 in aqueous solutions at sub-arc depth is restricted to
1239 1–2 wt% (e.g. Connolly, 2005) and experimental results (Yaxley and Brey, 2004)
1240 have shown that carbonate can be stable to pressures up to 3.5 GPa. 1 wt%
1241 CO_2 in solution converts, for an assumed flux of water into the mantle wedge of
1242 10^{11} kg year $^{-1}$ to a CO_2 flux of 2.3×10^{10} moles year $^{-1}$, which, with the four
1243 electron conversion to the mantle reference state, gives a redox budget flux of
1244 around 10^{11} moles year $^{-1}$. Such a flux is an order of magnitude smaller than
1245 the overall redox budget flux, but could induce sub-arc mantle oxidation on a
1246 suitably long timescale if the CO_2 were to be reduced to graphite in the sub-arc
1247 mantle. However, this seems unlikely, as the CO_2 output from arc volcanoes
1248 suggests that most of the CO_2 added to the sub-arc mantle is immediately
1249 recycled to the atmosphere via volcanism.

1250 Water has been proposed as a carrier for oxidation capacity (e.g. Brandon
1251 and Draper, 1996) but this is a very inefficient mechanism, as the solubility of
1252 O_2 in water is very small, so the redox budget of such fluids is tiny (Frost and
1253 Ballhaus, 1998) even when the potential for oxygen release by water dissociation
1254 is considered.

1255 Sulphur may also carry redox budget as suggested by Kelley and Cottrell
1256 (2009). Anyhrite is soluble in geological fluids, and solubility is positively cor-
1257 related with salinity (Newton and Manning, 2005). The eight electron difference
1258 between sulphate and the mantle reference state means that this element is an
1259 effective agent for changes in redox budget. If 10^{11} kg year $^{-1}$ of water fluxes

1260 through the mantle wedge, and anhydrite solubilities are 0.02 to 2 moles kg^{-1}
1261 (Newton and Manning, 2005) then the potential sulphate flux is $0.02 - 2 \times 10^{11}$
1262 moles year^{-1} , which is much less than the overall sulfur budget ($2 - 4 \times 10^{12}$
1263 moles year^{-1} (Table 6), and capable of carrying 0.016 to 1.6×10^{12} moles year^{-1} .
1264 A redox budget flux of 1.6×10^{12} moles year^{-1} can cause a measurable difference
1265 in subduction zone f_{O_2} on a 3 Ma timescale, and a 1 – 2 log unit change in 10
1266 Ma, so sulfur does provide a plausible transfer medium. The S content of arc
1267 magmas is generally relatively low, as discussed above, which could be taken
1268 to indicate that sulfur is not transferred to the sub-arc mantle. Alternatively,
1269 it can be also attributed to low S in the source zone, the relative insolubility
1270 of S in magmas at subduction zone redox conditions, or effective S degassing
1271 from magmas. A comparison between S contents in supra-subduction zone and
1272 typical mantle peridotites would be useful to help evaluate this possibility, but
1273 there is insufficient data for robust conclusions to be drawn.

1274 *4.5. Further work*

1275 It has been shown that subduction of oxidised material has the potential
1276 to oxidise sub-arc mantle on geological timescales, but the uncertainties are
1277 large. The implications of this possibility for the studies of temporal changes
1278 in the atmosphere, volcanism, ore deposit formation, and continental evolution
1279 are significant, so further work to better constrain the least well constrained
1280 parameters is justified. The largest uncertainties are introduced by the extent
1281 of serpentinisation of the lithospheric mantle. If this could be constrained, by a
1282 combination of seismic and geochemical techniques, then more reliable conclu-
1283 sions could be drawn. Additional restrictions are placed by the poorly known
1284 solubilities of many elements in slab-derived fluids. Substantial experimental
1285 work to determine the mobility of Fe, C and S in these fluids is required.

1286 **5. Conclusion**

1287 Fe, C and S and redox budget fluxes have been calculated for subduction
1288 zones from literature data. The largest uncertainties on the subduction zone

1289 redox budget are associated with the input of partially serpentinised mantle
1290 lithosphere, so new measurements for the composition of this material from New
1291 Caledonia and ODP leg 209 were presented. These data indicate that ophiolitic
1292 material can, in some cases, be used as a proxy for partially serpentinised mantle
1293 lithosphere from other environments, though the extent of serpentinisation was
1294 different in the two cases.

1295 Uncertainties on the calculations are large, but results indicate that Fe, C,
1296 S and redox budget are all added in significant quantities by subduction to the
1297 sub-arc and deep mantle. When other mantle outputs from MORB and plume-
1298 related magmatism are considered, the imbalances in Fe, C and S are accounted
1299 for, so cycling of these elements is within error of steady state on some geological
1300 timescale. Subduction zone redox budget inputs were not balanced by MORB
1301 and plume-related outputs, except for the most conservative estimates of redox
1302 budget influx.

1303 The fate of the redox budget added at subduction zones is difficult to deter-
1304 mine unambiguously. Some is almost certainly added to the sub-arc mantle, by
1305 transfer of dissolved sulphate, carbonate, and to a lesser extent, Fe^{3+} in aqueous
1306 fluids. This quantity is restricted by low solubilities of these elements to less
1307 than 2×10^{12} moles year^{-1} , which is a relatively low proportion of the added
1308 total. Nevertheless, such an addition is capable of producing the observed high
1309 f_{O_2} values above subduction zones on a Ma to 10 Ma timescale. The bulk of
1310 the redox budget is likely to be carried to the deep mantle by the slab, where it
1311 will be mixed on long (Ga) timescales into the bulk of the mantle. Such addi-
1312 tion may not have affected the redox state of the mantle at this point in time,
1313 because oxidised material only began to be subducted in the current quantities
1314 at 550 Ma, although changes are anticipated on a Ga timescale.

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1319 **7. References**

- 1320 Aitchison, J. C., Clarke, G. L., Meffre, S., Cluzel, D., 1995. Eocene Arc-
1321 Continent Collision in New-Caledonia and Implications for Regional South-
1322 west Pacific Tectonic Evolution. *Geology* 23: 161-164.
- 1323 Alt, J. C., 1995. Sulfur isotopic profile through the oceanic-crust - sulfur mobil-
1324 ity and seawater-crustal sulfur exchange during hydrothermal alteration.
1325 *Geology* 23: 585-588.
- 1326 Alt, J. C., 2003. Hydrothermal fluxes at mid-ocean ridges and on ridge flanks.
1327 *Compt. Rend. Geosc.* 335: 853-864.
- 1328 Alt, J. C., Shanks, W. C., 2003. Serpentinization of abyssal peridotites from
1329 the MARK area, Mid-Atlantic Ridge: Sulfur geochemistry and reaction
1330 modeling. *Geochim. Cosmochim. Acta.* 67: 641-653.
- 1331 Alt, J. C., Shanks, W. C., 2006. Stable isotope compositions of serpent-
1332 ite seamounts in the Mariana forearc: Serpentinization processes, fluid
1333 sources and sulfur metasomatism. *E.P.S.L.* 242: 272-285.
- 1334 Alt, J. C., Shanks, W. C., Bach, W., Paulick, H., Garrido, C. J., Beaudoin,
1335 G., 2007. Hydrothermal alteration and microbial sulfate reduction in peri-
1336 dotite and gabbro exposed by detachment faulting at the Mid-Atlantic
1337 Ridge, 15 degrees 20 ' N (ODP Leg 209): A sulfur and oxygen isotope
1338 study. *Geochem. Geophys. Geosys.* 8.
- 1339 Alt, J. C., Shanks, W. C., Jackson, M. C., 1993. Cycling of sulfur in subduction
1340 zones - the geochemistry of sulfur in the Mariana-Island Arc and Back-Arc
1341 Trough. *E.P.S.L.* 119: 477-494.
- 1342 Alt, J. C., Teagle, D. A. H., 1999. The uptake of carbon during alteration of
1343 ocean crust. *Geochim. Cosmochim. Acta.* 63: 1527-1535.
- 1344 Alt, J. C., Teagle, D. A. H., 2003. Hydrothermal alteration of upper oceanic
1345 crust formed at a fast-spreading ridge: mineral, chemical, and isotopic
1346 evidence from ODP Site 801. *Chem. Geol.* 201: 191-211.

