Volcanic deposits: an archive of nitrogen fixation by volcanic lightning at geological timescale

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Nitrogen (N) is a crucial element for life on Earth. However, almost all the readily accessible N is trapped in the form of the very stable atmospheric dinitrogen, N_2, which must be converted into biologically available forms (so called fixed N; e.g. ammonia, nitrates, nitrites) in order to be metabolised by living organisms. Nowadays, nearly all the N fixation is achieved through biological and anthropogenic processes (Ciais & Sabine, 2013; Fowler et al., 2013).

Though marginal in the present-day atmosphere, N fixation must have proceeded through natural abiotic processes on the early Earth. One of the most invoked natural abiotic sources is lightning discharges, notably those associated with volcanic activity (Navarro-Gonzalez & Segura, 2005; Navarro-Gonzalez et al., 1998). However, so far, no field evidence of substantial N fixation in volcanic records has been found.

Here we report for the first time on measurements of large levels of nitrates strongly correlated with sulphate and chlorine levels in massive Neogene volcanic deposits, in arid to semi-arid environments. The multi-isotopic composition of those nitrates, in particular the high $\Delta^{17}O$ signatures, demonstrates that a large part of the nitrate forms in the atmosphere, and does not originate from anthropogenic sources, biological sources, or even magmatic emissions. In addition, the slight correlation between the $\Delta^{17}O$ of nitrate and $\Delta^{17}O$ of sulphate confirms that nitrates are linked to large volcanic eruptions.

These volcanic nitrates most likely result from the oxidation of nitrogen oxides formed by volcanic lightning during intense explosive eruptions. Our preliminary estimations show that during a large caldera-forming eruption (volcanic explosivity index (VEI) about 7) up to about 300 Tg of N could be fixed by this mechanism. Our findings represent a unique evidence of the key role potentially played by volcanic lightning in N fixation during geological times, especially on the early Earth when volcanic activity was much more intense.

Keywords: isotopes, oxygen, nitrogen, volcanic lightning, nitrates, nitrogen fixation

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