

# Volcanic and anthropogenic contributions to global weathering budgets

J.C. Varekamp<sup>\*</sup>, E. Thomas<sup>1</sup>

*Department of Earth and Environmental Sciences, 265 Church Street, Wesleyan University, Middletown, CT 06459-0139, USA*

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## Abstract

We evaluate whether the global weathering budget is near steady state for the pre-anthropogenic modern environment by assessing the magnitude of acidity-generating volcanic exhalations. The weathering rate induced by volcanic acid fluxes, of which the CO<sub>2</sub> flux is the most important, can be expressed as an average release rate of dissolved silica, based on a model feldspar-weathering scheme, and the ratio of carbonate-to-silicate rock weathering. The theoretically predicted flux of silica from chemical weathering is slightly smaller than the estimated global riverine silica flux. After adjustment for carbonate weathering, the riverine dissolved bicarbonate flux is larger than the volcanic carbon degassing rate by a factor of about three. There are substantial uncertainties associated with the calculated and observed flux values, but the modern system may either not be in steady state, or additional, “**unknown**” carbon sources may exist. The closure errors in the predicted budgets and observed riverine fluxes suggest that continental weathering rates might have had an impact on atmospheric CO<sub>2</sub> levels at a time scale of 10<sup>3</sup>-10<sup>4</sup> years, and that enhanced weathering rates during glacial periods might have been a factor in the reduced glacial atmospheric CO<sub>2</sub> levels. Recent anthropogenic emissions of carbon and sulfur have a much larger acid-generating capacity than the natural fluxes. Estimated potential weathering budgets to neutralize these fluxes are far in excess of observed values. A theoretical scenario for a return to steady state at the current anthropogenic acidity emissions (disregarding the temporary buffering action of the ocean reservoir) requires either significantly lower pH values in continental surface waters as a result of storage of strong acids, and/or higher temperatures as a result of enhanced atmospheric CO<sub>2</sub> levels in order to create weathering rates that can neutralize the total flux of anthropogenic and natural background acidity. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Exchange processes between the endosphere and exosphere are part of the ongoing chemical differentiation of the Earth, but re-homogenization takes place through recycling of evolved materials from the exosphere back into the mantle. As part of the endospheric flux volcanic gases are expelled into the exosphere. Over geological time these gases have

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<sup>\*</sup> Corresponding author. Tel.: +1 203 347 9411; Fax: +1 203 343 3903.

<sup>1</sup> Also at: Center for the Study of Global Change, Department of Geology and Geophysics, 210 Whitney Avenue, Yale University, New Haven CT 06520-8109, USA.

accumulated as ‘excess volatiles’ in the exosphere, suggesting that their rate of recycling is smaller than their emission rate. A continuous mass exchange between the two major spheres of the Earth thus takes place, and it is a goal of ‘Earth System Science’ to quantify these fluxes and their variations over time.

One of the outstanding questions in Earth System Science is whether our natural environment (e.g., climate, water pH) is dominantly regulated by endospheric processes such as volcanism and mountain building, by exospheric processes as related to biotic productivity through its impact on the carbon cycle and through weathering processes, or by factors external to the Earth, such as variations in solar energy input (e.g., Berner, 1995). Apart from solar variations, the Earth’s climate is strongly influenced by the intensity of the ‘greenhouse’, which is a function of the atmospheric concentrations of several gases, including  $\text{CO}_2$ . It is generally considered likely that removal of greenhouse gases on geological time scales ( $> 10^5$  years) is modulated by chemical weathering rates, and the endogenic  $\text{CO}_2$  flux supposedly roughly balances the weathering and sedi-

mentation sink (e.g., Berner et al., 1983; Berner, 1994, 1995).

According to this concept, the terrestrial climate is partially dictated by the volcanic degassing rate (the endogenic flux), which may be a function of the rate of plate movements (see also Varekamp et al., 1992 for a discussion). In addition, exospheric feedback parameters such as runoff, ambient temperature and type of plant-cover modulate the weathering rate (e.g., Volk, 1989; Holmen, 1992; Velbel, 1993; Edmond et al., 1995). It is commonly assumed that the modern volcanic volatile flux is roughly balanced by the weathering flux, although the magnitude of the values that are used for these flux estimates by different authors varies substantially (e.g., Holland, 1984; Brantley and Koepnick, 1995). Extensive work by Berner (1991, 1993, 1994, 1995) reflects a quantitative approach of these concepts on a geological time scale.

We summarize and evaluate the most recent volcanic volatile flux estimates. These volatiles generate an acidity flux (as observed in the volcanogenic acid deposition in ice cores; e.g., Zielinski et al., 1994; Clausen et al., 1995), that is largely neutralized by

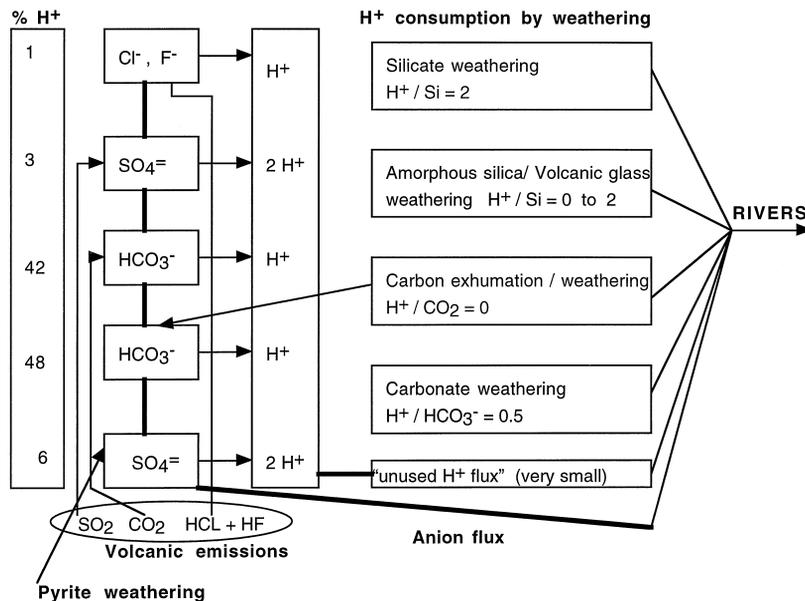


Fig. 1. Acid supply and consumption flow sheet for global weathering processes. Listed at the left side are the volcanic sources, the carbon exhumation and pyrite weathering fluxes. The different weathering reactions with the ratio of  $\text{H}^+$  consumed over the product generated are shown at the right. Also shown are the % of supplied  $\text{H}^+$  from the various sources.