- 1347 Ballhaus, C., Berry, R. F., Green, D. H., 1990. Oxygen fugacity controls in
1348 the Earths upper mantle. *Nature* 348: 437-440.
- 1349 Bebout, G. E., 1995. The impact of subduction-zone metamorphism on mantle-
1350 ocean chemical cycling. *Chem. Geol.* 126: 191-218.
- 1351 Berner, R. A., 2001. Modelling atmospheric O₂ over Phanerozoic time. *Geochim.*
1352 *Cosmochim. Acta.* 65: 685-694.
- 1353 Brandon, A. D., Draper, D. S., 1996. Constraints on the origin of the oxidation
1354 state of mantle overlying subduction zones: An example from Simcoe,
1355 Washington, USA. *Geochim. Cosmochim. Acta.* 60: 1739-1749.
- 1356 Canfield, D. E., 2004. The evolution of the Earth surface sulfur reservoir. *Am.*
1357 *J. Sci.* 304: 839-861.
- 1358 Cannat, M., 1996. How thick is the magmatic crust at slow spreading oceanic
1359 ridges? *J. Geophys. Res: Solid Earth.* 101: 2847-2857.
- 1360 Carlson, R. L., 2001. The abundance of ultramafic rocks in Atlantic Ocean
1361 crust. *Geophys. Journ. Int.* 144: 37-48.
- 1362 Charlou, J. L., Bougault, H., Appriou, P., Nelsen, T., Rona, P., 1991. Different
1363 Tdm/Ch₄ Hydrothermal Plume Signatures - Tag Site at 26-Degrees-N and
1364 Serpentinized Ultrabasic Diapir at 15-Degrees-05'n on the Mid-Atlantic
1365 Ridge. *Geochim. Cosmochim. Acta.* 55: 3209-3222.
- 1366 Charlou, J. L., Fouquet, Y., Bougault, H., Donval, J. P., Etoubleau, J., Jean-
1367 Baptiste, P., Dapigny, A., Appriou, P., Rona, P. A., 1998. Intense CH₄
1368 plumes generated by serpentinization of ultramafic rocks at the intersec-
1369 tion of the 15 degrees 20 ' N fracture zone and the Mid-Atlantic Ridge.
1370 *Geochim. Cosmochim. Acta.* 62: 2323-2333.
- 1371 Chester, R. 1990, *Marine Geochemistry*, Unwin Hyman, London, 698 pp.,

- 1372 Chiarenzelli, J., Lupulescu, M., Cousens, B., Thern, E., Coffin, L., Regan,
1373 S., 2010. Enriched Grenvillian lithospheric mantle as a consequence of
1374 long-lived subduction beneath Laurentia. *Geology* 38: 151-154.
- 1375 Connolly, J. A. D., 2005. Computation of phase equilibria by linear program-
1376 ming: A tool for geodynamic modeling and its application to subduction
1377 zone decarbonation. *E.P.S.L.* 236: 524-541.
- 1378 Crisp, J. A., 1984. Rates of Magma Emplacement and Volcanic Output. *J.*
1379 *Volc. Geotherm. Res.* 20: 177-211.
- 1380 Dasgupta, R., Hirschmann, M. M., Withers, A. C., 2004. Deep global cycling
1381 of carbon constrained by the solidus of anhydrous, carbonated eclogite
1382 under upper mantle conditions. *E.P.S.L.* 227: 73-85.
- 1383 de Hoog, J. C. M., Hattori, K. H., Hoblitt, R. P., 2004. Oxidized sulfur-rich
1384 mafic magma at Mount Pinatubo, Philippines. *Contrib. Mineral. Petrol.*
1385 146: 750-761.
- 1386 Delano, J. W., 2001. Redox history of the Earth's interior since similar to
1387 3900 Ma: Implications for prebiotic molecules. *Orig. Life. Ev. Bios.* 31:
1388 311-341.
- 1389 Depaolo, D. J., 1983. The mean-life of continents - estimates of continent
1390 recycling rates from Nd and Hf isotopic data and implications for mantle
1391 structure. *Geophys. Res. Lett.* 10: 705-708.
- 1392 Dixon, J. E., Stolper, E. M., 1995. An experimental study of water and carbon
1393 dioxide solubilities in mid-ocean ridge basaltic liquids .2. Applications to
1394 degassing. *J. Pet.* 36: 1633-1646.
- 1395 Ducea, M. N., Saleeby, J., Morrison, J., Valencia, V. A., 2005. Subducted
1396 carbonates, metasomatism of mantle wedges, and possible connections to
1397 diamond formation: An example from California. *Am. Min.* 90: 864-870.

- 1398 Dupuy, C., Dostal, J., Leblanc, M., 1981. Geochemistry of an ophiolitic com-
1399 plex from New-Caledonia. *Contrib. Mineral. Petrol.* 76: 77-83.
- 1400 Edmond, J. M., Measures, C., McDuff, R. E., Chan, L. H., Collier, R., Grant,
1401 B., Gordon, L. I., Corliss, J. B., 1979. Ridge crest hydrothermal activity
1402 and the balances of the major and minor elements in the ocean - Galapagos
1403 data. *E.P.S.L.* 46: 1-18.
- 1404 Evans, K. A., 2006. Redox decoupling and redox budgets: Conceptual tools
1405 for the study of earth systems. *Geology* 34: 489-492.
- 1406 Fischer, T. P., Marty, B., 2005. Volatile abundances in the sub-arc mantle: in-
1407 sights from volcanic and hydrothermal gas discharges. *J. Volc. Geotherm.*
1408 *Res.* 140: 205-216.
- 1409 Frost, B. R., Ballhaus, C., 1998. Comment on "Constraints on the origin of the
1410 oxidation state of mantle overlying subduction zones: An example from
1411 Simcoe, Washington, USA". *Geochim. Cosmochim. Acta.* 62: 329-331.
- 1412 Frost, B. R., Beard, J. S., 2007. On silica activity and serpentinization. *J. Pet.*
1413 48: 1351-1368.
- 1414 Ghiorso, M. S., Hirschmann, M. M., Reiners, P. W., Kress, V. C., 2002. The
1415 pMELTS: A revision of MELTS for improved calculation of phase relations
1416 and major element partitioning related to partial melting of the mantle to
1417 3 GPa. *Geochem. Geophys. Geosys.* 3.
- 1418 Giggenbach, W. F., 1992. Magma degassing and mineral deposition in hy-
1419 drothermal systems along convergent plate boundaries. *Economic Geology*
1420 87: 1927-1944.
- 1421 Gorman, P. J., Kerrick, D. M., Connolly, J. A. D., 2006. Modeling open system
1422 metamorphic decarbonation of subducting slabs. *Geochem. Geophys.*
1423 *Geosys.* 7.

