Redox decoupling and redox budgets: Conceptual tools for the study of earth systems

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ABSTRACT

Redox processes affect many aspects of geological systems. It is therefore useful to distinguish between chemical processes that result in changes in the capacities of reservoirs to oxidize or reduce from those that do not. Two terms are proposed to make this distinction. The first is redox decoupling: the transport of redox-sensitive elements (e.g., H, C, S, Fe) such that reservoirs experience a change in their capacity to oxidize or reduce other material. The second is electrochemical differentiation: the effect of one or more redox decoupling processes that change existing gradients in redox potential. Recognition of redox decoupling requires the use of an extensive rather than an intensive redox variable, because intensive variables do not provide information on fluxes. Redox budget, defined as the number of moles of negative charge that must be added to a sample to reach a reference state, is such a variable. Construction of redox budgets for mid-oceanic-ridge basalt (MORB) lavas and glasses reveals that redox decoupling occurs during crystallization at the Mid-Atlantic, Pacific, and Red Sea ridges, with net oxidation of the crystallized lava. The concepts of electrochemical differentiation, redox decoupling, and redox budget may be useful for researchers studying global cycling, the formation of ore deposits, volcanism, evolution of the mantle, crust and core, redox-related environmental problems, and biotic systems.

Keywords: global change, redox, MORB, cyclic processes.

INTRODUCTION

Earth's evolution has included the development of planet-scale gradients in the distribution of redox pairs (e.g., Fe^{3+}/Fe^{2+}), which reflect gradients in redox potential (e.g., Kuramoto and Matsui, 1996). The mantle is significantly more reduced than the ocean and atmosphere (e.g., Arculus, 1985), and changes in the distribution of redox-sensitive elements during Earth's early history have affected the composition of the atmosphere (e.g., Lowe and Tice, 2004). Redox-sensitive elements, particularly C, play a key role in global climate regulation (e.g., Wallman, 2001) and can limit the abundance of life (e.g., Petsch and Berner, 1998).

Redox-sensitive elements, such as H, C, N, S, P, Fe, and Mn, continue to be redistributed on a variety of scales. Lecuyer and Ricard (1999) noted a net flux of Fe^{3+} from crust to mantle, and suggested a consequent continuing net oxidation of the mantle and/or core. On a smaller scale, Sun et al. (2004) suggested that magnetite crystallization triggers sulfate to sulfide conversion in arc magmas associated with Cu-Au deposits. Redistribution of redox-sensitive elements can have significant consequences: Svensen et al. (2004) proposed that CH_4 released from sediments caused global warming in the Eocene; Selverstone and Gutzler (1993) attributed cooling ca. 125 Ma to the burial of sediment-hosted carbon.

However, it is difficult to determine if this continuous redistribution of redox-sensitive elements augments, maintains, or destroys existing gradients in redox potential. One reason for this difficulty is that the elements should not be considered separately. For example, Fe^{3+} may be added to the mantle by subduction, as suggested by Lecuyer and Ricard (1999), but if the Fe is reduced by C and CH_n compounds from subducted sediments, then the redox potential of the mantle could be unchanged. Studies of the consequences of transport of redox-sensitive elements considered in isolation are thus likely to be wrong. Further, the redistribution of redox-sensitive elements is discussed in terms used for chemical differentiation. Chemical differentiation has a large degree of control on the distribution of redox-sensitive elements, but chemical differentiation need not involve changes in redox potential. It is therefore necessary to develop vocabulary to allow discussion of the redistribution of redox-sensitive elements without chemical implication.

Intensive variables, such as $f(O_2)$, $f(S_2)$, *Eh*, or $f(H_2)$, are used to measure and record the redox characteristics of systems (e.g., Christie et al., 1986). Intensive variables are state variables that are capable of contact equilibrium; that is, they take the same value in adjacent phases (Munster, 1970), and they are appropriate when the quantity of material in the system described is not the primary subject of interest. This is not the case for studies of elemental fluxes, and an extensive redox variable, that is, a state variable that depends on the quantity of material considered, should be chosen instead. An analogy is the use of enthalpy, which is an extensive variable, instead of temperature, which is intensive, in phase equilibria calculations (Ussler and Glazner, 1992; Powell et al., 2005). Extensive variables have been previously used as proxies for $f(O_2)$ (e.g., Canil et al., 1994; Canil, 1997, Lee et al., 2005), but there is no widely used extensive redox variable that reflects the distribution of all redox-sensitive elements in a given system.