water–rock interaction. We calculate the theoretically induced chemical weathering fluxes, which we compare with the estimated global riverine fluxes, to evaluate whether an approximate steady state occurs. A flow sheet of our approach is given in Fig. 1. We investigate the various contributions of volcanic acids (endogenic flux) to global weathering budgets (exospheric processes) in two ways: (1) an evaluation of the amount of  $\text{HCO}_3^-$  in river water that was extracted from the atmosphere during weathering processes; and (2) an assessment of the flux of weathering products with respect to the calculated flux based on the volcanic acid yield. The first approach provides information on  $\text{CO}_2$  budgets only, whereas the second approach integrates information on the overall weathering process caused by all acid-producing volcanic gases. Subsequently, we compare the weathering rates from glacial to interglacial times and the associated acid demand. Finally, we compare the calculated weathering fluxes from anthropogenic volatile releases that generate acidity with those from volcanogenic releases, and estimate the exospheric conditions necessary for a return to steady state.

## 2. Volcanic processes: volatile emissions into the exosphere

Some volcanic gases ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ) become oxidized upon release and turn into strong acids, whereas others are released as strong acids ( $\text{HCl}$ ,  $\text{HF}$ );  $\text{CO}_2$  will become a weak acid upon dissolution in water. Volcanic emissions that create acidity will cause chemical weathering, and such emissions can be categorized into four groups: (1) subaerial gas fluxes from volcanic craters, flank fumaroles and diffuse gas seepage; (2) gas emissions into the stratosphere during explosive eruptions; (3) gases adsorbed as acids onto fine ashes from explosive eruptions; and (4) gases trapped in volcanic lakes and shallow hydrothermal systems.

Most active volcanoes are in a state of continuous, passive degassing, releasing substantial amounts of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HF}$  directly into the atmosphere (e.g., Symonds et al., 1994). The subaerial flux magnitude of volcanic  $\text{SO}_2$  emissions has been estimated based on COSPEC (Correlation Spectrometer) measurements at many individual volcanoes

(e.g., Stoiber et al., 1987). The associated volcanic  $\text{CO}_2$ ,  $\text{HCl}$  and  $\text{HF}$  fluxes are based on the estimated S fluxes and ratios of these gases to S in volcanic gas samples from active vents (e.g., Williams et al., 1992). In addition, direct  $\text{CO}_2$  flux measurements are made with infra-red absorption analyzers in volcanic plumes (e.g., Koepenick et al., 1996), and the  $\text{CO}_2$  flux by diffuse volcanic degassing is measured by analysis of soil gases (Allard et al., 1991). Satellite measurements (TOMS—total ozone measurement spectrometer) are made of  $\text{SO}_2$  emissions into the stratosphere during explosive eruptions (e.g., Bluth et al., 1993). In addition to these atmospheric yields, adsorbed acids on fine-grained ashes from explosive eruptions may constitute a substantial fraction of the total sulfur budget of an individual eruption (e.g., Rose, 1977; MacKinnon et al., 1984; Varekamp et al., 1984, 1986; Varekamp and Luhr, 1996). In about 12% of the world's volcanic systems, lakes or shallow hydrothermal systems trap a significant part of the volcanic gas flux and create very acid fluids, as found in crater lakes (Rowe and Varekamp, 1993), which may leak into local river systems. Each of these different sources of volcanic acidity will be considered.

The volcanic flux data for subaerial emissions (Table 1) are bulk values, independent of origin (recycled versus mantle volatiles), because all these emissions generate acidity that influences the weathering budgets. The volcanic gases from passive degassing are largely emitted into the troposphere and rain out predominantly on the surrounding continents or volcanic islands; e.g., the Kau desert on Hawaii is a result of acid rain from Kilauea degassing (Symonds et al., 1994). The stratospheric  $\text{SO}_2$  emissions rain out eventually over both continents and oceans, and the fluxes of  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HF}$  associated with explosive volcanism should thus be adjusted to account for fall-out over the oceans. This correction is very small, however, because the main fluxes derive from passive degassing.

All subaqueous volcanic degassing processes in the oceans are disregarded, because they do not contribute directly to the continental weathering processes. The 'weathering potential' of acids adsorbed onto fine ashes and the acid fluids in crater lakes is not expressed in the amount of acid generated, because much of the neutralization occurs in situ: in

Table 1  
Volcanic volatile fluxes, the carbon exhumation and pyrite weathering fluxes

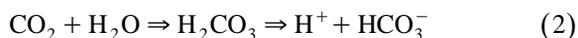
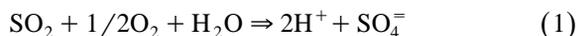
Element	Dominant species	Global flux (Tmol/a)	Equivalent H <sup>+</sup> (Tmol/a)	Sources
S (total)	SO <sub>2</sub> passive	0.2	0.53	adapt. <sup>a,b</sup>
	SO <sub>2</sub> explos.	0.07		
Cl + F	HCl + HF	0.25	0.25	corrected estimated
C	CO <sub>2</sub>	7	7	adapt. <sup>b</sup>
S from pyrite	SO <sub>4</sub> <sup>2-</sup>	0.5	1.0	<sup>c</sup>
C exhumation	CO <sub>2</sub>	8	8	<sup>d</sup>

<sup>a</sup>Symonds et al., 1994; <sup>b</sup>Brantley and Koepenick, 1995; <sup>c</sup>Berner and Berner, 1996; <sup>d</sup>Holmen, 1992.

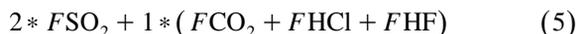
the lake or volcanic superstructure, and on the ashes. These contributions will be phrased directly as equivalent cation fluxes as a result of this in-situ weathering.