- 1424 Gurenko, A. A., Schmincke, H. U., 2000. S concentrations and its speciation
1425 in Miocene basaltic magmas north and south of Gran Canaria (Canary
1426 Islands): Constraints from glass inclusions in olivine and clinopyroxene.
1427 *Geochim. Cosmochim. Acta.* 64: 2321-2337.
- 1428 Hacker, B. R., Peacock, S. M., Abers, G. A., Holloway, S. D., 2003. Subduction
1429 factory - 2. Are intermediate-depth earthquakes in subducting slabs linked
1430 to metamorphic dehydration reactions? *J. Geophys. Res: Solid Earth.*
1431 108.
- 1432 Hattori, K. H., Guillot, S., 2007. Geochemical character of serpentinites as-
1433 sociated with high- to ultrahigh-pressure metamorphic rocks in the Alps,
1434 Cuba, and the Himalayas: Recycling of elements in subduction zones.
1435 *Geochem. Geophys. Geosys.* 8.
- 1436 Hay, W. W., Sloan, J. L., Wold, C. N., 1988. Mass age distribution and com-
1437 position of sediments on the ocean-floor and the global rate of sediment
1438 subduction. *J. Geophys. Res: Solid Earth.* 93: 14933-14940.
- 1439 Hayes, J. M., Waldbauer, J. R., 2006. The carbon cycle and associated redox
1440 processes through time. *Phil. Trans. Roy. Soc.* 361: 931-950.
- 1441 Hermann, J., Spandler, C., Hack, A., Korsakov, A. V., 2006. Aqueous fluids
1442 and hydrous melts in high-pressure and ultra-high pressure rocks: Impli-
1443 cations for element transfer in subduction zones. *Lithos* 92: 399-417.
- 1444 Hilton, D. R., Fischer, T. P., Marty, B. (2002), Noble gases and volatile recy-
1445 cling at subduction zones, in *Noble Gases in Geochemistry and Cosmo-*
1446 *chemistry*, edited, pp. 319-370.
- 1447 Hirschmann, M. M., 2009. Ironing out the oxidation of Earth's mantle. *Science*
1448 325: 545-546.
- 1449 Hoffman, N. R. A., McKenzie, D. P., 1985. The destruction of geochemi-
1450 cal heterogeneities by differential fluid motions during mantle convection.
1451 *Geophys. Jour. Roy. Astr. Soc.* 82: 163-206.

- 1452 Holland, H. D., 2002. Volcanic gases, black smokers, and the Great Oxidation
1453 Event. *Geochim. Cosmochim. Acta.* 66: 3811-3826.
- 1454 Holser, W. T., Schidlowski, M., Mackenzie, F. T., Maynard, J. B. (1988),
1455 Biogeochemical cycles of carbon and sulphur, in *Chemical cycles and the*
1456 *evolution of the Earth*, edited by C. B. Gregor, R. M. Garrels, F. T.
1457 Mackenzie and J. B. Maynard, pp. 105-175, John Wiley and Sons, New
1458 York.
- 1459 Honnorez, J., 2003. Hydrothermal alteration vs. ocean-floor metamorphism.
1460 A comparison between two case histories: the TAG hydrothermal mound
1461 (Mid-Atlantic Ridge) vs. DSDP/ODP Hole 504B (Equatorial East Pa-
1462 cific). *Compt. Rend. Geosc.* 335: 781-824.
- 1463 Ito, E., Harris, D. M., Anderson, A. T., 1983. Alteration of oceanic-crust and
1464 geologic cycling of chlorine and water. *Geochim. Cosmochim. Acta.* 47:
1465 1613-1624.
- 1466 Jarrard, R. D., 2003. Subduction fluxes of water, carbon dioxide, chlorine, and
1467 potassium. *Geochem. Geophys. Geosys.* 4.
- 1468 Johnson, H. P., Semyan, S. W., 1994. Age variation in the physical-properties
1469 of oceanic basalts - implications for crustal formation and evolution. *J.*
1470 *Geophys. Res: Solid Earth.* 99: 3123-3134.
- 1471 Kelley, K. A., Cottrell, E., 2009. Water and the oxidation state of subduction
1472 zone magmas. *Science* 325: 605-607.
- 1473 Kerrick, D. M., Caldeira, K., 1998. Metamorphic CO₂ degassing from orogenic
1474 belts. *Chem. Geol.* 145: 213-232.
- 1475 Kerrick, D. M., Connolly, J. A. D., 2001. Metamorphic devolatilisation of
1476 subducted marine sediments and the transport of volatiles into the Earth's
1477 mantle. *Nature* 411: 293-296.

- 1478 Kessel, R., Schmidt, M. W., Ulmer, P., Pettke, T., 2005. Trace element signa-
1479 ture of subduction-zone fluids, melts and supercritical liquids at 120-180
1480 km depth. *Nature* 437: 724-727.
- 1481 Kopf, A. J., 2002. Significance of mud volcanism. *Rev. Geophys.* 40. Article
1482 1005.
- 1483 Kopf, A. J., 2003. Global methane emission through mud volcanoes and its
1484 past and present impact on the Earth's climate. *Int. Jour. Earth. Sci.*
1485 92: 806-816.
- 1486 Kump, L. R., Holland, H. D., 1992. Iron in precambrian rocks - implications
1487 for the global oxygen budget of the ancient Earth. *Geochim. Cosmochim.*
1488 *Acta.* 56: 3217-3223.
- 1489 Kump, L. R., Kasting, J. F., Barley, M. E., 2001. Rise of atmospheric oxygen
1490 and the "upside-down" Archean mantle. *Geochem. Geophys. Geosys.* 2.
- 1491 Lecuyer, C., Ricard, Y., 1999. Long-term fluxes and budget of ferric iron:
1492 implication for the redox states of the Earth's mantle and atmosphere.
1493 *E.P.S.L.* 165: 197-211.
- 1494 Lee, C. T. A., Leeman, W. P., Canil, D., Li, Z. X. A., 2005. Similar V/Sc sys-
1495 tematics in MORB and arc basalts: Implications for the oxygen fugacities
1496 of their mantle source regions. *J. Pet.* 46: 2313-2336.
- 1497 Li, Z. X. A., Lee, C. T. A., 2004. The constancy of upper mantle fO(2) through
1498 time inferred from V/Sc ratios in basalts. *E.P.S.L.* 228: 483-493.
- 1499 Marchesi, C., Garrido, C. J., Godard, M., Belley, F., Ferre, E., 2009. Migration
1500 and accumulation of ultra-depleted subduction-related melts in the Massif
1501 du Sud ophiolite (New Caledonia). *Chem. Geol.* 266: 180-195.
- 1502 Marty, B., Jambon, A., Sano, Y., 1989. Helium-Isotopes and CO₂ in Volcanic
1503 Gases of Japan. *Chem. Geol.* 76: 25-40.

- 1504 Marty, B., Tolstikhin, I. N., 1998. CO₂ fluxes from mid-ocean ridges, arcs and
1505 plumes. *Chem. Geol.* 145: 233-248.
- 1506 McDonough, W. F., Sun, S. S., 1995. The composition of the Earth. *Chem.*
1507 *Geol.* 120: 223-253.
- 1508 McInnes, B. I. A., Gregoire, M., Binns, R. A., Herzig, P. M., Hannington, M.
1509 D., 2001. Hydrous metasomatism of oceanic sub-arc mantle, Lihir, Papua
1510 New Guinea: petrology and geochemistry of fluid-metasomatised mantle
1511 wedge xenoliths. *E.P.S.L.* 188: 169-183.
- 1512 Mevel, C., 2003. Serpentinization of abyssal peridotites at mid-ocean ridges.
1513 *Compt. Rend. Geosc.* 335: 825-852.
- 1514 Milkov, A. V., Claypool, G. E., Lee, Y. J., Xu, W. Y., Dickens, G. R., Borowski,
1515 W. S., 2003. In situ methane concentrations, at Hydrate Ridge, offshore
1516 Oregon: New constraints on the global gas hydrate inventory from an
1517 active margin. *Geology* 31: 833-836.
- 1518 Milkov, A. V., Sassen, R., Apanasovich, T. V., Dadashev, F. G., 2003. Global
1519 gas flux from mud volcanoes: A significant source of fossil methane in the
1520 atmosphere and the ocean. *Geophys. Res. Lett.* 30.
- 1521 Morner, N. A., Etiope, G., 2002. Carbon degassing from the lithosphere. *Glob.*
1522 *Plan. Chan.* 33: 185-203.
- 1523 Mottl, M. J., Wheat, C. G., Fryer, P., Gharib, J., Martin, J. B., 2004. Chem-
1524 istry of springs across the Mariana forearc shows progressive devolatiliza-
1525 tion of the subducting plate. *Geochim. Cosmochim. Acta.* 68: 4915-4933.
- 1526 Mungall, J. E., 2002. Roasting the mantle: Slab melting and the genesis of
1527 major Au and Au-rich Cu deposits. *Geology* 30: 915-918.
- 1528 Newton, R. C., Manning, C. E., 2005. Solubility of anhydrite, CaSO₄, in
1529 NaCl-H₂O solutions at high pressures and temperatures: Applications to
1530 fluid-rock interaction. *J. Pet.* 46: 701-716.

