

Sulfur and Oxygen Isotopic Records on Atmospheric Chemistry of Volcanic Gases

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Volcanic emission into the atmosphere has been an active process since the beginning of the Earth, although the process might have been more intensive in the early Earth than it is now. Emitted volcanic gases are out of equilibrium with atmospheric conditions, thus further reactions are expected. The reaction products, if preserved in rock records, should become some of the best probes for ancient atmospheric conditions. Here I report two cases where such records are revealed by mass-independent sulfur or oxygen isotopic compositions of some mineral phases that are directly related to volcanic emissions. It is intended to show that future research on this topic is urgently needed and is deemed fruitful.

Mass-independent S-33 isotopic anomalies in sulfide and sulfate phases in very old (older than 2.2 Ga) sedimentary rocks were discovered by Farquhar et al. (2000). As we know so far, only photochemical reactions can produce the observed mass-independent sulfur isotopic anomalies. The timing of the disappearance of the S-33 anomalies in sedimentary records is surprisingly well correlated with that of the rising of molecular oxygen in the atmosphere. The causal link between the two events is very tempting. Current speculation is that the early atmosphere was largely reduced and free of oxygen, thus the ozone layer was absent and short UV light was not blocked. Volcanic gases, for example H₂S and SO₂, were photolyzed by the short UV light penetrated deep into the Earth's atmosphere and produced the observed sulfur mass-independent anomaly. Once oxygen started to accumulate in the atmosphere since ~ 2.5 Ma, the photochemistry in question was shut down or greatly reduced. Thus, the S cycle shifted from a photochemistry-dominated one in the Archean to a biology-controlled one there after.

Once the atmosphere oxygenated and the ozone layer formed after the Archean eon, reduced sulfur gases from volcanic emission would involve mostly in oxidation reactions rather than UV photolysis. OH radical, H₂O₂, or O₃ are the major oxidants for volcanic SO₂ and H₂S. The only record so far that indicates the involvement of H₂O₂ and O₃ in the oxidation of volcanic gases is from the Oligocene-Miocene deposits in North America, where large O-17 anomalies were found in the water-soluble sulfate phases in volcanoclastic deposits on land (Bao et al, 2000, 2001). The intriguing thing, however, is the

absence of such O-17 anomalies in a dozen of fresh volcanic ash samples from Recent eruptions.