A new insight into the climatic impact of volcanic explosion: A lesson from the sulfur stable isotopes

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Large violent volcanic explosions throughout Earth's history, such as the eruption of Tambora in Indonesia in 1815, have significantly impacted human societies, killing thousands of people directly by the blast or indirectly by famine, shaping religion in Hawaii, mythology in Greece, folklore, poetry and literature in all societies. During the massive energy release, megatons of ash, liquid and gaseous materials from the Earth's interior are directly injected into the stratosphere in just a few days. Mainly sul$fur-containing volcanic gases are responsible for the climate effects of explosive volcanic eruptions. The formation of a sulfuric acid cloud that can reside in the stratosphere for years and cover the entire globe profoundly modifies the radiative budget of the atmosphere and seriously impacts the ozone layer. There is no other internal Earth process that disturbs the atmosphere with the power, the speed, and the extent of a stratovolcano, and massive cooling resulting eventually in starvation is definitely a possibility, even today.

It is estimated that at least once every 2 years, a volcanic eruption penetrates the tropopause, thus, the long-term impact of volcanoes on natural climate variability must also be considered. But such an exercise is difficult for the past. Ice core records have been intensively used to assess such climate effects because they have the capability to record the fingerprint of volcanic events in the form of unusually high sulfuric acid levels in snow and ice layers (Hammer, 1977). Figure 1 shows an example of a sulfate concentration profile as recorded in a Greenland ice core. For the past 800 years, with the notable exception of the 20th century, due to anthropogenic emissions, the background concentration of sulfate has been rather stable and comes equally from the oxidation of dimethylsulfide (DMS), a product of the marine biota, and non-eruptive volcanic emissions. On top of this background, spikes of sulfate concentration represent a violent volcanic eruption. However, despite such high-resolution records of volcanic events, it is very difficult to establish a volcanic climatic effect (Zielinski, 1995). No obvious distinction between global stratospheric and regional tropospheric eruptions can be made, and quantification of the amount of sulfate emitted by a volcano is not directly linked to the depositional flux of sulfate to the ice surface. Thus, two major issues persist with ice cores: Identification and quantification; both severely limit the use of volcanic glaciological records to reconstruct the volcanic forcing in the past.

Sulfur isotopic chemistry

Stable isotopic chemistry has been used for decades to constrain source emission. Sulfur is characterised by 4 stable isotopes or 3 isotopic ratios: $^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$. Classically, these ratios are expressed in δ notation, where $\delta\,xS\ (‰) = [(^{x}S/^{32}S)_{sample}/(^{x}S/^{32}S)_{CDT}) - 1] \times 1000$ and CDT (Canyon Diablo Triolite) is the international sulfur isotope standard. The δ scale expresses the deviation of a given sulfur isotope ratio of a sample from the CDT standard. Thermodynamic, kinetic and biological processes produce isotopic fractionations that depend on the relative mass differences between the different isotopes of sulfur. As