- 1531 Parkinson, I. J., Arculus, R. J., 1999. The redox state of subduction zones:
1532 insights from arc-peridotites. *Chem. Geol.* 160: 409-423.
- 1533 Paul, H. J., Gillis, K. M., Coggon, R. M., Teagle, D. A. H., 2006. ODP Site
1534 1224: A missing link in the investigation of seafloor weathering. *Geochem.*
1535 *Geophys. Geosys.* 7.
- 1536 Paulick, H., Bach, W., Godard, M., De Hoog, J. C. M., Suhr, G., Harvey,
1537 J., 2006. Geochemistry of abyssal peridotites (Mid-Atlantic Ridge, 15
1538 degrees 20 ' N, ODP Leg 209): Implications for fluid/rock interaction in
1539 slow spreading environments. *Chem. Geol.* 234: 179-210.
- 1540 Peacock, S. M., 1990. Fluid processes in subduction zones. *Science* 248: 329-
1541 337.
- 1542 Petsch, S. T., Berner, R. A., 1998. Coupling the geochemical cycles of C, P, Fe,
1543 and S: The effect on atmospheric O₂ and the isotopic records of carbon
1544 and sulfur. *Am. J. Sci.* 298: 246-262.
- 1545 Plank, T., Langmuir, C. H., 1998. The chemical composition of subducting
1546 sediment and its consequences for the crust and mantle. *Chem. Geol.*
1547 145: 325-394.
- 1548 Prinzhofer, A., Nicolas, A., Cassard, D., Moutte, J., Leblanc, M., Paris, J.
1549 P., Rabinovitch, M., 1980. Structures in the New-Caledonia Peridotites-
1550 Gabbros - Implications for Oceanic Mantle and Crust. *Tectonophysics* 69:
1551 85-112.
- 1552 Raiswell, R., Canfield, D. E., 1998. Sources of iron for pyrite formation in
1553 marine sediments. *Am. J. Sci.* 298: 219-245.
- 1554 Ranero, C. R., Sallares, V., 2004. Geophysical evidence for hydration of the
1555 crust and mantle of the Nazca plate during bending at the north Chile
1556 trench. *Geology* 32: 549-552.

- 1557 Rea, D. K., Ruff, L. J., 1996. Composition and mass flux of sediment entering
1558 the world's subduction zones: implications for global sediment budgets,
1559 great earthquakes, and volcanism. *E.P.S.L.* 140: 1-12.
- 1560 Ronov, A. B., Yaroshevsky, A. A., 1976. A new model for the chemical struc-
1561 ture of the Earth's crust. *Geochem. Int.* 13: 89-121.
- 1562 Rupke, L. H., Morgan, J. P., Hort, M., Connolly, J. A. D., 2004. Serpentine
1563 and the subduction zone water cycle. *E.P.S.L.* 223: 17-34.
- 1564 Russell, M. J., Hall, A. J., Boyce, A. J., Fallick, A. E., 2005. 100th anniversary
1565 special paper: On hydrothermal convection systems and the emergence of
1566 life. *Economic Geology* 100: 419-438.
- 1567 Saal, A. E., Hauri, E. H., Langmuir, C. H., Perfit, M. R., 2002. Vapour under-
1568 saturation in primitive mid-ocean-ridge basalt and the volatile content of
1569 Earth's upper mantle. *Nature* 419: 451-455.
- 1570 Salters, V. J. M., Stracke, A., 2004. Composition of the depleted mantle.
1571 *Geochem. Geophys. Geosys.* 5.
- 1572 Sano, Y., Nishio, Y., Gamo, T., Jambon, A., Marty, B., 1998. Noble gas and
1573 carbon isotopes in Mariana Trough basalt glasses. *App. Geochem.* 13:
1574 441-449.
- 1575 Sano, Y., Williams, S. N., 1996. Fluxes of mantle and subducted carbon along
1576 convergent plate boundaries. *Geophys. Res. Lett.* 23: 2749-2752.
- 1577 Schneider, M. E., Eggler, D. H., 1986. Fluids in equilibrium with peridotite
1578 minerals - implications for mantle metasomatism. *Geochim. Cosmochim.*
1579 *Acta.* 50: 711-724.
- 1580 Shaw, A. M., Hilton, D. R., Fischer, T. P., Walker, J. A., Alvarado, G. E., 2003.
1581 Contrasting He-C relationships in Nicaragua and Costa Rica: insights into
1582 C cycling through subduction zones. *E.P.S.L.* 214: 499-513.

- 1583 Skelton, A., Whitmarsh, R., Arghe, F., Crill, P., Koyi, H., 2005. Constraining
1584 the rate and extent of mantle serpentinization from seismic and petrologi-
1585 cal data: implications for chemosynthesis and tectonic processes. *Geofluids*.
1586 5: 153-164.
- 1587 Skelton, A. D. L., Valley, J. W., 2000. The relative timing of serpentinisation
1588 and mantle exhumation at the ocean-continent transition, Iberia: con-
1589 straints from oxygen isotopes. *E.P.S.L.* 178: 327-338.
- 1590 Staudigel, H., Albarede, F., Blichert-Toft, J., Edmond, J., McDonough, B.,
1591 Jacobsen, S. B., Keeling, R., Langmuir, C. H., Nielsen, R. L., Plank, T.,
1592 Rudnick, R., Shaw, H. F., Shirey, S., Veizer, J., White, W., 1998. Geo-
1593 chemical Earth Reference Model (GERM): description of the initiative.
1594 *Chem. Geol.* 145: 153-159.
- 1595 Staudigel, H., Hart, S. R., Schmincke, H. U., Smith, B. M., 1989. Cretaceous
1596 ocean crust at DSDP Site-417 and Site-418 - carbon uptake from weath-
1597 ering versus loss by magmatic outgassing. *Geochim. Cosmochim. Acta*.
1598 53: 3091-3094.
- 1599 Sun, W., Arculus, R. J., Kamenetsky, V. S., Binns, R. A., 2004. Release of
1600 gold-bearing fluids in convergent margin magmas prompted by magnetite
1601 crystallization. *Nature* 431: 975-979.
- 1602 Svensen, H., Planke, S., Malthe-Sorensen, A., Jamtveit, B., Myklebust, R.,
1603 Eidem, T. R., Rey, S. S., 2004. Release of methane from a volcanic basin
1604 as a mechanism for initial Eocene global warming. *Nature* 429: 542-545.
- 1605 Vils, F., Pelletier, L., Kalt, A., Muntener, O., Ludwig, T., 2008. The Lithium,
1606 Boron and Beryllium content of serpentinized peridotites from ODP Leg
1607 209 (Sites 1272A and 1274A): Implications for lithium and boron budgets
1608 of oceanic lithosphere. *Geochim. Cosmochim. Acta.* 72: 5475-5504.
- 1609 von Huene, R., Scholl, J. W., 1991. Observations at convergent margins con-
1610 cerning sediment subduction, subduction erosion and the growth of con-