Sources of acidity other than volcanic emissions in the exosphere include H<sub>2</sub>S generation in coastal marsh systems, CO<sub>2</sub>-emissions from the oceans through several loops in the short carbon cycle, and oceanic biogenic sulfur emissions in the form of dimethylsulfide (DMS; e.g., Charlson et al., 1992; LeGrand, 1995). All these processes are part of the exospheric cycling of these elements; we will disregard these fluxes because their fall-out rates on land are relatively small (e.g., Berner and Berner, 1996).

The acid production from volcanic gas releases is symbolized by the reactions:



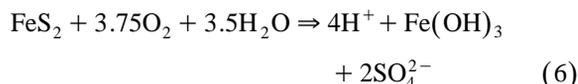
The total volcanic emission-related H<sup>+</sup> balance can now be phrased as:



in which *F* denotes flux. Obviously, CO<sub>2</sub> is the major volcanic flux leading to acidity, whereas S, Cl and F contribute only a small fraction. The CO<sub>2</sub> flux estimate of Brantley and Koepenick (1995) assumes a power-law distribution of the measured flux values. Earlier estimates of the subaerial volcanic CO<sub>2</sub> flux using a gaussian flux distribution are much smaller: 1.8 Tmol CO<sub>2</sub>/a (Gerlach, 1991), 1.5 + 1.0 Tmol CO<sub>2</sub>/a (Williams et al., 1992); 3.5 Tmol CO<sub>2</sub>/a (Varekamp et al., 1992). The annual acidity yield

from the volcanic fluxes in Table 1 sums up to 7.8 Tmoles H<sup>+</sup>/a, a 'high estimate' that we will use here.

Fluxes that constitute a release of acid from the lithosphere are of the same nature as the high-temperature degassing flux. Many sulfide deposits formed from volcanic gases at depth are weathered when they reach the exosphere after uplift and erosion e.g., creating acid mine drainage. The generalized reaction may have the form:

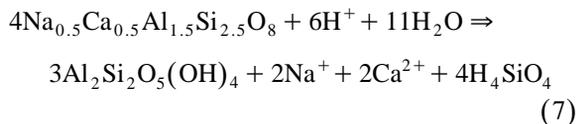


and the produced acid is largely used for the weathering of the host shale-deposit (Meybeck, 1987). The magnitude of the pyrite weathering flux is estimated at 0.5 Tmol S/a, yielding 1.0 Tmol H<sup>+</sup>/a (Berner and Berner, 1996). The weathering of organic carbon or elemental carbon from the lithosphere also provides a CO<sub>2</sub> flux to the atmosphere, although this flux has a positive feedback. If the weathering rate decreases, the flux decreases as well and this process thus can not serve in the greenhouse 'thermostat operation' of the Earth. The elemental C weathering flux is estimated at 8 Tmol C/a, yielding 8 Tmol H<sup>+</sup>/a (Holmen, 1992). The total of the acid yielding processes from volcanoes and exhumation sums up to 16.8 Tmol/a.

### 3. Calculated versus observed weathering fluxes

The exospheric process consuming acidity is water–rock interaction or chemical weathering. The neutralization of acid can be symbolized by a feldspar

weathering reaction of the form: feldspar +  $H^+$  +  $H_2O \Rightarrow$  clay + cations + dissolved silica, which for the reaction of an intermediate plagioclase to kaolinite gives:



This reaction produces 0.66 moles of dissolved Si for each  $H^+$  consumed. Weathering of intermediate plagioclase to gibbsite and smectite gives respectively 1.66 Si and 0.37 Si per  $H^+$  consumed. Alkalifeldspar weathers to the same assemblage under production of 1 (smectite), 2 (kaolinite) or 3 (gibbsite) silica per  $H^+$  consumed, but alkalifeldspar weathering is slower than plagioclase weathering (Berner and Berner, 1996). The composition of many natural waters reflects plagioclase and alkalifeldspar weathering to a mixture of kaolinite and smectite, so we take that on average about 0.5 Si is produced for each  $H^+$  consumed. This would produce a  $HCO_3^-/SiO_2$  ratio of about 2, if carbonic acid is the main agent (Garrels, 1967; Garrels and MacKenzie, 1967). Weathering of glassy volcanic rocks might generate more dissolved silica (Drever, 1988; Berner and Berner, 1996) but data from Hawaiian watersheds show not significantly different  $HCO_3^-/SiO_2$  ratios (between 1.5 and 3, Bluth and Kump, 1994).

We use the amount of dissolved silica in rivers as a proxy for the global silicate weathering flux, because only little silica is precipitated on the continents (some silica is removed by fresh water diatoms), no silica adsorption reactions occur and almost all rivers are undersaturated in silica (e.g., Drever, 1988). Dissolved silica fluxes from geothermal can be large, because silica solubility is a strong function of temperature (Fournier and Rowe, 1966; Fournier, 1970). Most of that dissolved silica is precipitated upon cooling as sinter terraces in geothermal regions, and thus does not contribute substantially to the global riverine silica budget.

The weathering of biogenic opaline silica in limestones (radiolarians, diatoms, sponges) is an additional source of dissolved Si without associated  $H^+$  demand, which may be approximately canceled by the magnitude of terrestrial biogenic silica deposition (both estimated at about 8% of the total Si flux,

Berner and Berner, 1996). Bluth and Kump (1994), however, suggest that the dissolution of silica from limestones could possibly produce a more substantial Si flux. The amount of  $H^+$  transported by rivers is very small compared to other fluxes ('unused  $H^+$ ' in Fig. 1), so this flux value can be neglected.

The observed riverine Si flux is estimated by cumulating the average riverine water fluxes and their Si contents, leading to a value of about 5.3 Tmol Si/a (Meybeck, 1987) to 6.5 Tmol Si/a (Berner and Berner, 1996). A modeled estimate of the global weathering-related Si flux, using weathering yields after Bluth and Kump (1994), is about 5.4 Tmol/a (Sloan et al., 1997).