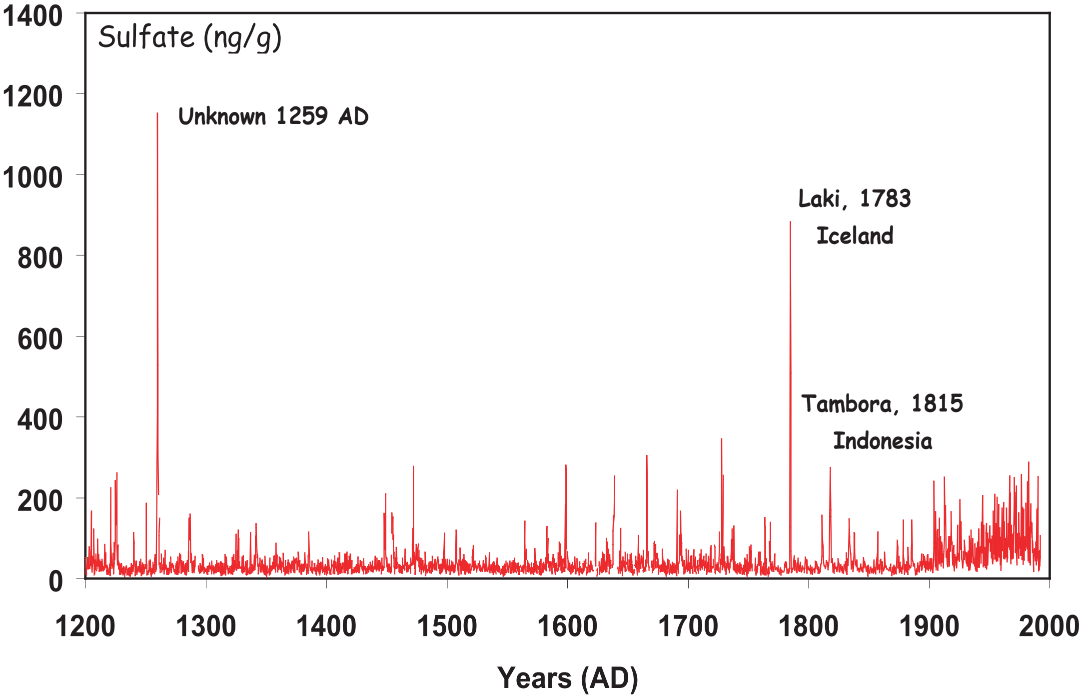

Figure 1: Sulfate concentration profile of a Greenland ice core. Except during the 20th century, which is dominated by anthropogenic emissions, the background sulfate concentration is rather stable. Sharp peaks are the manifestation of volcanic events recorded in the ice. For Greenland, most of them are tropospheric eruptions from Iceland and North America. However, few of them are clearly identified as stratospheric eruptions (1259: unknown; 1815: Tambora, for instance). From such concentration measurements alone, it is a very difficult task to estimate the impact of volcanoes on climate because the peak height is not directly linked to the magnitude of the eruption (Joël Savarino, unpublished data).

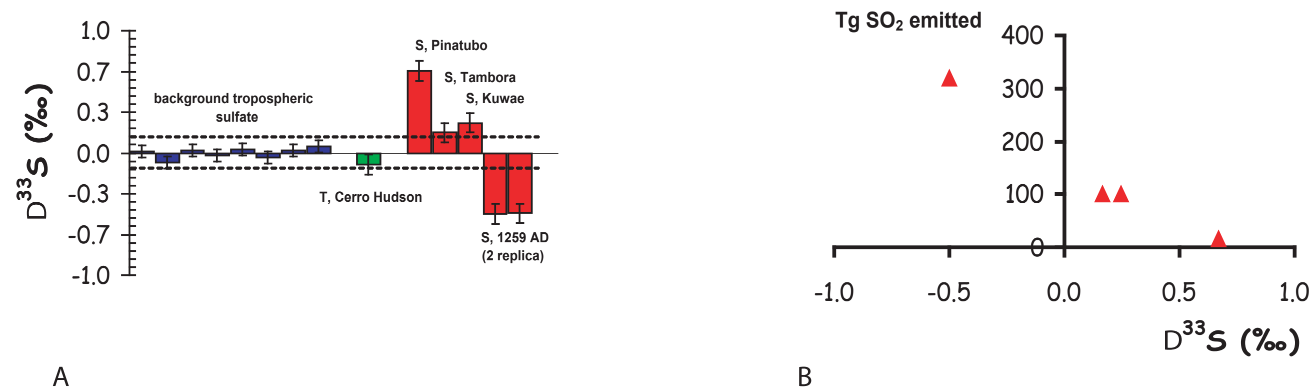

Figure 2: A) Sulfur isotopic anomalies of stratospheric and tropospheric sulfate. From this limited data set, we can clearly see that only stratospheric volcanic sulfate carries a $\Delta^{33}S$ that is significantly different than 0. This isotopic fingerprint might be used to classify the nature of any volcanic eruption independently of its depositional flux. The two dashed lines represent the two standard deviations (± 0.1 ‰) of the isotopic references. S and T stand for stratosphere and troposphere. B) Plot of $\Delta^{h}S$ versus amount of sulfur injected into the stratosphere. This kind of plot might be used in the future to quantify unknown volcanic explosions and assess their climatic impact; information that is unavailable so far.

