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Are Volcanic Gases Serial Killers?

Bruno Scaillet*

Volatiles released by volcanic eruptions are often cited as a possible cause of major environmental changes. On a decadal time scale, at least, the connection between volcanic eruptions and climate was firmly established after the 1991 eruption of Mount Pinatubo, Philippines, whose climate aftermaths have been extensively documented and modeled (1). The remaining debate concerns the effect of magmatic volatiles on long-term climate trends (2). On page 1654 of this issue, Self *et al*. (3) fill in the picture of what gases have been released by volcanoes, and how much, during the so-called flood events. Such events are the most important volcanic eruptions that occurred on Earth. They are produced by mantle upwelling and its partial melting, resulting in massive basalt (a magma poor in silica) outpouring with volumes often exceeding 1 million $km³$.

Earth volcanic activity is one of the two leading scenarios proposed to explain the pattern of mass extinctions in the Phanerozoic (the last 545 million years), the other involving asteroid impacts (4). To assess the volcanic hypothesis, we need to know the age and duration of volcanic events and the mass and nature of volatiles being released. Although decisive progress has been made in recent years concerning age and duration, confirming the geologically narrow interval (less than 1 million years) during which most flood basalt is discharged (5), almost no information is available on the latter aspects. As a result, the volatile yields of volcanic activity have been estimated by assuming that the volatile content of flood basalts is similar to that of their modern counterparts at mid-ocean ridges. However, there is no a priori reason why this should be so.

Self *et al.* (3) report the first analyses of sulfur in glass inclusions found in the Deccan basalts in west-central India. These ancient eruptions have been proposed by some as one of the important players of the Cretaceous-Tertiary mass extinction (6). The finding demonstrates unambiguously that the capacity of Deccan basalts to discharge sulfur into the atmosphere was similar to that of present-day erupting basalts. Trivial though this piece of evidence may seem, it now allows us to use with some confidence climate scenarios derived from the study of recent basalt outbursts, such as the 1783-1784 Laki eruption in Iceland (7), as a proxy for the likely environmental consequences related to catastrophic flood events (8), albeit on a much smaller scale.

This understanding of volatiles from the work of Self *et al*., although clearly a decisive step forward, is far from complete, however. The authors have reasonably focused on quantifying one of the species to which climate is highly sensitive. Sulfur, along with $CO₂$, indeed reigns supreme in almost all models proposed so far to correlate mass extinctions with flood events, although each has opposite effects (2). Other volatiles may also have altered the climate, however, in particular halogens (F, Cl, Br, I). In addition to having regional devastating effects (9), halogens may dramatically affect both tropospheric and stratospheric chemistries, with severe impacts on the ozone layer.

According to Self *et al*., the Deccan basalts were quite rich in Cl, and possibly in other halogens as well, as compared to their oceanic counterpart. Yet, their derived figure of 1 Tg (10^{12} g) of HCl per km³ of erupted magma may well be a lower bound. Some researchers have proposed on the basis of calculations that basalt-forming floods may have been extremely $H₂O$ and $CO₂$ rich, with combined amounts of up to 4 weight % (10). A consequence of such

an elevated volatile content is that basalts may be saturated with gas at depth (see the figure), in which case the gas phase will store a considerable, if not dominant, part of the halogen budget, a factor not considered in climate models. Yet, given the colossal amounts of magma erupted, the amount of halogens delivered to the atmosphere may have been dramatic as well, and it is not certain that lessons derived from the Pinatubo eruption (11), which was three orders of magnitude smaller than the Deccan eruptions, equally apply to flood events. Quantitative evaluation of the amounts of F, Cl, and Br released during magmatic flood activity, and of their possible effects on atmospheric chemistry, should be a priority for future research.

Several uncertainties remain, unfortunately. So far, attention has been focused on the volatiles released by the basalt component. Yet, the composition of several flood provinces has two peaks (12), with a more or less prominent silicic component, whose volatile yield must also be evaluated. Contrary to the perceived wisdom (2), it has been shown that some silicic floods may have propelled enormous amounts of sulfur into the atmosphere, equivalent to those released by basalt (13). The reason lies in the different modes of silicic magma flood production, which in turn depend, among other things, on the locus of plumes that give rise to flood magmas (beneath the continental or oceanic crust), and on the frequency of basalt intrusion in the crust (14). A last complicating factor is due to thermal effects of basalt intrusion on crustal rocks: Upon heating, these may release additional volatiles such as CH4 (15) or $CO₂$ (16), in amounts much larger than the pristine content of the magma.

Thus, the geological evidence suggests that the volatile-induced climate response to a flood event may not be unique, and the above list of potential influential factors has to be evaluated on a case-by-case basis. The possible large variation in release of volatiles from flood basalt eruptions offers an explanation as to why some of these massive magma outbursts are associated with worldwide biological crisises while others are not (2). Besides highly precise geochronological and mass data, the complete elucidation of this particular volcano-climate connection needs careful and detailed petrological understanding of magmas erupted and of the rocks they have passed through, in addition to the determination of how the eruptions occurred. When such a consolidated database is available for each of the dozen or so flood sequences so far documented, then climate models may come into play and tackle the environmental consequences associated with these massive magma floods that have punctuated the last 350 million years. Then, and only then, will the geological community be in position to prove either right or wrong that putative causal link between mass extinctions and volcanism.

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Volatile situation. The mantle plume hits the base of the crust, whether oceanic or continental, which, via dykes intrusion, heats up, and eventually partially melts, producing magmas rich in silica (rhyolites). Local basalt accumulation in the upper crust produces reservoirs whose cooling may also yield rhyolite. Both basalt and rhyolite magmas, in addition to crystals hosting melt inclusions, may contain gas bubbles (**inset**) in which some volatile species (HCl, HBr, $CO₂$) may be concentrated. Heating by magmatic intrusions may release CH_4 or CO_2 species.