- 1611 timental crust. *Rev. Geophys.* 29: 279-316.
- 1612 Wallace, P., Carmichael, I. S. E., 1992. Sulfur in basaltic magmas. *Geochim.*
1613 *Cosmochim. Acta.* 56: 1863-1874.
- 1614 Wallace, P. J., 2005. Volatiles in subduction zone magmas: concentrations and
1615 fluxes based on melt inclusion and volcanic gas data. *J. Volc. Geotherm.*
1616 *Res.* 140: 217-240.
- 1617 Wallman, K., 2001. Controls on the Cretaceous and Cenozoic evolution of sea-
1618 water composition, atmospheric CO₂ and climate. *Geochim. Cosmochim.*
1619 *Acta.* 65: 3005-3025.
- 1620 Wood, B. J., Bryndzia, L. T., Johnson, K. E., 1990. Mantle oxidation-state
1621 and its relationship to tectonic environment and fluid speciation. *Science*
1622 248: 337-345.
- 1623 Wood, B. J., Wade, J., Kilburn, M. R., 2008. Core formation and the oxidation
1624 state of the Earth: Additional constraints from Nb, V and Cr partitioning.
1625 *Geochim. Cosmochim. Acta.* 72: 1415-1426.
- 1626 Wykes, J. L., Newton, R. C., Manning, C. E., 2008. Solubility of andradite,
1627 Ca₃Fe₂Si₃O₁₂, in a 10 mol% NaCl solution at 800 degrees C and 10 kbar:
1628 Implications for the metasomatic origin of grandite garnet in calc-silicate
1629 granulites. *Am. Min.* 93: 886-892.
- 1630 Wysoczanski, R. J., Wright, I. C., Gamble, J. A., Hauri, E. H., Luhr, J. F.,
1631 Eggins, S. M., Handler, M. R., 2006. Volatile contents of Kermadec Arc-
1632 Havre Trough pillow glasses: Fingerprinting slab-derived aqueous fluids
1633 in the mantle sources of arc and back-arc lavas. *J. Volc. Geotherm. Res.*
1634 152: 51-73.
- 1635 Yaxley, G. M., Brey, G. P., 2004. Phase relations of carbonate-bearing eclogite
1636 assemblages from 2.5 to 5.5 GPa: implications for petrogenesis of carbon-
1637 atites. *Contrib. Mineral. Petrol.* 146: 606-619.

- 1638 Zhang, Z. M., Shen, K., Sun, W. D., Liu, Y. S., Liou, J. G., Shi, C., Wang, J.
1639 L., 2008. Fluids in deeply subducted continental crust: Petrology, mineral
1640 chemistry and fluid inclusion of UHP metamorphic veins from the Sulu
1641 orogen, eastern China. *Geochim. Cosmochim. Acta.* 72: 3200-3228.
- 1642 Zhou, W. M., Van der Voo, R., Peacor, D. R., Wang, D. M., Zhang, Y.
1643 X., 2001. Low-temperature oxidation in MORB of titanomagnetite to ti-
1644 tanomaghemite: A gradual process with implications for marine magnetic
1645 anomaly amplitudes. *J. Geophys. Res: Solid Earth.* 106: 6409-6421.

1646 **8. Figure Captions**

1647 Figure 1. (a) conceptual model; (b) box model representation of conceptual
1648 model

1649 Figure 2. Results of analysis of serpentinised mantle lithosphere from the
1650 MARK fracture zone and New Caledonia: (a) MgO vs. Al_2O_3 ; (b) S vs.
1651 loss on ignition; (c) $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ vs. loss on ignition; (d) C vs. loss on
1652 ignition; (e) RB_M versus loss on ignition; (f) RB_C versus loss on ignition.

1653 Figure 3. Graphical representation of element fluxes. Δ indicates the net
1654 addition of each element to the mantle. Units for all fluxes are $\times 10^{12}$
1655 moles year $^{-1}$.

1656 Figure 4. Estimates of input and output subduction zone redox budgets for
1657 minimum and maximum crustal oxidation and minimum and maximum
1658 mantle oxidation

1659 Figure 5. Comparison of net subduction zone input with MORB, plume and
1660 the sum of MORB, plume and arc outputs

1661 Figure 6. Calculated relationship between mantle $\log f\text{O}_2$ relative to QFM
1662 and Fe_2O_3 content at 1200°C and 1 GPa. Calculations were made using
1663 pMelts (Ghiorso et al. 2002). Line shows best fit to arbitrary equation
1664 shown in equation 2.

1665 Figure 7. Calculated evolution of mantle $\log f\text{O}_2$ relative to QFM with time
1666 for different redox budget fluxes and mantle mixing scenarios: (a) redox
1667 budget added only to subduction zones; (b) redox budget added only
1668 to the upper mantle; (c) redox budget added to the whole mantle; (d)
1669 redox budget added to the whole mantle with a linear increase in mixing
1670 efficiency up to 1 Ga.

1671 **9. Tables**

Table 1: Serpentinised peridotite analyses

Element (wt%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	LOI	Cl	C	S	Total
NC07-01	34.72	0.04	4.16	3.42	42.58	0.05	0.02	b.d.l.	12.74	0.016	0.12	0.019	98.31
NC07-02	34.28	0.09	6.33	1.21	40.01	0.01	0.02	b.d.l.	16.08	b.d.l.	0.38	0.005	98.90
NC07-03	34.8	0.09	2.94	4.31	43.92	0.04	0.02	b.d.l.	11.48	0.007	0.15	0.02	98.31
NC07-04	41.24	0.39	3.75	3.71	39.09	1.34	0.03	b.d.l.	8.07	b.d.l.	0.07	0.013	98.22
NC07-05	36.49	0.22	3.89	3.6	41.96	0.07	0.02	b.d.l.	11.25	b.d.l.	0.1	b.d.l.	98.17
NC07-06	39.07	0.39	4.15	3.62	40.18	0.2	0.02	b.d.l.	9.94	b.d.l.	0.07	0.013	98.28
NC07-07	34.57	0.26	3.57	3.89	42.86	0.06	0.02	b.d.l.	11.5	b.d.l.	0.11	0.019	97.80
NC07-08	38.79	0.4	3.08	3.97	41.16	0.33	0.02	b.d.l.	9.56	b.d.l.	0.09	0.007	98.08
NC07-09	39.22	0.36	3.33	3.7	40.77	0.37	0.02	b.d.l.	10.63	b.d.l.	0.1	0.005	99.06
NC07-10	37.63	0.35	5.46	2.04	38.75	0.08	0.02	b.d.l.	13.23	b.d.l.	0.15	0.017	98.34
NC07-11	35.11	0.08	3.25	4.25	43.98	0.05	0.02	b.d.l.	10.99	b.d.l.	0.1	0.018	98.38
NC07-012	38.93	0.36	3.46	4.74	41.73	0.23	0.02	b.d.l.	8.91	b.d.l.	0.09	0.013	99.16
NC07-014	38.32	0.25	3.62	4.49	42.36	0.19	0.03	b.d.l.	9.34	b.d.l.	0.1	0.006	99.19
69427	38.94	0.62	3.10	4.06	40.81	0.65	0.04	b.d.l.	11.27	0.081	0.19	0.025	100.31
69332	41.18	0.58	4.05	2.76	36.05	0.01	0.14	0.01	12.56	0.07	0.19	1.307	99.37
69430	32.78	0.59	4.76	2.82	41.22	0.09	0.04	b.d.l.	14.93	0.084	0.19	0.031	98.47
69431	37.17	0.62	4.03	2.96	39.67	0.61	0.04	b.d.l.	13.2	0.094	0.19	0.037	99.17
69432	36.72	0.57	3.99	2.96	39.32	0.46	0.05	b.d.l.	14.03	0.096	0.21	0.05	98.96
69321	41.28	0.78	3.01	3.62	36.98	0.02	0.1	0.06	11.7	0.021	0.08	0.629	98.78
69433	35.86	0.59	3.36	3.42	38.57	0.5	0.05	b.d.l.	15.62	0.081	2.13	0.116	100.82
69434	34.09	0.24	4.95	2.5	40.49	0.08	0.05	b.d.l.	15.46	0.184	0.2	0.064	98.81
69322	40.67	0.75	2.80	3.65	37.46	0.02	0.1	0.02	11.95	0.01	0.13	0.749	98.85
69435	35.28	0.29	4.52	2.67	40.34	0.14	0.05	b.d.l.	14.96	0.175	0.16	0.055	99.12
69495	36.28	0.74	3.77	2.76	38.66	0.15	0.06	b.d.l.	15.37	0.17	1.25	0.107	99.86
69323	45.56	0.97	3.27	2.73	34.7	0.24	0.14	0.01	10.18	0.044	0.21	0.326	98.93
69324	40.78	0.76	3.87	2.76	38.7	0.01	0.14	b.d.l.	12.21	0.049	0.14	0.155	100.23
69327	40.88	0.65	2.26	3.88	37.89	0.05	0.08	0.01	12.11	0.016	0.08	0.264	98.67
69497	36.62	0.81	4.10	3.04	38.41	0.17	0.3	0.01	14.89	0.285	1.05	0.129	100.45
69498	36.73	0.56	4.33	2.7	39.78	0.02	0.08	b.d.l.	15.01	0.494	0.33	0.169	100.72
69499	36.41	0.56	4.08	2.7	39.39	0.12	0.08	b.d.l.	15.76	0.423	0.93	0.125	101.09