a result, observed isotope variations are highly correlated with $\delta^{33}S \approx 0.515\ \delta^{34}S$ and $\delta^{36}S \approx 1.90\ \delta^{34}S$, so that usually only $\delta^{34}S$ is reported, since the two other isotopic ratios are redundant information. In pioneer work, Farquhar et al. (2000) discovered that such correlations were violated for minerals older than 2.2 billion years. The quantities $\Delta^{33}S$ and $\Delta^{36}S$ reflect the deviation of measured isotopic compositions from mass fractionation arrays ($\Delta^{33}S \approx \delta^{33}S$ - $0.515\ \delta^{34}S$ and $\Delta^{36}S \approx 36S - 1.90\ \delta^{34}S$). Soon after, we showed that those sulfur isotopic anomalies ($\Delta 33S$ and $\Delta 36S \neq 0$) could be reproduced in the laboratory when SO_2 gas was subjected to intense UV photolysis (Farquhar et al., 2001). As a way to test the causality between UV and sulfur isotopic anomalies, we decided to sample well-known stratospheric volcanic horizons buried in South Pole snow and ice. Indeed, before being converted to sulfate, SO_2 is intensively subjected to UV radiation in the stratosphere, similar to the Archean troposphere. Our first strategy was to test Farquhar's proposition, which has important implications for the oxygenation of the atmosphere.

Snow and ice signatures

We extracted volcanic and background sulfate from South Pole snow and ice (Savarino et al., 2003). Because of the quantity needed to perform such isotopic analyses, only major events could be sampled. Ion chromatography is used to isolate, concentrate and purify the volcanic and background sulfate. After chemical operations, sulfate is converted to SF_6, from which all sulfur isotopes can be measured (fluorine is a mononuclear element). Five volcanoes were sampled: The well-observed stratospheric Pinatubo eruption (June 1991, Indonesia) and tropospheric Cerro Hudson (September 1991, Chili), the Tambora (1815, Indonesia), the Kuwae (1450, Vanuatu) and the biggest eruption of the past 1,000 years but still unidentified, the stratospheric 1259 eruption. Backgrounds were extracted from ice surrounding the volcanoes and from tropospheric aerosol filters. Isotopic results are displayed in Figure 2a. It seems evident that based on this limited data set, sulfates produced in the stratosphere show an anomalous ^{33}S isotopic composition, while all other sulfate samples have $\Delta^{33}S$ not significantly different than zero. The precise mechanism responsible for this unique isotopic composition is not yet well understood but it undoubtedly takes place in the stratosphere where short wavelengths are present. Therefore, it should be kept in mind that the sulfur isotopic anomaly is independent of the starting isotopic composition of the volcanic source. As far as we know, no sulfur isotopic anomalies have been reported for sulfur oxides produced in the troposphere.

Another interesting feature of the sulfur isotopes is the linear correlation between the ^{33}S anomaly and the estimated amount of sulfur emitted by the stratovolcano (Fig. 2b). We do not know exactly why such correlation exists but we can reasonably argue that the penetration of UV photons into the SO_2cloud will dependent both on the amount of SO_2 present and on the altitude of the cloud; two parameters closely linked to the power of the eruption. If such observations prove to be correct in the future, then sulfur isotopic measurements might constrain the two major uncertainties in estimating the climatic impact of volcanoes from ice cores; that is the stratospheric or tropospheric nature of a volcano and the amount of sulfur injected into the stratosphere. More work is needed before a new, more sensitive tracer for stratospheric eruptions can be claimed but sulfur isotope measurements at least provide new direction to tackle this important issue of the volcano-climate relationship. To confirm these preliminary observations, other well-identified stratospheric eruptions such as Krakatoa (1883) or the Toba (~ 75 ky BP) must be examined, as well as the spatial and temporal homogeneities of such isotopic signatures; two research directions that are currently underway in our lab.

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Land–surface changes: feedbacks and climate forcing

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Climate changes affect vegetation productivity and distribution, surface hydrology including the extent of lakes and wetlands, and soil moisture regimes and, through these, susceptibility to erosion by wind and water. These changes in land-surface conditions in turn affect the physical properties which control water- and energy-fluxes between the land and the atmosphere, and hence can amplify or mitigate the impact of the original climate change. In this sense, land-surface changes can be regarded as feedbacks within the climate system. However, anthropogenic changes in land-surface conditions, caused for example by urbanization, deforestation or agricultural exploitation, produce similarly large changes in physical properties and such changes must be regarded as an independent forcing of the climate system.