When we apply our calculated acid yield to global weathering processes, we first have to separate silicate weathering from carbonate weathering. The proportion of weathered carbonate rocks to that of silicates is generally estimated between 55/45 and 70/30 (Meybeck, 1987). We assume that a 60/40 proportion between carbonate and silicate weathering is a reasonable approximation for most acid consuming reactions, except the  $H^+$  generated from pyrite-weathering which is completely used in weathering the silicate host-shale of the pyrite (Meybeck, 1987). Using these proportions, we obtain a theoretical dissolved silica flux of 3.7 Tmol Si/a. If we assume that about 10% of the total Si flux is derived from carbonate weathering (Meybeck, 1987), our estimate is lower than the observed Si fluxes by 1.3–2.5 Tmol Si/a.

We can approach the same processes by considering the carbonate mass balance, realizing that the bulk of the weathering reactions is fueled by carbonic acid. The riverine  $HCO_3^-$  flux equals about 31.9 Tmol/a; about 20.4 Tmol/a of that amount was derived from the atmosphere (Berner and Berner, 1996). The remainder is derived from calcite and dolomite weathering. The riverine bi-carbonate balance suggests that about 11.8 Tmol/a (58%) of the 20.4 Tmol/a comes from silicate rock weathering, which would produce 5.9 Tmol/a of dissolved Si according to our average feldspar weathering scheme. The remainder is 'fixed' atmospheric  $CO_2$  from carbonate weathering. The riverine flux values of  $HCO_3^-$  and dissolved Si for an average feldspar weathering scheme as that given above are thus internally consistent, but the whole global weather-

ing process demands about 20.4 Tmol atmospheric C/a.

The volcanic carbon flux of about 7 Tmol/a is thus a factor of 3 too small to explain the riverine atmosphere-derived bicarbonate flux. The carbon exhumation flux of about 8 Tmol C/a provides an additional flux of CO<sub>2</sub>, which makes for a final shortfall of about 5.4 Tmol C/a. Such a carbon shortfall is well in line with the above described deficit in the calculated silica weathering budget, because an additional 5 Tmol C/a would generate about 1 Tmol Si/a from silicate weathering. Shifting the proportion of weathering between silicates and limestones will not significantly alter the above relations, so most likely, an additional carbon flux on the order of 5 Tmol C/a must exist. It is outside the scope of this paper to review the details of the marine carbon cycle, but calcite precipitation in the oceans leads to shifts in carbonate equilibria with the potential release of CO<sub>2</sub> to the atmosphere. The marine organic carbon burial flux constitutes a net sink for exospheric carbon. Considerable uncertainties exist on the magnitude of these fluxes (e.g., Berner, 1991; François and Walker, 1992), but this could make up for the calculated CO<sub>2</sub> deficit.

The riverine SO<sub>4</sub><sup>2-</sup> flux (4.5 Tmol/a) would be another measure to check for mass balance in the global weathering budget, but many sources contribute to dissolved riverine sulfate (e.g., Charlson et al., 1992; MacKenzie et al., 1993). Berner and Berner (1996) estimate that about 8% of the total riverine sulfate budget is derived from volcanic sources, but this value was calculated taking a volcanic SO<sub>2</sub> flux into account. As a result, we can not use the sulfur budgets to independently balance the extent of weathering processes.

Other potential sources of acidity derive from acids adsorbed on freshly fallen ashes and magmato-hydrothermal systems. The very sulfur-rich eruption of El Chichon (1982) was probably not a typical event, but substantial amounts of Ca, Na and K were released from its freshly fallen ash by adsorbed acids upon wetting by rain (Varekamp et al., 1984). Short-lived, dissolved-element pulses produced by volcanic eruptions of easily weathered ashes may escape detection in monitoring programs of river-water chemistry and thus may not be adequately represented in the global riverine budgets of

dissolved elements. The average rate of fine-ash production is about 1250 Tg/a (Fisher and Schmincke, 1984), leading to a potential 'ash weathering flux' of Ca and Na on the order of respectively 0.5 and 0.1 Tg/a (J.C. Varekamp and J.F. Luhr, unpubl. data). These amounts are small compared with the global riverine fluxes and do not make a big difference in the overall weathering budget.

The chemical weathering in crater lake systems and hydrothermal fluids was studied quantitatively at Poas Lake, Costa Rica (Rowe and Brantley, 1993), leading to an estimate of an annual mass transfer from that volcano on the order of 5000 m<sup>3</sup> of dissolved rock. The global chemical denudation rate is on the order of 10<sup>9</sup> m<sup>3</sup> of rock (Berner and Berner, 1996): even if such a mass transfer rate was common at all crater lake volcanoes (12% of the 620 active volcanoes in the world; Rowe and Varekamp, 1993), this would not contribute much more than 0.1% to the global weathering budget. These volcanic weathering processes thus may have a dramatic local impact, but do not seem to contribute substantially to the global weathering budgets.

We conclude that the calculated weathering flux induced by volcanic acids and the exhumed carbon and pyrite flux is close to the observed chemical denudation rate. Our calculations indicate that the overall weathering mass balance can be approached reasonably well with our averaged feldspar weathering scheme, but there is a calculated shortfall of about 5 Tmol C/a. This calculated shortfall probably did not result from underestimating the active volcanic CO<sub>2</sub> output, because we used a maximum estimate of volcanic CO<sub>2</sub> emissions (Brantley and Koepnick, 1995). Possibly, volcanic CO<sub>2</sub> trapped in geothermal systems is carried away from the volcanoes to emerge in springs and seeps (Varekamp et al., 1992; D'Allesandro et al., 1997). Other CO<sub>2</sub> sources could be present, e.g., a significant degassing flux from metamorphic regions through cold CO<sub>2</sub> springs and the above-mentioned possible evasion of CO<sub>2</sub> from the oceans.

Another hypothesis would be that the exosphere is not in steady state with respect to the volcanic influxes. A sustained shortfall of about 5 Tmol C/a would be significant at time scales of 10<sup>3</sup>–10<sup>4</sup> years, given that the pre-anthropogenic atmospheric CO<sub>2</sub> budget was about 6.2 × 10<sup>4</sup> Tmol C (about a 12,000

year supply at the rate of such a shortfall). We therefore think that this hypothesis is not very likely: if the exosphere would not be in steady state, we would see changes in atmospheric CO<sub>2</sub> levels over the last 1000 years, but the record over that time as preserved in Antarctic ice cores shows no changes (Houghton et al., 1996).