This work develops an initial vocabulary for use in discussion of redox-redistribution processes, proposes an appropriate extensive variable for study of movement and redistribution of redox-sensitive elements, and presents an example of its use.

VOCABULARY

Redox Decoupling

The transport of redox-sensitive elements such that reservoirs experience a net increase or decrease in their capacity to oxidize other material is referred to here as redox decoupling. An example of redox decoupling is the transport of Fe^{3+} to the mantle by subduction.

Electrochemical Differentiation

Electrochemical differentiation occurs when one or more redox decoupling process changes existing gradients in redox potential. Electrochemical differentiation is generally accompanied by chemical differentiation, but need not be. An example of electrochemical differentiation is the establishment of a reduced iron core by a combination of redox decoupling processes that include melting and devolatilization.

Scaling Issues

Any study of redox decoupling and/or electrochemical differentiation needs to define time and length scales carefully. This is because processes that may be steady state and redox-neutral on long time or distance scales can involve redox decoupling when examined on a smaller scale.

REDOX BUDGET

The key criteria for an extensive redox variable are that it should provide a measure of a sample's ability to oxidize or reduce that is dependent on the quantity of the sample, and that it should be measurable. Oxidation and reduction involve a redistribution of electrons, so the extensive variable should be based in some way on the availability of electrons. The total number of moles of electrons present in any sample is unsuitable, because the number of electrons is simply equal to the number of protons in uncharged samples. An alternative is the number of electrons present in the sample relative to a reference state. This is more practical, because the reference state can then be chosen to optimize convenience for the system of interest, and the

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TABLE 1. EXAMPLES OF REDOX BUDGET (RB) CALCULATIONS

Example 1: Redox budget for 2 moles of FeO. Reference state is Fe as Fe^{3+}, O as O^{2-}.

i	Hosts	v_i	n_i	$v_i n_i$
Fe^{2+}	FeO	−1	2	$(-1 \times 2) = -2$
O^{2-}	FeO	0	1	$(0 \times 1) = 0$
Total *RB (moles)*				−2

Example 2: Redox budget for 2 moles of FeO, 4 moles of Fe_2O_3 and 3 moles of FeS. Reference state is Fe as Fe^{2+}, O as O^0 and S as S^{2-}.

i	Hosts	v_i	n_i	$v_i n_i$
Fe^{2+}	FeO and FeS	0	$(2 + 3) = 5$	$(0 \times 5) = 0$
Fe^{3+}	Fe_2O_3	1	$2 \times 4 = 8$	$(1 \times 8) = 8$
O^{2-}	FeO, Fe_2O_3	−2	$2 + (4 \times 3) = 14$	$(-2 \times 14) = -28$
S^{2-}	FeS	0	3	$(0 \times 3) = 0$
Total *RB (moles)*				−20

Example 3: Redox budget for 2 moles of FeO, 4 moles of Fe_2O_3 and 3 moles of FeS. Reference state is Fe as Fe^{3+}, O as O^{2-} and S as S^{6+}.

i	Hosts	v_i	n_i	$v_i n_i$
Fe^{2+}	FeO, FeS	−1	$(2 + 3) = 5$	$(-1 \times 5) = -5$
Fe^{3+}	Fe_2O_3	0	$2 \times 4 = 8$	$(0 \times 8) = 0$
O^{2-}	FeO, Fe_2O_3	0	$2 + (4 \times 3) = 14$	$(0 \times 14) = 0$
S^{2-}	FeS	−8	3	$(-8 \times 3) = -24$
Total *RB (moles*				−29

Note: *i* is the redox state considered, v_i is the number of electrons that need to be added to one mole of oxidation state *i* for it to reach the reference state; n_i is the number of moles of oxidation state *i*.

variable can be measured either by addition of measured quantities of an oxidizing or reducing agent until some predefined redox state is reached (redox titration) or by measurement of the distribution of redox-sensitive elements. The redox budget of a rock is defined as the number of moles of electrons that need to be added to the rock to reach the reference state:

$$RB = \sum_i n_i v_i. \quad (1)$$

RB is the redox budget, v_i is the number of electrons required to take one mole of redox state *i* to the reference redox state, and n_i is the number of moles of redox state *i* present in the sample of interest. For example, the redox budget of two moles of FeO with respect to a reference state of Fe as Fe^{3+} and O as O^{2-} is −2 (Table 1, example 1); 2 moles of electrons would need to be removed to oxidize the Fe^{2+} to Fe^{3+}.