Table 2: Selected trace element contents in ppm
b.d.l.: below detection limit

	Co	Cr	Cu	Ni	V	Zn	P	Mn	Ti
NC07-01	120	668	36	2540	b.d.l.	40	20	820	b.d.l.
NC07-02	114	1556	40	2383	b.d.l.	45	20	710	b.d.l.
NC07-03	122	1709	39	2626	b.d.l.	46	20	810	b.d.l.
NC07-04	110	1795	65	2091	36	51	20	930	100
NC07-05	119	2223	36	2444	b.d.l.	48	20	830	b.d.l.
NC07-06	115	2920	32	2190	22	50	20	920	b.d.l.
NC07-07	120	5809	30	2571	b.d.l.	54	20	820	b.d.l.
NC07-08	110	3513	35	2227	b.d.l.	46	20	830	b.d.l.
NC07-09	113	2324	46	2163	25	54	20	860	b.d.l.
NC07-10	112	2842	31	2215	b.d.l.	45	20	870	b.d.l.
NC07-11	122	1641	27	2671	b.d.l.	44	20	810	b.d.l.
NC07-012	129	3103	47	2335	23	58	20	950	100
NC07-014	135	1283	41	2370	b.d.l.	50	20	930	b.d.l.
69319	b.d.l.	552	47	267	196	147	20	1700	3500
69321	105	1954	52	2089	25	67	40	520	200
69322	b.d.l.	2157	48	2152	24	46	20	880	b.d.l.
69323	b.d.l.	1284	1009	1580	42	71	30	980	500
69324	102	3662	91	2039	29	48	20	540	b.d.l.
69325	b.d.l.	b.d.l.	56	70	169	82	40	840	3000
69326	b.d.l.	b.d.l.	33	112	205	92	30	1540	2900
69327	102	2120	88	2116	30	42	20	490	b.d.l.
69328	b.d.l.	b.d.l.	41	113	190	83	20	1420	2700
69329	b.d.l.	b.d.l.	41	96	176	59	60	1210	3300
69331	b.d.l.	b.d.l.	37	92	194	59	100	1200	3600
69332	111	1610	85	2114	22	44	20	510	100
69427	125	1875	89	2247	23	59	20	840	b.d.l.
69430	129	5806	99	2412	28	71	20	830	b.d.l.
69431	122	2097	93	2224	32	59	20	840	b.d.l.
69432	110	1759	76	2188	22	91	20	810	b.d.l.
69433	111	1889	84	2112	27	73	20	770	200
69434	118	1667	68	2311	b.d.l.	62	20	780	b.d.l.
69435	117	1197	98	2321	b.d.l.	79	20	710	200
69495	105	2148	66	2057	29	68	20	860	100
69497	120	2586	70	2150	40	69	50	860	400
69498	106	1737	82	2245	b.d.l.	58	20	720	200
69499	101	1886	97	2147	b.d.l.	61	20	690	100

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Table 3: Summary of S content measurements in serpentinised peridotite

Site	Source	n	S ²⁻	S ⁻	S ^{2-+S-}	S ⁶⁺	S(total)
MAR	Alt et al. (2007)	36	0.04(5)	0.05(14)		0.08(7)	
15°20'	Vils et al. (2008)	13					0.11(6)
	Paulick et al. (2006)	13					0.32(56)
	This study	18					0.26(34)
Izu-Bonin Forearc	Alt and Shanks (2006)	27			0.006(15)	0.03(7)	
MAR Kane Fracture Zone	Alt and Shanks (2003)	22			0.12(21)	0.05(2)	
New Caledonia	This Study	13					0.01(1)

n:number of analyses
figure in brackets is one standard deviation on the value

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Table 4: Estimates of compositions and uncertainties of input and output reservoirs for subduction zones

wt% element	C ⁰	C ⁴⁺	Fe ²⁺	Fe ³⁺	S ²⁻	S ⁻	S ⁶⁺
Sediments	0.50	3.00	0.72	3.28	n.a.	1.15	n.a.
σ	0.25	1.40	0.06	0.26	n.a.	0.58	n.a.
Altered Ocean Crust	n.a.	0.21	4.90	1.40	n.a.	0.071	0.036
σ	n.a.	0.04	0.59	0.62	n.a.	0.014	0.018
Serpentinised Lithosphere	n.a.	0.28	2.39	2.88	0.041	0.048	0.078
σ	n.a.	0.28	0.40	0.40	0.055	0.140	0.073
Arc Rocks	n.a.	0.0007	4.62	3.09	n.a.	0.050	n.a.
σ	n.a.	0.0003	1.39	1.39	n.a.	0.040	n.a.
n.a.: not applicable							

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Table 5: Estimates of fluxes and uncertainties of input and output to subduction zones

	Reservoir Flux $\times 10^{15} \text{ g yr}^{-1}$	C^{4-}	C^0	C^{4+}	Fe^{2+}	Fe^{3+}	S^{2-}	S^-	S^{4+}	S^{6+}	H^0
		$\times 10^{12} \text{ mol yr}^{-1}$									
Sediments	1.73	n.a.	0.72	1.18	0.22	1.02	n.a.	0.62	n.a.	n.a.	n.a.
σ	0.35	n.a.	0.39	0.60	0.05	0.22	n.a.	0.33	n.a.	n.a.	n.a.
Altered Ocean Crust	45.60	n.a.	n.a.	2.18	40.01	11.43	n.a.	1.01	n.a.	0.51	n.a.
σ	9.12	n.a.	n.a.	0.62	9.34	5.55	n.a.	0.28	n.a.	0.28	n.a.
Serpentinised Lithosphere	13	n.a.	n.a.	3.03	5.56	6.70	0.17	0.20	n.a.	0.32	n.a.
σ	10	n.a.	n.a.	3.83	4.38	5.24	0.26	0.59	n.a.	0.38	n.a.
Arc Gases	n.a.	n.a.	n.a.	1.41	n.a.	n.a.	n.a.	n.a.	0.32	n.a.	0.17
σ	n.a.	n.a.	n.a.	0.28	n.a.	n.a.	n.a.	n.a.	0.06	n.a.	0.03
Arc Rocks	7.50	n.a.	n.a.	0.0044	6.20	4.15	n.a.	0.12	n.a.	n.a.	n.a.
σ	1.20	n.a.	n.a.	0.0020	2.11	1.98	n.a.	0.10	n.a.	n.a.	n.a.
Non-volcanic	n.a.	1.00	n.a.	0.06	n.a.	n.a.	n.a.	n.a.	n.a.	0.041	n.a.
σ	n.a.	0.70	n.a.	0.04	n.a.	n.a.	n.a.	n.a.	n.a.	0.029	n.a.