Now that we have considered the modern-day weathering rates, we will assess the magnitude of variations in weathering rates during glacial times. How much higher a weathering rate than today's is needed to depress atmospheric CO<sub>2</sub> levels to glacial concentrations?

#### 4. Glacial / interglacial times

Ice core data indicate that glacial atmospheric CO<sub>2</sub> levels were at least about 30% lower than modern pre-anthropogenic levels (180–200 ppmv vs. 280 ppmv; e.g., Lorius et al., 1992; Raynaud et al., 1992). These records show that levels of about 280 ppmv are among the highest reached during the last several 100 ka, and it has been suggested that the pre-anthropogenic environment might have been close to reaching the peak of an interglacial cycle (Imbrie and Imbrie, 1979, fig. 48). It has been hotly debated whether the lower atmospheric CO<sub>2</sub> concentration was a result of the ice ages, or a contributing cause of the ice age by magnifying the effects of the Milankovitch-forcing (e.g., Berger, 1992; Broecker and Peng, 1993).

Volcanic input of CO<sub>2</sub> and silicate weathering have been said to be out of equilibrium at time scales of more than 10<sup>6</sup> years (e.g., over the Cenozoic as a whole), and that increased weathering as a result of the Himalayan uplift and its effects of lowering atmospheric  $p_{\text{CO}_2}$  caused the long-term Cenozoic cooling trend (Raymo, 1991; Edmond, 1992; François et al., 1992; François and Walker, 1992; Raymo and Ruddiman, 1992; Molnar et al., 1993). The hypothesis that tectonic events are the main driver of global weathering rates (Edmond et al., 1995), however, is contradicted by geochemical models which predict that chemical weathering is driven by temperature and  $p_{\text{CO}_2}$  (Berner et al., 1983; Velbel, 1993; Berner, 1995). If increased weathering (driven by tectonic uplift) could have occurred at lower temperatures

and  $p_{\text{CO}_2}$ , there is a major question regarding the nature of the required negative feedback; after all, runaway cooling leading to an extreme 'icehouse' Earth has not occurred over the Phanerozoic (e.g., Berner, 1995).

Several possibilities for such a negative feedback mechanism have been mentioned, e.g., changing burial rates of organic carbon to carbonate, precipitation of silicate minerals on the ocean floor, and sea floor weathering of the basaltic crust, but there is not much evidence favoring one specifically, and several authors do not agree on their relative importance (e.g., Raymo and Ruddiman, 1992; François et al., 1992). The Sr-isotope record appears to indicate that weathering rates indeed increased during the Cenozoic, and especially during the Neogene (e.g., Elderfield, 1986; Hess et al., 1986), as supported by the Ge/Si record (Shemesh et al., 1989). The Sr isotope record, however, may be explained not just by weathering increasing quantities of rock over the Cenozoic, but also by weathering rocks with increased contents of Sr as well as high Sr-isotope ratios, as exposed in the uplifted Himalayan Mountains (e.g., Berner and Rye, 1992; Edmond et al., 1995).

On shorter (10<sup>4</sup>–10<sup>5</sup> years) time scales the possible lack of negative feedback can not be seen as a major impediment (e.g., Berner, 1995). At these time scales the Sr-isotope record can not give information on weathering intensity because of the long marine residence time of that element (> 10<sup>6</sup> years; Richter and Turekian, 1993). There is evidence for increased weathering of silicate rocks during the last few glacial epochs from Ge/Si ratios in oceanic diatoms, with the data requiring riverine Si fluxes to have been higher by at least a factor of 2.5 during glacials (Froehlich et al., 1992). This proxy can be expected to show evidence for variations at glacial/interglacial time scales, because the oceanic residence time of Si is on the order of 104 years.

As discussed by these authors, increased weathering during colder periods with lower atmospheric  $p_{\text{CO}_2}$  appears to be 'not only counter-intuitive, but bordering on heresy', but we agree with Froehlich et al. (1992) that increased silicate weathering during glacials appears to be at least a possibility. Data on glacial/interglacial weathering rates are contradictory, because there are limited data on glacial solute

fluxes. In addition, we are uncertain about ice-sheet conditions, especially about whether the glacial continental ice sheets were dominantly wet- or dry-based (Anderson et al., 1997). Gibbs and Kump (1994) derived weathering rates by modeling of lithology and hydrology during the last glacial maximum, and estimated that glacial rates may have been higher by about 20%. This could have been an under-estimate, because they assumed that no weathering occurs under ice sheets. Sharp et al. (1995) and Anderson et al. (1997), however, found high cation denudation rates under alpine glaciers, and suggested that weathering rates during glacial times were high. Glacial weathering rates of soils have also been estimated to have been higher than modern rates (Taylor and Blum, 1995).

Such increased glacial weathering may have been caused by dropping sea-levels, exposing shelves to erosion, but only if the shelves would contain a high proportion of unweathered primary silicates (Gibbs and Kump, 1994; Berner, 1995). The drop in sea-level would lower the base-level of rivers, having a similar effect as tectonic uplift and possibly leading to increased weathering on the steeper slopes (Edmond et al., 1995). In addition, eolian (physical) weathering may have increased during glacial times when wind speeds were higher, reducing more rocks to smaller grains more susceptible to chemical weathering (e.g., Mayewski et al., 1994; Yung et al., 1996) as well as effects of physical erosion by the glacier movements.

If the weathering rates indeed increased during glacial times, the decrease in atmospheric CO<sub>2</sub> could be a result of changes in the continental weathering regime. Small imbalances of the carbon cycle such as the 5 Tmol/a suggested above, would be sufficient to have caused fluctuations in atmospheric CO<sub>2</sub> contents on the order as observed from glacial times to modern times in a few thousand years. In conclusion, our preliminary analysis suggests that glacial–interglacial atmospheric CO<sub>2</sub> variations may have part of their origin in continental weathering processes, even though weathering fluxes are generally regarded as modulating the atmospheric CO<sub>2</sub> contents only at 10<sup>6</sup> year time scales. We could not arrive at a simple mass balance for the modern (A.D. 1850) world, so it seems unlikely that we can back-estimate the magnitude of CO<sub>2</sub> fluxes for glacial times. Direct proxies for weathering rates (such as

Ge/Si ratios) seem a more promising avenue to determine past weathering rates.