The notional addition or removal of electrons to/from a sample will lead to a charged sample. The reference state is thus hypothetical, but this does not detract from its utility. Some choices of reference state can be unhelpful. For instance, in example 2 (Table 1), a large proportion of the redox budget is associated with the change between O^{2-} and O^0. O^0 is not common in minerals under normal geological conditions, so the O^0-related part of the redox budget does not indicate a real redox capacity, and a reference state of O^{2-}, as shown in example 3 (Table 1), might be more useful. A reference state in which all elements are uncharged is not recommended, because the redox budget of any uncharged sample with respect to this reference state must be zero. It can be useful to choose a reference state composed of redox states that do not occur in the sample, because it is possible to add any quantity of an element in the reference redox state to a sample without changing the redox budget of the sample. For instance, if 2 moles of Fe_2O_3 were added to the sample in example 3 (Table 1), then the redox budget would be unchanged. The choice of reference state can also depend on the methods used to measure the redox budget. Possible methods include titration, spectophotometric methods, Mossbauer, electron microprobe, and synchrotron techniques.

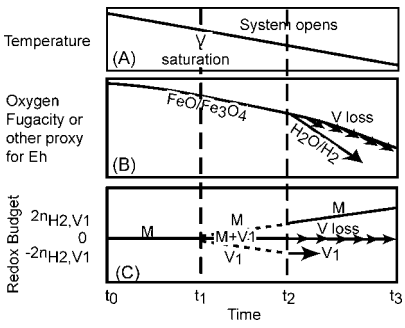

Figure 1. Schematic representation of evolution in (A) temperature, (B) $f(O_2)$, and (C) redox budget of a hypothetical cooling magma. Evolution of hydrogen-bearing fluid begins at t_1, but system remains closed. System opens to release volatiles at t_2 and remains open. M—magma, V—fluid.

COMPARISON OF INTENSIVE AND EXTENSIVE REDOX VARIABLES

A description of the evolution of intensive and extensive redox variables during cooling, crystallization, and vapor evolution of a hypothetical Fe-bearing mid-oceanic-ridge basalt (MORB)–like magmatic system illustrates the principal differences between the two types of variables. The temperature-time evolution of the hypothetical system is shown in Figure 1A. At t_0, the system comprises melt and crystals. Between t_0 and t_1, cooling drives crystallization of phases that include magnetite, but fluid is not evolved. At t_1, H_2-bearing fluid begins to exsolve but does not leave the system. At t_2, the melt chamber opens, and a volume of fluid, V1, which contains n_{H_2} moles of hydrogen, is lost. Between t_2 and t_3, fluid is released from the melt, but the open system now allows each increment of fluid to escape.

Intensive redox variables in the melt (m) and crystal (c) part of the system, and in fluid (aq) in contact with the melt, are buffered by:

$$3FeO(m) + H_2O(m/aq) = Fe_3O_4(m/c) + H_2(m/aq), \quad (2)$$

(e.g., Holloway and O'Day, 2000; Holloway, 2004), and in fluid isolated from the melt by:

$$H_2O(aq) = H_2(aq) + \tfrac{1}{2}O_2(aq). \quad (3)$$

Intensive redox variables in melt and fluid evolve along the FeO/Fe_3O_4 buffer (equation 2) between t_0 and t_2 (Fig. 1B); evolution of fluid at t_1 does not affect redox because buffer equation 2 controls equation 3. The evolution of intensive redox variables in the melt is

largely unaffected by vapor loss at t_2, and by the continuing vapor loss between t_2 and t_3, so long as the FeO/Fe_3O_4 buffer is not exhausted. Each fluid increment evolves along the buffer in equation 3.

Redox budgets for this example can be calculated relative to Fe as Fe^{2+}, O as O^{2-}, and H as H^{1+}. The redox budgets (*RB*) of melt and fluid, for a melt with an initial redox budget of zero ($nFe^{3+} + 2nO^0 = nH^0$) , and for Fe-free fluids, are, therefore,

$$RB(\mathrm{m} + \mathrm{c}) = nFe^{3+} - nH^0 + 2nO^0 = 2nFe_3O_4(\mathrm{m} + \mathrm{c}) - 2nH_2(\mathrm{m}) + 4nO_2(\mathrm{m}), \quad (4)$$

and

$$RB(\mathrm{fluid}) = -nH^0 + 2nO^0 = -2nH_2\ (\mathrm{aq}) + 4nO_2\ (\mathrm{aq}). \quad (5)$$

Crystals are assumed to remain within the melt, and specific reference to them is omitted from here onward. While no fluid is exsolved (t_0–t_1), the redox budget of the system remains constant (Fig. 1C). Exsolution of fluid at t_1 has no net effect on the redox budget of the combined melt/fluid system (M + V1 on Fig. 1C), although the redox budget of the melt increases ($nFe^{+3} + n[O_2] > nH^0$), and that of the fluid decreases ($nH^0 > 0$). These changes are shown by the dotted lines on Figure 1C. The loss of fluid at t_2 increases the redox budget of the melt to $2nH_2$,V1, while that of the fluid is $-2nH_2$,V1 (Fig. 1C). Further fluid evolution between t_2 and t_3 causes a continuous increase in the redox budget of the melt, while the redox budget of the fluid increments is small and negative, because of the H^0 borne by the fluid.

This example demonstrates the principal advantages of the redox budget: it is insensitive to changes in pressure and temperature, and it reflects open-system processes. The redox budget is unaffected by chemical differentiation that does not redistribute redox-sensitive elements, e.g., changes in Fe/(Fe + Mg) due to Mg loss or gain. The redox budget can be used quantitatively; changes on Figure 1C obey the lever rule. Intensive redox variables, on the other hand, are sensitive to pressure, temperature, and redox-neutral chemical differentiation; for example, changes in Fe/(Fe + Mg), regardless of cause, of the melt would change the activity of FeO, and hence the position of the FeO/Fe_3O_4 buffer.

CASE STUDY: IS REDOX DECOUPLING ASSOCIATED WITH MORB CRYSTALLIZATION?

Christie et al. (1986) performed analyses of Fe^{3+}/Fe_{tot} ratios on MORB glasses and lavas from a wide range of different spreading ridges. Their results showed that the glasses record $f(O_2)$ values two orders of magnitude less than the crystalline lavas, which record $f(O_2)$ close to the synthetic $f(O_2)$ buffer of fayalite-magnetite-quartz (FMQ). This increase was attributed to H_2 loss (Christie et al., 1986), possibly via reaction equation 2 (Holloway and O'Day, 2000). Oxidation of the lava, with a consequent reduction of the crustal reservoir(s) that receive the H_2, would change the redox budget of at least two different chemical subsystems within the Earth and provide an example of redox decoupling. However, subsequent work by Bezos and Humler (2005) suggests that Christie et al. (1986) may have underestimated $f(O_2)$ in the glasses.

MORB Crystallization Data

Redox budget calculations can be used to test the hypothesis that crystallized MORBs have been oxidized relative to the original magma. Glass analyses from 104 MORBs (Bezos and Humler, 2005) and 380 spreading-center basalt lava analyses from the PETDB online database (PETDB, 2005) were used to create histograms of the redox budget for the Mid-Atlantic, Indian, and Pacific Ridges (Fig. 2). Redox budgets were taken per 100 g of material, and were referenced to H as H^{1+}, Fe as Fe^{2+}, and O as O^{2-}, and it was assumed that Fe was the only significant contributor to the redox budget. The redox budget is therefore