Table 6: Summary of element fluxes

	Fe	C	S
	$\times 10^{12} \text{ mol yr}^{-1}$		
Sediments	1.24	1.90	0.62
σ	0.22	0.71	0.33
Altered Ocean Crust	51.44	2.18	1.52
σ	10.87	0.62	0.40
Serpentinised Lithosphere	12.27	3.03	0.68
σ	6.83	3.83	0.75
Arc Gases	0.00	1.41	0.32
σ	0.00	0.28	0.06
Arc Rocks	10.35	0.00	0.12
σ	2.90	0.00	0.10
Non-volcanic	0.00	1.06	0.04
σ	0.00	0.70	0.03
IN	64.94	7.11	2.82
σ	12.84	3.94	0.91
OUT	10.35	2.47	0.48
σ	2.90	0.75	0.12
Net addition	54.59	4.64	2.35
σ	13.16	4.01	0.92
% recycled	15.94	34.74	16.93
σ	5.46	21.99	6.88

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Table 7: Contributions to redox budget fluxes

		C ⁴⁻	C ⁰	C ⁴⁺	Fe ²⁺	Fe ³⁺	S ²⁻	S ⁻	S ⁴⁺	S ⁶⁺	H ⁰
					x 10 ¹² mol yr ⁻¹						
Mantle Reference State											
Sediments	Max mantle oxidation	n.a.	0.00	7.11	0.00	1.23	n.a.	0.96	n.a.	n.a.	n.a.
	Min mantle oxidation	n.a.	0.00	2.32	0.00	0.80	n.a.	0.29	n.a.	n.a.	n.a.
AOC	Max mantle oxidation	n.a.	n.a.	11.17	0.00	16.99	n.a.	1.30	n.a.	6.31	n.a.
	Min mantle oxidation	n.a.	n.a.	6.24	0.00	5.88	n.a.	0.73	n.a.	1.89	n.a.
Serp Lith	Max mantle oxidation	n.a.	n.a.	27.44	0.00	11.94	n.a.	0.78	n.a.	5.61	n.a.
	Min mantle oxidation	n.a.	n.a.	0.00	0.00	1.46	n.a.	0.00	n.a.	0.00	n.a.
Arc Gases	Max mantle oxidation	n.a.	n.a.	4.52	0.00	n.a.	n.a.	n.a.	1.54	n.a.	-0.20
	Min mantle oxidation	n.a.	n.a.	6.76	0.00	n.a.	n.a.	n.a.	2.30	n.a.	-0.14
Arc Rocks	Max mantle oxidation	n.a.	n.a.	0.01	0.00	2.17	n.a.	0.02	n.a.	n.a.	n.a.
	Min mantle oxidation	n.a.	n.a.	0.03	0.00	6.13	n.a.	0.21	n.a.	n.a.	n.a.
Non-volcanic	Max mantle oxidation	-6.80	n.a.	0.07	0.00	n.a.	n.a.	n.a.	n.a.	0.10	n.a.
	Min mantle oxidation	-1.20	n.a.	0.38	0.00	n.a.	n.a.	n.a.	n.a.	0.56	n.a.
Crustal Reference State											
Sediments	Max Crustal Oxidation	n.a.	-4.44	0.00	-0.27	0.00	n.a.	-6.70	n.a.	n.a.	n.a.
	Min Crustal Oxidation	n.a.	-1.33	0.00	-0.17	0.00	n.a.	-2.01	n.a.	n.a.	n.a.
AOC	Max Crustal Oxidation	n.a.	n.a.	0.00	-49.35	0.00	n.a.	-9.07	n.a.	0.00	n.a.
	Min Crustal Oxidation	n.a.	n.a.	0.00	-30.67	0.00	n.a.	-5.09	n.a.	0.00	n.a.
Serp Lith	Max Crustal Oxidation	n.a.	n.a.	0.00	-9.94	0.00	-3.39	-5.48	n.a.	0.00	n.a.
	Min Crustal Oxidation	n.a.	n.a.	0.00	-1.18	0.00	0.00	0.00	n.a.	0.00	n.a.
Arc Gases	Max Crustal Oxidation	n.a.	n.a.	0.00	n.a.	n.a.	n.a.	n.a.	-0.51	n.a.	-0.14
	Min Crustal Oxidation	n.a.	n.a.	0.00	n.a.	n.a.	n.a.	n.a.	-0.77	n.a.	-0.20
Arc Rocks	Max Crustal Oxidation	n.a.	n.a.	0.00	-4.09	0.00	n.a.	-0.15	n.a.	n.a.	n.a.
	Min Crustal Oxidation	n.a.	n.a.	0.00	-8.32	0.00	n.a.	-1.49	n.a.	n.a.	n.a.
Non-volcanic	Max Crustal Oxidation	-2.40	n.a.	0.00	n.a.	n.a.	n.a.	n.a.	n.a.	0.00	n.a.
	Min Crustal Oxidation	-13.60	n.a.	0.00	n.a.	n.a.	n.a.	n.a.	n.a.	0.00	n.a.

Table 8: Summary of redox budget fluxes

	Max		Min		Max		Min		Monte Carlo Normal	Monte Carlo Log Normal
	Mantle Oxidation	Mantle Oxidation	Mantle Oxidation	Mantle Oxidation	Crustal Oxidation $\times 10^{12}$ mol yr $^{-1}$	Crustal Oxidation	Crustal Oxidation	Crustal Oxidation		
Sediments	9.31	3.41	-11.40	-3.51						
Altered Ocean Crust	35.76	14.74	-58.42	-35.76						
Serpentinised Lithosphere	45.77	1.46	-18.82	-1.18						
Arc Gases	5.85	8.93	-0.65	-0.97						
Arc Rocks	2.20	6.37	-4.24	-9.81						
Non-volcanic	-6.63	-0.26	-2.40	-13.60						
Total	89.42	4.58	81.35	16.08				46	46 - 58	
σ								12		
% returned	1.56	76.67	8.22	60.26				27	14 - 34	
σ								7		

Table 9: Summary of other mantle fluxes

	C ⁴⁺	Fe ²⁺	Fe ³⁺ wt%	S ²⁻	S ⁶⁺	Reservoir Flux x 10 ⁻¹⁵ g year ⁻¹
MORB	0.08	5.86	0.44	0.09	0.00	45.60
σ	0.02	2.29	0.26	0.01	0.00	9.12
OIB	2.30	4.90	2.00	0.33	0.06	4.56
σ	1.15	1.02	0.92	0.10	0.02	0.91
Flux x 10 ⁻¹² moles year ⁻¹	C ⁴⁺	Fe ²⁺	Fe ³⁺	S ²⁻	S ⁶⁺	
		x 10 ⁻¹² moles year ⁻¹				
MORB	0.86	47.85	3.59	1.22	0.06	
σ	0.24	20.97	2.24	0.28	0.07	
OIB	2.38	4.00	1.63	0.47	0.09	
σ	1.28	1.15	0.82	0.17	0.04	
Element Fluxes x 10 ⁻¹² moles year ⁻¹						
	Fe	C	S			
MORB	51.44	0.86	1.28			
σ	21.09	0.24	0.29			
OIB	5.63	2.38	0.56			
σ	1.42	1.28	0.18			
Total	57.07	3.24	1.84			
σ	21.14	1.31	0.34			
RB _M x 10 ⁻¹² moles year ⁻¹						
MORB	7.53					
σ	2.49					
OIB	11.88					
σ	5.21					
Total	19.40					
σ	5.77					