## 5. Anthropogenic contributions

Anthropogenic gas emissions have similarities to endogenic fluxes: an oxygen demand from sulfide roasting and fossil fuel burning, and acidity generation from CO<sub>2</sub> and SO<sub>2</sub> emissions (e.g., Charlson et al., 1992; MacKenzie et al., 1993; Houghton et al., 1996). The magnitude of these annual fluxes is estimated at 500 Tmol carbon and 2.5 Tmol SO<sub>2</sub>, the latter largely from coal burning and sulfide-ore roasting (e.g., Charlson et al., 1992; MacKenzie et al., 1993). The oxygen demand is greatly in excess of the annual C<sub>org</sub> burial rate (1 Tmole/a), and atmospheric O<sub>2</sub> contents are thus decreasing (Bender et al., 1996). The atmospheric O<sub>2</sub> reservoir is so large that these effects are not of direct interest for our time scale.

The exospheric carbon cycle post A.D. 1900 is greatly out of steady state as a result of the anthropogenic fluxes, as witnessed by the build-up of CO<sub>2</sub> in the atmosphere and possibly in the oceans and/or biosphere (e.g., Houghton et al., 1996). The weathering flux potentially generated by the anthropogenic SO<sub>2</sub> emissions (e.g., 2.5 Tmol Si/a) has not yet materialized because the strong acids are still largely stored in the hydrosphere, e.g., acidified lakes as a result of acid rain. Although the weathering rates as a result of this acidification have increased and a small part of the acid rain is neutralized, these systems are still far from steady state. Probably, the pH of most river waters has slightly declined over this century as a result of these SO<sub>2</sub> releases.

The potential dissolved Si-generating capacity of the anthropogenic emissions at steady state is on the order of 250 Tmol Si/a. Such a large flux is unlikely to occur because the amorphous silica solubility at ambient temperatures is exceeded at about 10<sup>-2.3</sup> mol Si/l, and silica deposits would possibly form in many areas. For steady state to be re-established at the current anthropogenic CO<sub>2</sub> and SO<sub>2</sub> fluxes, the weathering rates need to increase by a factor of about 50. Studies of feldspar weathering rates indicate a logarithmic dependency on the pH and an Arrhenius relationship with temperature (Blum

and Stillings, 1995). The pH of surface waters has to drop about 2 units (from 6 to 4) to reach rates that are 50–100 times larger than current rates. This produces the unpleasant scenario that long-term steady state for CO<sub>2</sub> can only be reached if the exosphere becomes acidified to a much lower average pH, although this may be offset by higher ambient temperatures.

## 6. Conclusions

The currently estimated chemical weathering fluxes as expressed by dissolved Si are of the same order as those expected from the acid generating capacity of endogenic emissions. Both the carbonate and silica budgets resulting from weathering processes are somewhat larger than those predicted from endogenic emissions, including the pyrite, C and C<sub>org</sub> weathering flux. Although relatively large uncertainties are associated with these estimates, we derive a consistent shortfall in the CO<sub>2</sub> influxes on the order of several Tmol/a. Fluxes of this order of magnitude should have an impact on atmospheric CO<sub>2</sub> levels within a few thousand years, which has not been observed over the last millennium. Another CO<sub>2</sub> source must exist, most likely the oceans and possibly a metamorphic degassing flux. Models and observations invoking high global weathering rates during glacial intervals suggest that continental weathering processes might have modulated atmospheric CO<sub>2</sub> contents on time scales of 10<sup>4</sup>–10<sup>5</sup> years.

The impact of anthropogenic emissions on global weathering is presumably barely felt until now: the strong acids accumulate in the hydrosphere and generate lower pH levels, but rates of neutralization are still far from a steady-state condition. The excess CO<sub>2</sub> is still being stored in the atmosphere, biosphere and oceans, and the neutralization of its acid-generating capacity has barely begun. The scenario of a steady-state world at current anthropogenic emission strengths is unpleasant: pH values of about 4 in continental surface waters may be needed to restore the carbon cycle to steady state at current CO<sub>2</sub> emission rates. We did not consider the possible temperature effects of a CO<sub>2</sub> greenhouse, which will tend to diminish the extent of the required acidification.

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## References

- Allard, P., Carbonelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M.C., Maurenas, J.M., Faivre-Pierret, R., Martin, D., Sabroux, J.C., Zettwoog, P., 1991. Eruptive and diffuse emissions of CO<sub>2</sub> from Mount Etna. *Nature* 1351, 387–391.
- Anderson, S.P., Drever, J.I., Humphrey, N., 1997. Chemical weathering in glacial environments. *Geology* 25, 399–402.
- Bender, M., Ellis, T., Tans, P., Francey, R., Lowe, D., 1996. Variability in the O<sub>2</sub>/N<sub>2</sub> ratio of southern hemisphere air, 1991–1994: implications for the carbon cycle. *Global Biogeochem. Cycles* 10, 9–21.
- Berger, W.H., 1992. The CO<sub>2</sub>/CH<sub>4</sub> climate connection. In: Moore, B., Schimmel, D. (Eds.), *Trace Gases and the Biosphere*. UCAR Office for Interdisciplinary Earth Studies, Boulder, CO (USA), pp. 13–40.
- Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air and Geochemical Cycles*. Prentice-Hall, Englewood Cliffs, N.J., 376 pp.
- Berner, R.A., 1991. A model for atmospheric CO<sub>2</sub> over Phanerozoic time. *Am. J. Sci.* 291, 339–376.
- Berner, R.A., 1993. Paleozoic atmospheric CO<sub>2</sub>: importance of solar radiation and plant evolution. *Science* 261, 68–70.
- Berner, R.A., 1994. 3GEOCARBII: a revised model of atmospheric CO<sub>2</sub> over Phanerozoic time. *Am. J. Sci.* 294, 56–91.
- Berner, R.A., 1995. Chemical weathering and its effect on atmospheric CO<sub>2</sub> and climate. *Rev. Mineral.* 31, 565–583.
- Berner, R.A., Rye, D.M., 1992. Calculation of the Phanerozoic Strontium isotope record of the oceans from a carbon cycle model. *Am. J. Sci.* 292, 136–148.
- Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate–silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* 283, 641–683.
- Blum, A.E., Stillings, L.L., 1995. Feldspar dissolution kinetics. *Rev. Mineral.* 31, 291–351.
- Bluth, G.J.S., Kump, L.R., 1994. Lithologic and climatologic controls on river chemistry. *Geochim. Cosmochim. Acta* 58, 2341–2359.
- Bluth, G.J.S., Schnetzler, C.C., Krueger, A.J., Walter, L.S., 1993. The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations. *Nature* 366, 327–329.
- Brantley, S.L., Koepenick, K.W., 1995. Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes. *Geology* 23, 933–936.
- Broecker, W.S., Peng, T.H., 1993. What caused the glacial to interglacial CO<sub>2</sub> change? In: Heimann, M. (Ed.), *The Global Carbon Cycle*. NATO–ASI Series I, 15, Kluwer, Dordrecht, pp. 95–115.

- Charlson, R.J., Anderson, T.L., McDuff, R.E., 1992. The Sulfur Cycle. In: Butcher, S.S., Charlson, R.J., Orians, G.H., Wolfe, G.V. (Eds.), *Global Biogeochemical Cycles*. Academic Press, New York, pp. 285–300.
- Clausen, H.B., Hammer, C.U., Christensen, J., Schøtt Hvidberg, C., Dahl-Jensen, D., Legrand, M., Steffenson, J.P., 1995. 1250 years of global volcanism as revealed by central Greenland ice cores. In: Delmas, R.J. (Ed.), *Ice Core Studies of Biogeochemical Cycles*. NATO–ASI Series I, 30, Kluwer, Dordrecht, pp. 175–194.
- D'Allesandro, W., Giammanco, S., Parello, F., Valenza, M., 1997. CO<sub>2</sub> output and  $\delta^{13}\text{C}(\text{CO}_2)$  from Mount Etna as indicators of degassing of shallow asthenosphere. *Bull. Volcanol.* 58, 455–458.
- Drever, J., 1988. *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, N.J., 436 pp.
- Edmond, J.M., 1992. Himalayan tectonics, weathering processes, and the strontium isotope record in marine limestones. *Science* 258, 1594–1597.
- Edmond, J.M., Palmer, M.R., Measures, C.I., Grant, B., Stallard, R.F., 1995. The fluvial geochemistry and denudation rate of the Guyana Shield in Venezuela, Colombia and Brazil. *Geochim. Cosmochim. Acta* 16, 3301–3325.
- Elderfield, H.E., 1986. Strontium isotope stratigraphy. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 57, 71–90.
- Fisher, R.V., Schmincke, H.-U., 1984. *Pyroclastic Rocks*. Springer-Verlag, Berlin, 472 pp.
- Fournier, R.O., 1970. Silica in thermal waters: laboratory and field investigations. In: *Proc. Symp. Hydrogeochemistry and Biogeochemistry*, Vol. 1. Clark Co., Washington D.C., pp. 122–140.
- Fournier, R.O., Rowe, J.J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Am. J. Sci.* 264, 685–697.
- François, L.M., Walker, J.C.G., 1992. Modeling the Phanerozoic carbon cycle and climate: constraints from the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio of sea water. *Am. J. Sci.* 292, 81–135.
- François, L.M., Walker, J.C.G., Opdyke, B.N., 1992. The history of global weathering and the chemical evolution of the ocean–atmosphere system. In: Takahashi E., Jeanloz, R. (Eds.), *Chemical Evolution of the Earth and Planets*. Am. Geophys. Union, pp. 1–17.
- Froehlich, P.N., Blanc, V., Mortlock, R.A., Chillrud, S.N., 1992. River fluxes of dissolved Silica to the oceans were higher during glacials: Ge/Si in diatoms, rivers and oceans. *Paleoceanography* 7, 739–767.
- Garrels, R.M., 1967. Genesis of some ground waters from igneous rocks. In: Abelson, P.H. (Ed.), *Researches in Geochemistry*. John Wiley and Sons, New York, p. 412.
- Garrels, R.M., MacKenzie, F.T., 1967. Origins of the chemical composition of some springs and lakes. In: *Equilibrium Concepts in Natural Water Systems*. Am. Chem. Soc. Adv. Chem. Ser. 67, 222–232.
- Gerlach, T., M., 1991. Present-day CO<sub>2</sub> emissions from volcanoes. *EOS, Trans. Am. Geophys. Union* 72: 249–255.
- Gibbs, M.T., Kump, L.R., 1994. Global chemical erosion during the last glacial maximum and the present: sensitivity to changes in lithology and hydrology. *Paleoceanography* 9, 529–543.
- Hess, J., Bender, M.L., Schilling, J.-G., 1986. Evolution of the rate of strontium-87 to strontium-86 in sea water from the Cretaceous to Present. *Science* 231, 979–984.
- Holland, H.D., 1984. *The Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, N.J., 582 pp.
- Holmen, K., 1992. The global carbon cycle. In: Butcher, S.S., Charlson, R.J., Orians, G.H., Wolfe, G.V. (Eds.), *Global Biogeochemical Cycles*. Academic Press, New York, pp. 239–262.
- Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A., Maskell, K., 1996. *Climate Change 1995: The Science of Climate Change*. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental panel on Climate Change, Cambridge University Press, Cambridge, 572 pp.
- Imbrie, J., Imbrie, K.P., 1979. *Ice Ages: Solving the Mystery*. Enslow Publ., Garden City, N.J., p. 113.
- Koepnick, K.W., Brantley, S.L., Thompson, J.M., Rowe, G.L., Nyblade, A.A., Moshy, C., 1996. Volatile emissions from the crater and flank of Oldoinyo Lengai volcano, Tanzania. *J. Geophys. Res.* 101, 13819–13830.
- LeGrand, M., 1995. Sulphur-derived species in polar ice: a review. In: Delmas, R.J. (Ed.), *Ice Core Studies of Global Biogeochemical Cycles*. NATO–ASI Ser. I, 30, pp. 91–119.
- Lorius, C., Jouzel, J., Raynaud, D., 1992. The ice core record: past archive of the climate and signpost to the future. *Philos. Trans. R. Soc. London* 338, 227–234.
- MacKenzie, F.T., Ver, L.M., Sabine, C., Lane, M., Lerman, A., 1993. C, N, P, S biogeochemical cycles and modeling of global change. In: Wollast, R., MacKenzie, F.T., Chou, L. (Eds.), *Interactions of C, N, P, S Biogeochemical Cycles and Global Change*. NATO–ASI Ser. I, 4, pp. 1–61.
- MacKinnon, I.D.R., Gooding, J.L., McKay, D.S., Clanton, U.S., 1984. The El Chichon stratospheric cloud: solid particulates and settling rates. *J. Volcanol. Geotherm. Res.* 23, 125–146.
- Mayewski, P.A., Meeker, L.D., Whitlow, S., Twickler, M.S., Morrison, M.C., Bloomfield, P., Bond, G.C., Alley, R.B., Gow, A.J., Grootes, P.M., Meese, D.A., Ram, M., Taylor, K.C., Wumkes, W., 1994. Changes in atmospheric circulation and ocean ice cover over the North Atlantic during the last 41,000 years. *Science* 263, 1747–1751.
- Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am. J. Sci.* 287, 401–428.
- Molnar, P., England, P., Marinod, J., 1993. Mantle dynamics, uplift of the Tibetan Plateau, and the Indian Monsoon. *Rev. Geophys.* 31, 357–396.
- Raymo, M.E., 1991. Geochemical evidence supporting T.C. Chamberlin's theory of glaciation. *Geology* 19, 344–347.
- Raymo, M.E., Ruddiman, W.F., 1992. Tectonic forcing of late Cenozoic climate. *Nature* 359, 117–122.
- Raynaud, D., Barnola, J.M., Chapellaz, J., Zardini, D., Jouzel, J., Lorius, C., 1992. Glacial–interglacial evolution of greenhouse gases as inferred from ice core analysis: a review of recent results. *Quat. Sci. Rev.* 11, 381–386.
- Richter, F.M., Turekian, K.K., 1993. Simple models for the geochemical response of the ocean to climatic and tectonic forcing. *Earth Planet. Sci. Lett.* 199, 121–131.
- Rose, W.I. Jr., 1977. Scavenging of volcanic aerosol by ash:

- atmospheric and volcanologic implications. *Geology* 5, 621–624.
- Rowe, G.L., Brantley, S.L., 1993. Estimation of the dissolution rates of andesitic glass, plagioclase and pyroxene in a flank aquifer of Poas Volcano, Costa Rica. *Chem. Geol.* 105, 71–87.
- Rowe, G.L., Varekamp, J.C., 1993. Solicitations for comments, suggestions and data contributions to the IWGCL volcanic lake database from IWGCL members. *IWGCL Newsl.* 6, 56–61.
- Sharp, M., Tranter, M., Brown, G.H., Skidmore, M., 1995. Rates of chemical denudation and CO<sub>2</sub> drawdown in a glacier-covered alpine catchment. *Geology* 23, 61–64.
- Shemesh, A., Mortlock, R.A., Froehlich, P., 1989. Late Cenozoic Ge/Si record of marine biogenic opal: implications for variations of riverine fluxes to the ocean. *Paleoceanography* 4, 221–234.
- Sloan, L.C., Bluth, G.J.S., Filipelli, G.M., 1997. A comparison of spatially resolved and global mean reconstructions of continental denudation under ice-free and present conditions. *Paleoceanography* 12, 147–160.
- Stoiber, R.E., Williams, S.N., Huebert, B.J., 1987. Annual contribution of sulphur dioxide to the atmosphere by volcanoes. *J. Volcanol. Geotherm. Res.* 33, 1–8.
- Symonds, R.B., Rose, W.I., Bluth, G.J.S., Gerlach, T.M., 1994. Volcanic-gas studies: methods, results, and applications. *Rev. Mineral.* 30, 1–66.
- Taylor, A., Blum, J.D., 1995. Relation between soil age and silicate weathering rates determined from the chemical evolution of a glacial chronosequence. *Geology* 23, 979–982.
- Varekamp, J.C., Luhr, J.F., 1996. Volatile element budgets of explosive eruptions: contributions from volatiles absorbed on ashes. Abstract Chapman Conference, Crater Lake (OR), 4–9 Sept. 1996.
- Varekamp, J.C., Luhr, J.F., Prestegard, K., 1984. The 1982 eruptions of El Chichon volcano (Chiapas, Mexico): character of the eruptions, ash-fall deposits, and gas phase. *J. Volcanol. Geotherm. Res.* 23, 39–68.
- Varekamp, J.C., Thomas, E., Germani, M.S., Buseck, P.R., 1986. Particle geochemistry of volcanic plumes of Etna and Mount St. Helens. *J. Geophys. Res.* 91, 12233–12248.
- Varekamp, J.C., Kreulen, R., Poorter, R.P.E., van Bergen, M.J., 1992. Carbon sources in arc volcanism, with implications for the carbon cycle. *Terra Nova* 4, 373–373.
- Velbel, M.A., 1993. Temperature dependence of silicate weathering in nature: how strong a negative feedback on long term accumulation of atmospheric CO<sub>2</sub> and global greenhouse warming?. *Geology* 21, 1059–1062.
- Volk, T., 1989. Rise of angiosperms as a factor in long-term cooling. *Geology* 17, 107–110.
- Williams, S.N., Schaefer, S.J., Calvache, M.L., Lopez, D., 1992. Global carbon dioxide emission to the atmosphere by volcanoes. *Geochim. Cosmochim. Acta* 56, 1765–1770.
- Yung, Y.L., Lee, T., Wang, C.-H., Shieh, Y.-T., 1996. Dust: a diagnostic of the hydrologic cycle during the last glacial maximum. *Science* 271, 962–963.
- Zielinski, G.A., Mayewski, P.A., Meeker, L.D., Whitlow, S., Twickler, M.S., Morrison, M., Meese, D.A., Gow, A.J., Alley, R.B., 1994. Record of volcanism since 7000 BC. from the GISP2 ice core and implications for the volcano–climate system. *Science* 264, 948–952.