The palaeorecord leaves us in no doubt that there have been substantial and often dramatic changes in land-surface conditions (e.g. Kohfeld and Harrison, 2000). The dramatic conversion of the Sahara into a landscape with large lakes, extensive wetlands and shrubby vegetation during the earlier part of the Holocene (ca 11,000 to 5500 years ago), or the large-scale replacement of boreal and temperate forests by steppe-tundra vegetation across Eurasia during the last glacial maximum (ca 21,000 years ago), are well documented. Palaeoenvironmental and isotopic evidence document the existence of freshwater lakes and moisture-demanding vegetation in central Australia between 30,000 and 65,000 years ago. During the last interglacial (ca 125,000 years before present) boreal forests extended to the Arctic coastline and wetter conditions associated with expansion of the northern hemisphere monsoons produced large lakes in northern Africa. Earlier periods in the Earth's history provide even more dramatic examples of land-surface changes, including the existence of forest in polar regions until ca 3 million years ago. It is hardly surprising, then, that some of the earliest work to demonstrate the importance of land-surface feedbacks in the climate system were concerned with past times.

Investigations of the role of land-surface changes on regional palaeoclimates have tended to focus on iconic features, for example, the amplification during interglacial periods of arctic warming by northward extension of boreal forest and of northern-hemisphere monsoons by the expansion of moisture-demanding vegetation (see e.g. Kutzbach et al., 2001; Wohlfahrt et al., 2004). Despite the very different types of models and experimental approaches used in these studies, a number of robust conclusions about the way land-surface changes affect climate have emerged.

In the high latitudes, the most important influence of land-surface conditions on the climate system is through changes in surface albedo. Albedo during the winter season is much lower in regions characterized by tall vegetation (high shrubs, trees) than in regions without such vegetation because of the masking effect of vegetation on the underlying snow. Northward expansion of forest vegetation, in response to orbitally-induced warming in the mid-Holocene or last interglacial, resulted in a reduction in albedo and hence increased surface warming. The impact of this vegetation-snow-albedo feedback is most marked during spring, when radiation receipts are increasing but the ground is still snow covered, but has a non-negligible effect during other seasons such that vegetation reduces the cooling due to orbital forcing in winter and produces year-round warming in the high northern latitudes. There is still considerable uncertainty about the magnitude of the warming due to vegetation feedback: early experiments suggested that vegetation-induced changes were substantially larger than those due to orbital forcing, but later studies indicate that realistic changes in vegetation cover produce a summer warming of 50-90% of that induced by orbital changes alone.

Albedo changes are also important in monsoonal regions. Studies of the impact of land-surface changes in northern Africa during the mid-Holocene, initially induced by orbitally-forced changes in the monsoon, indicate that vegetation-induced lowering of albedo led to warming of the continent, enhancing land-sea contrast and increasing onshore advection of moisture. When compared to the effects of mid-Holocene insolation changes, the presence of vegetation enhances warming in spring and hence initiates an early onset of monsoonal precipitation. Vegetation cover also prolongs the monsoon season in autumn, in large part because it decreases the reliance on moisture advection and maintains monsoonal conditions through enhanced moisture recycling. Other land-surface changes, including the expansion of lakes and wetlands, also increase moisture recycling. The impact of land-surface changes on the African monsoon is comparable in magnitude to the increase due to orbital forcing during the mid-Holocene.

Given the importance of land-surface feedbacks in regional palaeoclimates, it is natural to expect that climate-induced changes in natural vegetation will play a role in future climate change. Recent warming in the Arctic has indeed led to reductions in snow cover and the expansion of shrub and tree cover. Chapin et al. (2005) have suggested that these changes in land-surface conditions have led to local increases in atmospheric heating by up to 3 Wm-2 per decade. However, considerably more attention has been focused on the potential impacts of direct anthropogenic modification of land-surface conditions on the climate system. There have been large changes in the nature of