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1677 **10. Figures**

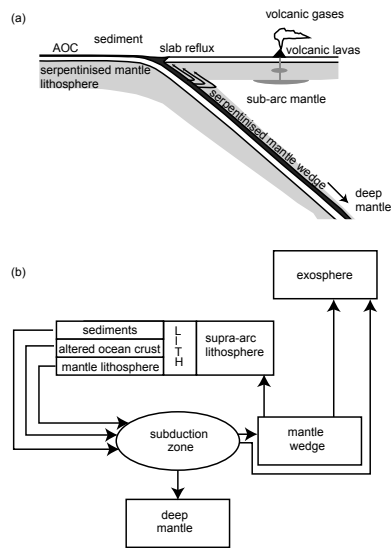


Figure 1:

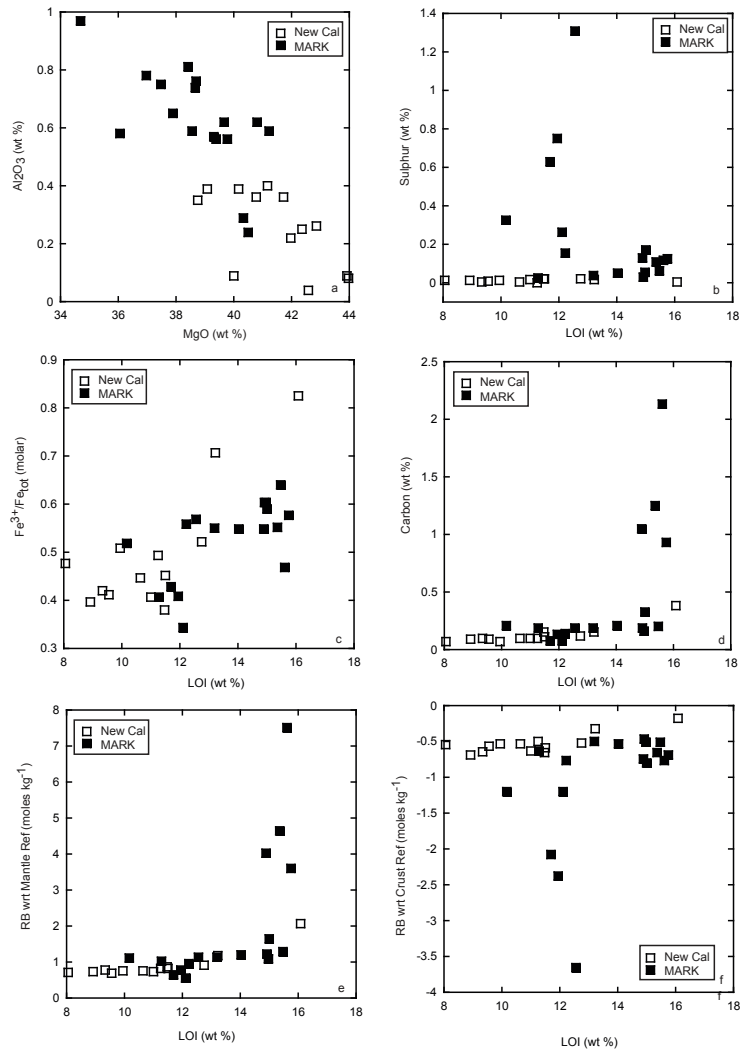


Figure 2:

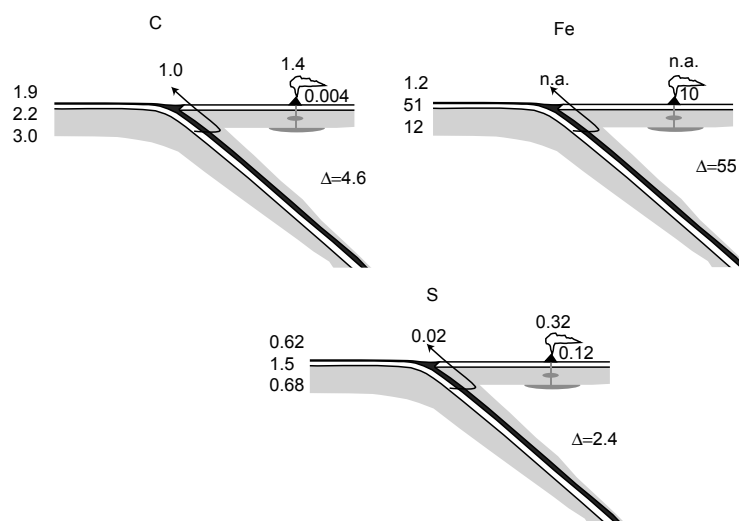


Figure 3:

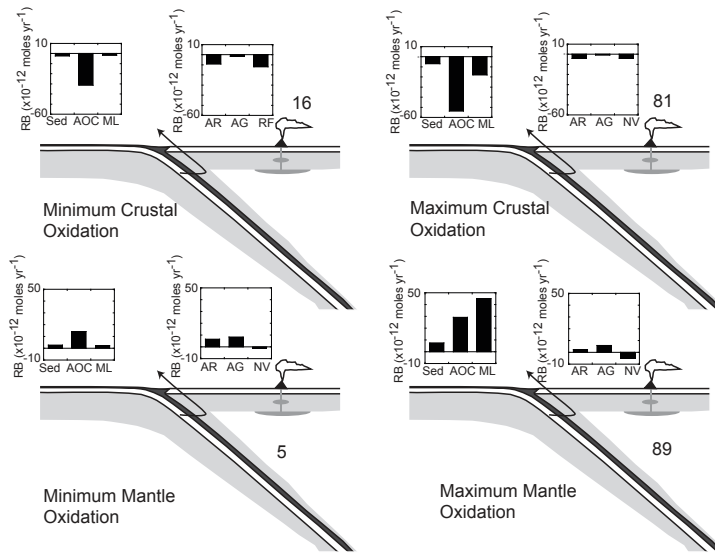


Figure 4:

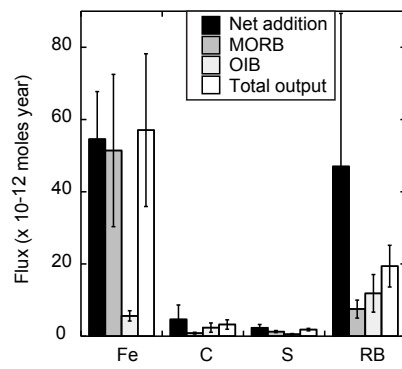


Figure 5:

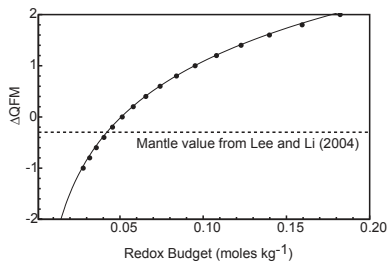


Figure 6:

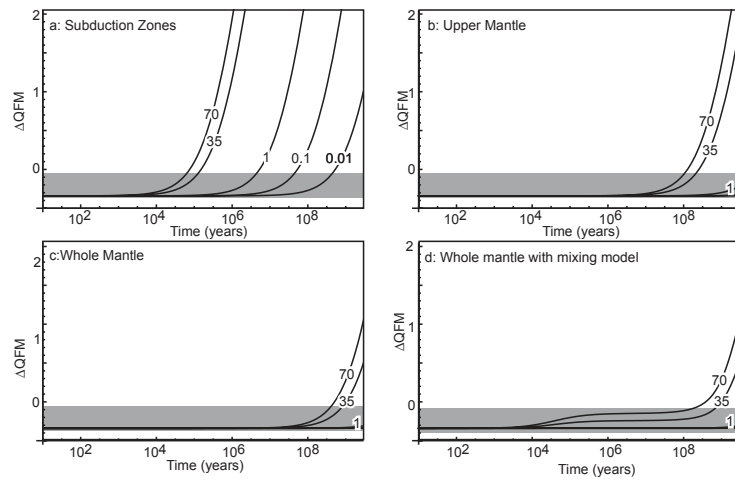


Figure 7: