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INCLUSION OF THE WEATHERING OF VOLCANIC ROCKS IN THE GEOCARBSULF MODEL

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ABSTRACT. The carbon cycle model GEOCARBSULF is extended by dividing the weathering of silicates into volcanic and non-volcanic rocks. The proportion of volcanic weathering is calculated as a function of time from the oceanic record of $^{87}Sr/^{86}Sr$. The volcanic proportion is then used to modify the equations for calculating atmospheric CO_2 by the addition of a new non-dimensional volcanic weathering factor. The effect of uplift and physical erosion on weathering is also modified by using only the distribution over time of the abundance of sandstones and shales, and not Sr isotopic data that had been used previously. Results indicate moderate change from GEOCARBSULF in the distribution of atmospheric CO_2 over Phanerozoic time. This includes an increased minimum in CO_2 during the Late Ordovician, in agreement with the presence of a continental glaciation at that time, and a shift of maximum Mesozoic values from the Jurassic to the Early Cretaceous.

INTRODUCTION

Recent studies (Taylor and Lasaga, 1999; Gaillardet and others, 1999; Dessert and others, 2003; Louvat and others, 2005) have shown that the weathering of volcanic rocks, including those on oceanic islands, may be an important component of total global silicate weathering. This is especially true because it is the chemical weathering of Ca and Mg silicate minerals, abundant in volcanic rocks, that dominate the uptake of atmospheric CO_2 during weathering (Berner, 2004). Also, volcanic rocks weather faster than non-volcanic silicate rocks (Meybeck, 1987; Taylor, ms, 2000). Recent estimates (Dessert and others, 2003) are that volcanic weathering may represent as much as 30 to 35 percent of total silicate weathering. It is the major purpose of this short note to attempt to quantify the weathering of volcanic rocks over Phanerozoic time using the strontium isotope record.

The average $^{87}Sr/^{86}Sr$ value of volcanic rocks is approximately 0.703 whereas that for other silicate rocks generally have much higher average values. If one assumes that the $^{87}Sr/^{86}Sr$ value for seawater, as recorded in limestones and calcareous fossils, represents a mixture of inputs from volcanic silicate rock weathering, basalt-seawater reaction, and other non-volcanic rock weathering (Brass, 1976; Kump, 1989; Berner and Rye, 1992; Taylor and Lasaga, 1999), one can use the Sr isotopic record to quantify the proportion of volcanic rock weathering as it has changed over time.

Use of Sr isotopes as a volcanic weathering indicator is more appropriate than their use as an indicator of mountain uplift and the resulting rate of erosion-assisted weathering. This is because the Sr isotopic composition of rocks undergoing chemical weathering undoubtedly undergoes change with time as volcanism varies and as old radiogenic rocks are uplifted into the zone of weathering. An example is the formation of the highly radiogenic rocks of the Himalayas during the Cenozoic (for example, Edmond, 1992). Thus, the interpretation of changes in $^{87}Sr/^{86}Sr$ of the oceans is not due simply to changes in the total weathering flux to the sea of Sr (and proportionately Ca and Mg) as a result of global mountain building (Raymo, 1991; Richter and others, 1992). A more direct indicator of past uplift and enhanced erosion, leading to accelerated weathering, is the abundance of the erosion products, sandstones and shales, over time (Berner and Kothavala, 2001).

METHOD

An expression for the volcanic fraction of Ca-Mg silicate rocks undergoing weathering over time, based on strontium isotope data, (see Appendix I for a derivation) is:

$$X_{volc} = [f_{sr}(t)F_{bo}(0)(R_v - R_{oc}) + F_{wcy}R_{cy} + F_{wca}R_{ca} - R_{oc}F_{bc} + R_{nv}F_{wsi}] / [F_{wsi}(R_{nv} - R_v)] \quad (1)$$

where: X_{volc} = fraction of total Ca and Mg silicate weathering derived from volcanic rocks
R_v = average value for $^{87}Sr/^{86}Sr$ of sub-aerial and submarine volcanic rocks
R_{nv} = average value for $^{87}Sr/^{86}Sr$ of non-volcanic silicate rocks
R_{oc} = average value for $^{87}Sr/^{86}Sr$ of seawater as recorded in carbonates
R_{cy} = average value of $^{87}Sr/^{86}Sr$ for "young" carbonates undergoing weathering (for a definition of young vs old see Berner 2004, 2006)
R_{ca} = average value of $^{87}Sr/^{86}Sr$ for "old" carbonates undergoing weathering
$f_{sr}(t)$ = seafloor spreading rate(t)/seafloor spreading rate (0) (from Berner, 2004)
$F_{bo}(0)$ = rate of exchange of Ca and Mg between basalt and seawater at present
F_{bc} = burial flux of Ca and Mg carbonates
F_{wcy} = weathering flux for young Ca and Mg carbonates
F_{wca} = weatheriing flux for old Ca and Mg carbonates
F_{wsi} = weathering flux for all Ca and Mg silicates

Values of the various fluxes F are determined from the GEOCARBSULF model (Berner, 2006). Values of R_{oc} over the Phanerozoic are taken from the compilation of Burke and others (1982). The average value for $R_v = 0.703$; the value of R_{nv} is chosen so that the value of $X_{volc} = 0.30$ at $x = 0$ (pre-human present) (Dessert and others, 2003). It is $R_{nv} = 0.717$ and is allowed to vary with time as discussed below. The value 0.717 reflects the fact that according to the GEOCARBSULF model, carbonates of isotopic composition more radiogenic than that of the present day oceans are being weathered at present. A simple mass balance between silicates, ignoring carbonate weathering, results in the erroneous present value of $R_{nv} = 0.713$.

In equation (1) the value of $F_{bo}(0)$ is derived by analogy with strontium mass balance. Davis and others (2003) have shown that the present rate of exchange of Sr between submarine basalts, at both high and low temperatures, is about $3x10^{15}$ mol/my. The imbalance in the oceanic Sr cycle is stated by Davis and others to be about 11×10^{15} mol/my. Assuming that the difference is made up by sub-aerial basalt weathering (Louvat and others, 2005), this means that the present volcanic Sr weathering flux is about 8×10^{15} mol/my or about $8/3 = 2.67$ times that of basalt-seawater Sr exchange. It is assumed here that this ratio also applies to the ratio of the flux of Ca and Mg from volcanic weathering relative to exchange of the same elements between basalt and seawater. The volcanic weathering flux at present is estimated to be about 30 percent of total silicate weathering (Dessert and others, 2003), From the present value for total Ca and Mg silicate weathering $F_{wsi}(0) = F_{bc} - F_{wc} = 6.7x10^{18}$ mol/my (Berner, 2004) , the present volcanic flux $F_{volc}(0)$ is, therefore, estimated to be about $0.3 \times 6.7 = 2.0 \times 10^{18}$ mol/my. Using this and the factor of 2.67

given above, the present basalt-seawater exchange Ca-Mg flux $F_b(0)$ is calculated to be about 0.75 x 10^{18} mol/my.

The rate expression for Ca-Mg silicate rock weathering (Berner, 2004), modified here by adding a new term $f_{volc}(t)$ expressing the effects of volcanic weathering, is:

$$F_{wsi} = f_{volc}(t)f_{Bt}(CO_2)f_{Bb}(CO_2)f_R(t)f_E(t)f_{AD}(t)^{0.65}F_{wsi}(0) \quad (2)$$

where: F_{wsi} = flux in 10^{18} mol/my for sub-aerial Ca and Mg silicate weathering with (0) referring to the pre-human present; $F_{wsi} = F_{bc} - F_{wcy} - F_{wca}$

$f_{volc}(t)$ = volcanic weathering effect (t)/volcanic weathering effect (0)

$f_{Bt}(CO_2)$ = effect of temperature on weathering rate(t)/effect of temperature on weathering rate (0) combining the effects of the CO_2 greenhouse, solar radiation, and paleogeography on temperature

$f_{Bb}(CO_2)$ = effect of CO_2 on plant assisted weathering(t)/effect of CO_2 on plant assisted weathering(0)

$f_E(t)$ = effect of plants on weathering rate(t)/effect of plants on weathering rate(0)

$f_D(t)$ = runoff (t)/runoff (0) due to changes in paleogeography

$f_A(t)$ = land area (t)/land area(0)

$f_{AD}(t)$ = $f_A(t)$ $f_D(t)$

$f_R(t)$ = physical erosion (t)/physical erosion (0)

The expression for the new term $f_{volc}(t)$ is given by:

$$f_{volc}(t) = [W_vX_{volc} + W_{nv}(1 - X_{volc})]/[W_vX_{volc} + W_{nv}(1 - X_{volc})](0) \quad (3)$$

where: (0) = pre-human present

W_v = weatherability of volcanics (weathering rate per unit mass)

W_{nv} = weatherability of non-volcanics

The work of Meybeck (1987) and Taylor (ms, 2000), the latter based on weathering of adjacent basalt and granite under the same conditions of climate, slope *et cetera*, suggests that the weatherability of volcanics is about twice that for non-volcanics. Assuming this, then $W_v = 2W_{nv}$. Substituting this and X_{volc} for the present = 0.3 (Dessert and others, 2003) into (3) yields:

$$f_{volc} = (X_{volc} + 1)/1.3 \quad (4)$$

The expression $f_{volc}(t) = (X_{volc}+1)/\ 1.3$ is introduced to indicate that an increased proportion of volcanic rocks leads to faster global weathering. If $f_{volc}(t) = 1$ equation (2) reduces to the same expression used in GEOCARBSULF (Berner, 2006) and GEOCARB III (Berner and Kothavala, 2001).

The term for physical erosion assisted weathering, $f_R(t)$, is here based solely on a cubic fit to the sandstone and shale abundance data of Ronov (1993) and not on Sr isotope ratios which nevertheless give similar results (Berner and Kothavala, 2001; Berner, 2004). A re-analysis of the Ronov data gives the expression:

$$f_R(t) = 25.269(t/1000)^3 + 26.561(t/1000)^2 + 6.894(t/1000) + 1.063 \quad (5)$$

where t = time (-570 Ma to 0)

Variation of R_{nv}, the $^{87}Sr/^{86}Sr$ of non-volcanic silicates, would be expected to occur with time. This allows for the weathering of radiogenic strontium from very old rocks exposed as a result of the uplift and erosion of mountain belts (for example, Himalayas during the Cenozoic, Edmond, 1992). To account for this phenomenon the abundance of shales and sandstones over time (Ronov, 1993) is used as an indicator not only of erosion and enhanced silicate weathering, as discussed above, but also of

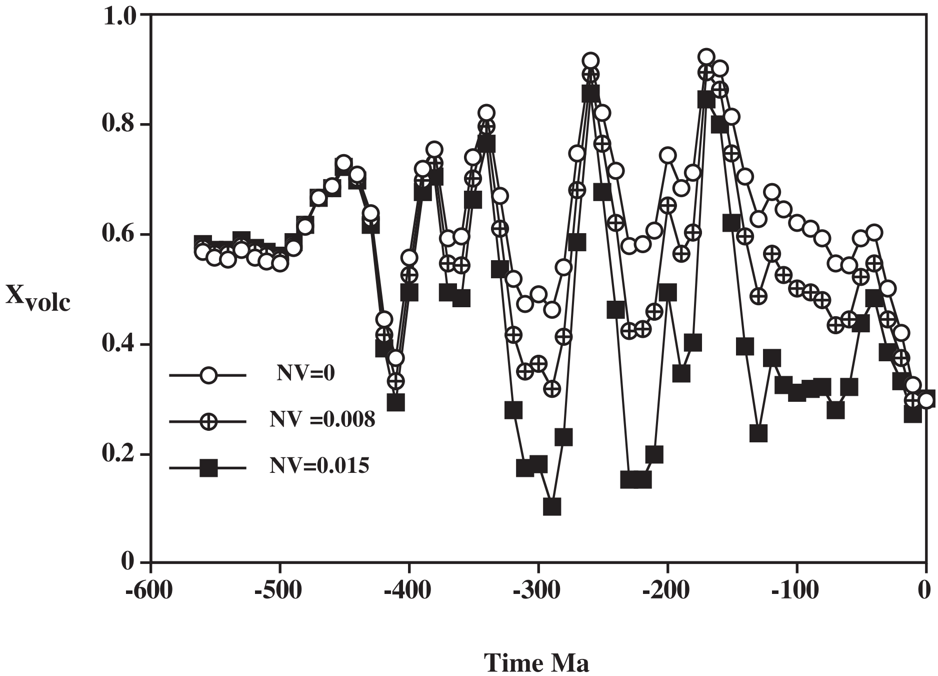

Fig. 1. Plot of X_{volc}, the proportion of total Ca and Mg silicate weathering derived from volcanic rocks vs time for various values of $^{87}Sr/^{86}Sr$ for non-volcanic silicates undergoing weathering R_{nv} (see fig. 2). The parameter NV is given in the expression $R_{nv} = 0.717 - NV(1\text{-}f_R(t))$ where $f_R(t)$ represents the effect of physical erosion on the weathering of silicates (see text).

the exposure of old radiogenic rocks to weathering. This is manifested again by the weathering uplift factor $f_R(t)$. The expression used for varying $^{87}Sr/^{86}Sr$ of the non-volcanic silicates is:

$$R_{nv} = 0.717 - NV[1 - f_R(t)]$$

where: NV = an arbitrary parameter which is allowed to vary in this paper from 0 to 0.015.

RESULTS AND DISCUSSION

A plot of the fraction of total silicate weathering derived from terrestrial volcanics X_{volc} as a function of varying values of R_{nv}, is shown in figure 1 (time scale of Gradstein, Ogg, and Smith, 2004). The different values shown for R_{nv} in figure 1 are presented in figure 2 and compared with values of R_{oc}, those recorded for the oceans. The large variations in Rnv, compared to Roc, are permissible because the oceanic value of $^{87}Sr/^{86}Sr$ at any time is buffered by carbonates, whose weathering fluxes and precipitation from seawater dominate over those of silicates (Meybeck, 1987; Berner and Berner, 1996), and carbonates show little variation of $^{87}Sr/^{86}Sr$ with time.

The variations of X_{volc} in figure 1 agree with some independent observations. The high Mesozoic values for NV=0 and the peak at around 250 Ma agree with the abundance of volcanic rocks over time determined by Ronov (1993) as discussed in Berner (2004). Another check is supplied by a comparsion with the data of Bluth and Kump (1991) for land areas of volcanics exposed to weathering over time. Bluth and Kump's data can be recast in terms of the ratio of volcanic land exposure to total land

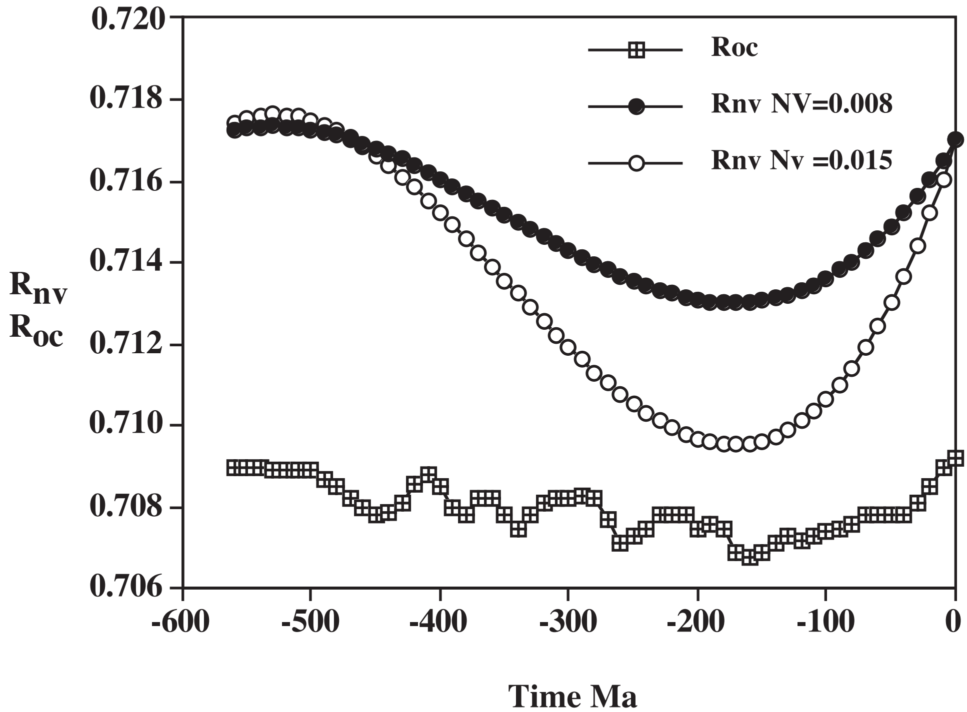

Fig. 2. Plots of $^{87}Sr/^{86}Sr$ of the ocean R_{oc} and of non-volcanic silicates undergoing weathering R_{nv} as a function of time. See caption to figure 1 for definition of NV.

for all silicates (total land minus carbonates) denoted as $X_{volcland}$. Figure 3 shows a comparison of X_{volc} and $X_{volcland}$ for the past 130 Ma using NV=0.015. There is a similarity in the two trends and, in fact, the ratio of $X_{volc}/X_{volcland}$ is about two, in agreement with the assumption earlier that volcanics weather about twice as fast as non–volcanics. Before 130 Ma there is much disagreement, however, between the trends of X_{volc} and $X_{volcland}$ which may be due to a combination of errors in values of R_{nv} and estimates of land area exposed to weathering further back in time. This is especially true of volcanic land area exposed to weathering. There could be large errors due to the lack of preservation of island arcs (where much volcanic weathering takes place at present —Louvat and others, 2005) because of subsequent loss due to subduction.

Plots of RCO_2 (the ratio of atmospheric CO_2 for a past time to that at the pre-human present) are shown in figure 4. The new plot, based on the inclusion of volcanic weathering and the use of sandstone plus shale abundance to determine $f_R(t)$, results in RCO_2 values only broadly similar to those for the GEOCARBSULF paper where weathering of volcanics is not considered and $f_R(t)$ is based on Sr isotope data. This shows that factors other than volcanic weathering are still important in the overall trend of the curves. However, there are notable differences for the Ordovician and the Mesozoic plus Cenozoic (past 200 million years). The larger RCO_2 minimum near 450 Ma for the (GEOCARBSULF) volc curves than for the (GEOCARBSULF) no volc curve accords with the observation of the Late Ordovician glaciation at this time. Another major difference is that Mesozoic RCO_2 values show the Mesozoic maximum shifting from the Jurassic to the Cretaceous for the volc curves.

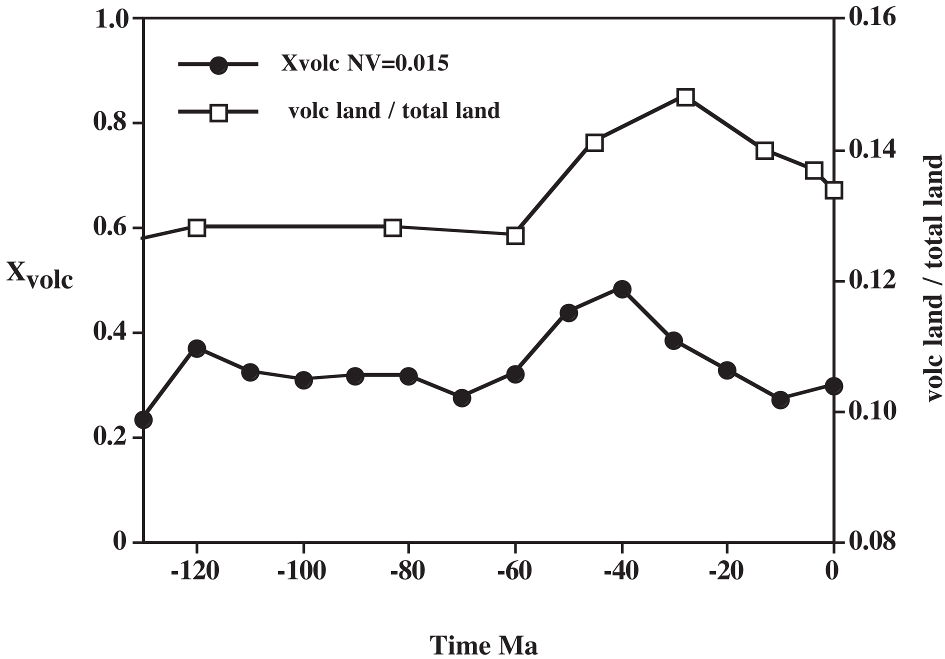

Fig. 3. Comparison of values of X_{volc} and $X_{volcland}$ for the past 130 million years. $X_{volcland}$ is the ratio of land underlain by volcanics to land underlain by all silicates derived from the data of Bluth and Kump (1991).

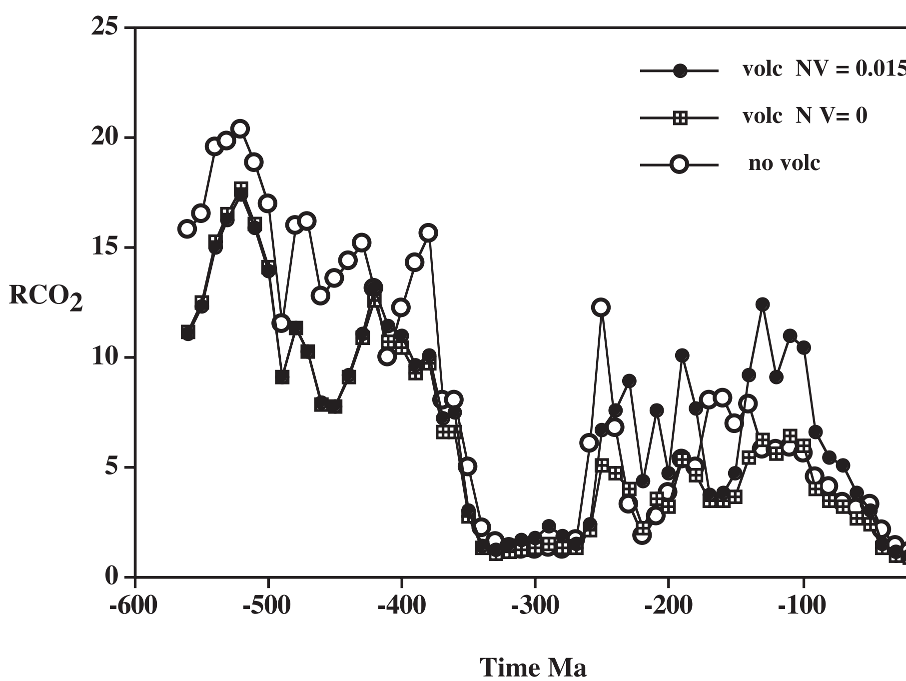

Fig. 4. Plot of RCO_2 (ratio of mass of atmospheric CO_2 at a past time to that at the pre-human present), calculated via the GEOCARBSULF model, with and without inclusion of the term for volcanic rock weathering. See caption to figure 1 for definition of NV.

These results indicate that it is important to attempt to continue to improve the GEOCARB model. The present results show the effects of considering volcanic weathering, which has gained relevance because of its recently discovered quantitative importance (Dessert and others, 2003). Deriving the uplift-erosion weathering factor $f_R(t)$ directly from geologic evidence (sandstone and shale abundance), rather than indirectly from arguments concerning the use of strontium isotopes, is another improvement. The author feels that strontium isotopes are better used to deduce the relative importance of volcanic weathering (Berner and Rye, 1992), as is done here, than to estimate the effects of mountain uplift on chemical weathering.

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Appendix

Derivation of equation (1)

The mass balance for ^{87}Sr input and output from the oceans (ignoring minor diagenesis) is given by the expression (Berner and Rye, 1992):

$$F_{wv}r_vR_v + F_{wnv}r_{nv}R_{nv} + F_{bo}r_bR_b + F_{wcy}r_{cy}R_{cy} + F_{wca}r_{ca}R_{ca} = F_{bc}r_{oc}R_{oc} + F_{ob}r_{oc}R_{oc} \quad (1A)$$

where: F = fluxes
R = $^{87}Sr/^{86}Sr$
r = Sr/(Ca+Mg)

and subscripts are:

bo = submarine basalt to ocean ; ob = ocean to submarine basalt
wv = weathering of terrestrial volcanics
wnv = weathering of other terrestrial silicates (non-volcanics)
wcy = weathering of young (Berner, 2006) carbonates
wca = weathering of old (Berner, 2006) carbonates
bc = burial of carbonates in ocean; b = submarine basalt
cy = young carbonates; ca = old carbonates
v = terrestrial volcanic rocks; nv = terrestrial non-volcanics
oc = ocean

It can be shown that all values of r are approximately equal, that $F_{ob} \approx F_{bo}$ and $R_b \approx R_v$ (Berner and Rye, 1992; Davis and others, 2003). Thus, (1-A) simplifies to:

$$F_{wv}R_v + F_{wnv}R_{nv} + F_{bo}(R_v - R_{oc}) + F_{wcy}R_{cy} + F_{wca}R_{ca} = F_{bc}R_{oc} \quad (2A)$$

Let:

$$X_{volc} = F_{wv}/F_{wsi}$$

$$1 - X_{volc} = F_{wnv}/F_{wsi} \quad (3A)$$

The term F_{wsi} represents the weathering of all Ca and Mg silicates, including both volcanics and non-volcanics. It is given by (Berner, 2004):

$$F_{wsi} = F_{bc} - (F_{wcy} + F_{wca}) \quad (4A)$$

Also, assuming that basalt-seawater reaction varies with the rate of sea floor spreading (Berner, 2004):

$$F_{bo} = f_{sr}(t)F_{bo}(0) \quad (5A)$$

where: (0) refers to the present and $f_{sr}(t)$ = spreading rate/spreading rate at present
Dividing (2A) by F_{wsi} and substituting (3A) in (2A) we obtain:

$$X_{volc}R_v + (1 - X_{volc})R_{nv} + A(R_v - R_{oc}) + BR_{cy} + DR_{ca} = ER_{oc} \quad (6A)$$

where: $A = f_{SR}(t)\ F_{bo}(0)/F_{wsi}$
$B = F_{wcy}/F_{wsi}$
$D = F_{wca}/F_{wsi}$
$E = F_{bc}/F_{wsi}$

Solving for X_{volc}:

$$X_{volc} = [A(R_v - R_{oc}) + BR_{cy} + DR_{ca} - ER_{oc} + R_{nv}]/(R_{nv} - R_v) \tag{5A}$$

or substituting for A, B, D, and E:

$$X_{volc} = [f_{sr}(t)F_{bo}(0)(R_v - R_{oc}) + F_{wcy}R_{cy} + F_{wca}R_{ca} - R_{oc}F_{bc} + R_{nv}F_{wsi}]/F_{wsi}(R_{nv} - R_v) \tag{6A}$$

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