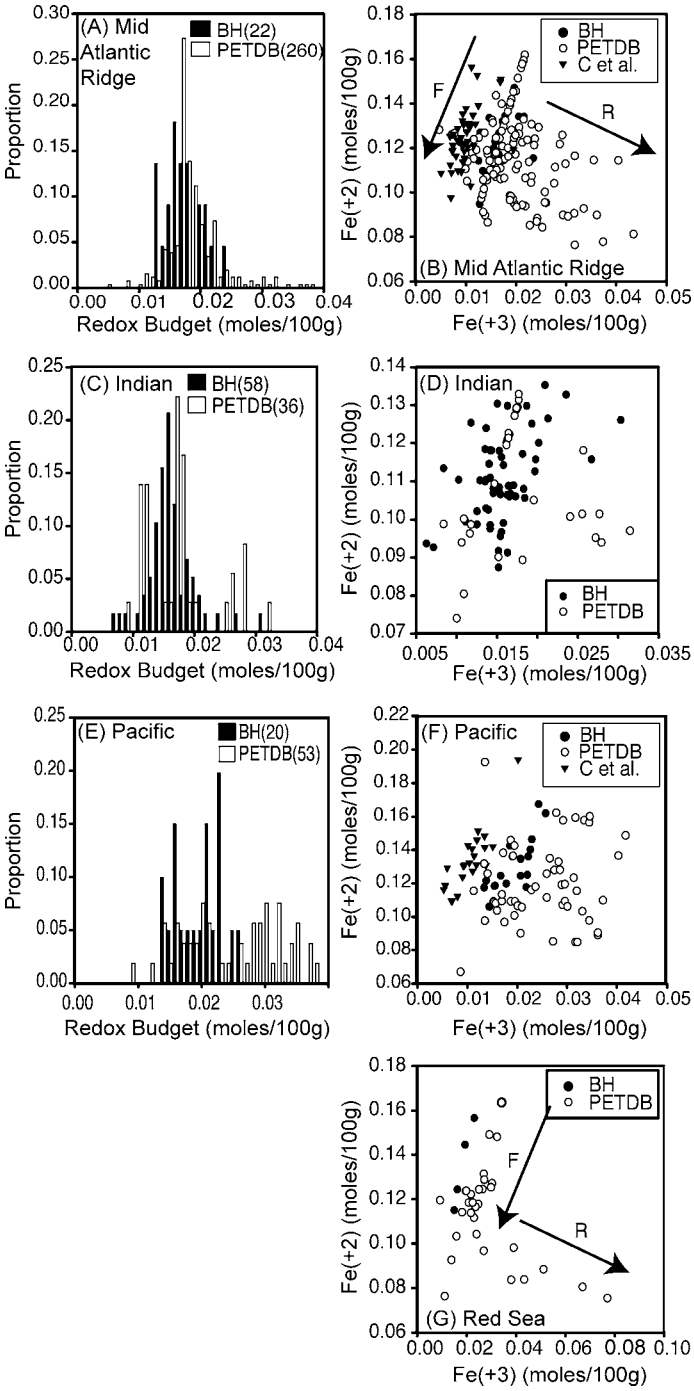

Figure 2. Comparison of the redox budget, referenced to Fe^{2+}, for mid-ocean-ridge basalt (MORB) glasses (black) and lavas (white). A–B: Mid-Atlantic Ridge; C–D: Indian Ridge; E–F: Pacific Ridge; G: Red Sea. Results are normalized to allow comparison of dissimilar sample sizes. F—fractionation trend; R—Fe oxidation trend; BH—data from Bezos and Humler (2005); PETDB—data from the online PETDB database (PETDB, 2005); C et al.—data from Christie et al. (1986).

$$RB(\mathrm{lava/glass}) = nFe^{3+}\ \text{per 100 g} = 2\ \text{wt\%}\ Fe_2O_3/159.69. \quad (6)$$

Inspection of the histograms (Figs. 2A, 2C, and 2E) reveals that the median redox budget for the glasses is consistently at a slightly lower value than that for the lavas, and there is an apparent skewing of the lava data to higher redox budgets, but the distributions appear

similar, and visual inspection is not conclusive. The normality of each of the data sets was tested using a Kolmogirnov-Smirnov normality test, which was passed in each case. The hypothesis that the sample means were different was then tested using a Student-t test for samples of unequal variance, and they were found to be significantly different at the 95% confidence level for the Mid-Atlantic and Pacific Ridges, but not for the Indian Ridge (75% confidence). Data for the Red Sea spreading center were also collected (5 glasses, 31 lavas), and the glasses were found to have a lower average redox budget than the lavas (not shown), although this data set was too small for statistical tests to produce a meaningful result. These results suggest that Mid-Atlantic and Pacific lavas are more oxidized than the glasses.

This conclusion is supported by plots of Fe^{2+} against Fe^{3+} for the four ridge systems (Figs. 2B, 2D, 2F, and 2G). The data of Christie et al. (1986) are also shown for the Atlantic and Pacific Ridges (Figs. 2B and 2F). Their data lie at systematically higher Fe^{2+} and lower Fe^{3+} contents than those of Bezos and Humler (2005). Two trends can be identified on these plots. The first, marked F in Figure 2B, has a positive slope and reflects the effects of redox-neutral fractionation—the total Fe content changes at a constant Fe^{2+}/Fe^{3+} ratio. The second, marked R in Figure 2B, is consistent with conversion of Fe^{2+} to Fe^{3+}, a process that imparts a negative slope to the trend: $Fe^{2+} + Fe^{3+} =$ constant, therefore $Fe^{2+} =$ constant $- Fe^{3+}$. This could be attributed to the loss of H_2, or to oxidation by seawater. The Red Sea lavas (Fig. 2G) lie at higher Fe^{3+}, and hence at higher redox budget, than the glasses.

It is interesting that the slowest spreading ridge, the Indian Ridge (Figs. 2C and 2D), shows the least difference between the redox budgets of lava and glass, while the fastest spreading ridge, the Pacific Ridge (Figs. 2E and 2F), exhibits the most pronounced difference between redox budgets of the two phases. However, speculation on this topic is beyond the scope of this work.

The evidence and redox budget calculations presented here support the assertions of Christie et al. (1986), and suggest that MORB crystallization induces redox decoupling between the crystallizing melt and the exsolving vapor. This decoupling would result in electrochemical differentiation, with net oxidation of the mantle and reduction of the atmosphere/oceans if other processes do not act to balance the flux of reductant into the atmosphere/ocean system. Further work is required to constrain the extent and implications of this redox decoupling, and to assess the likelihood of electrochemical differentiation.

APPLICATIONS

The redox-related concepts introduced here can be applied to any field where redox processes occur. Examples include global cycling (e.g., Lecuyer and Ricard, 1999), the formation of ore deposits (e.g., Phillips and Evans, 2004), volcanism (de Hoog et al., 2004), the evolution of the mantle, crust, and core (Arculus, 1985), treatment of certain types of pollution (e.g., Christensen et al., 2000), and biotic systems (e.g., Bottrell et al., 2000). The concepts of redox decoupling, electrochemical differentiation, and redox budgets are probably not new to many researchers in these fields. However, their explicit definition provides a potentially new set of tools that may be used to gain new insights.

CONCLUSIONS

The ubiquity of redox processes in earth systems at a variety of scales necessitates a vocabulary that allows processes that redistribute redox-sensitive elements to be distinguished from processes that do not. It is proposed here that redox decoupling should be used to describe the transport of redox-sensitive elements such that a reservoir experiences a net increase or decrease in its capacity to oxidize on some time scale, and that electrochemical differentiation should be used to describe the net result of one or more redox decoupling processes that change existing gradients in redox potential.

Intensive variables, such as *Eh* and $f(O_2)$, cannot be used to measure fluxes of material. The redox budget, which is the number of moles of electrons that must be added to the rock to reach a defined reference state, is more suitable for such calculations. Redox budget calculations show that MORB lavas from the Pacific and Mid-Atlantic Ridges have a higher redox budget than MORB glasses; this is consistent with the results of Christie et al. (1986). This increase in redox budget records redox decoupling between the ocean floor and the ocean/atmosphere. The concepts presented here may be useful to workers in a variety of fields, including, but not limited to global cycling, the formation of ore deposits, volcanism, the compositional and redox evolution of the mantle, crust, and core, redox-related environmental problems, and biotic systems.

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