The multi oxygen isotope analyses on black crust from Sicily highlight the volcanic emission influence from Mount Etna on urban areas

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This study reports on measurements of Δ\(^{17}\)O (derived from the triple oxygen isotopes) in sulphate from black crust sampled in Sicily. Atmospheric oxidants, such as O\(_3\), H\(_2\)O\(_2\), OH and O\(_2\) carry specific \(^{17}\)O-anomalies, which are partly transferred to the sulphate during sulphur gas (e.g. SO\(_2\)) oxidation. Hence, the Δ\(^{17}\)O in sulphate can be used as a tracer of sulphur oxidation pathways. So far, this method has been mostly applied on sulphate from aerosols, rainwaters, volcanic deposits and ice cores. Here we propose a new approach, that aims to investigate the dominant oxidants of gaseous sulphur precursors into sulphate extracted from black crust material. Black crusts are mostly found on building/monument/sculpture and are the result of the reaction between sulphur compounds (SO\(_2\), H\(_2\)SO\(_4\)) and carbonate (CaCO\(_3\)) from the substrate, which leads to the formation of gypsum (CaSO\(_4\), 2H\(_2\)O). Sicilian black crust from sites under different emission influences (anthropogenic, marine and volcanic) were collected. Multi oxygen and sulphur isotope analyses were performed to better assess the origins of black crust sulphate in these different environments. This is crucial for both a better understanding of the sulphur cycle and the preservation of historical monument.

Multi sulphur isotopes show mostly negative values ranging from -0.4 ‰ to 0.02 ‰ ± 0.01 and from -0.59 ‰ to 0.41‰ ± 0.3 for Δ\(^{33}\)S and Δ\(^{36}\)S respectively. This is unique for natural samples and different from sulphate aerosols measured around the world (Δ\(^{33}\)S > 0‰). This tends to indicate that sulphate from black crust is not generated by the same processes as sulphate aerosols in the atmosphere. Instead of SO\(_2\) oxidation in the atmosphere, dry deposition of SO\(_2\) and its oxidation on the substratum is preferred. The multi oxygen isotopes show a clear dependence with the geographical repartition of the samples. Indeed, black crusts from Palermo (the biggest Sicilian city) show small \(^{17}\)O-anomalies ranging between -0.16 ‰ to 1.02 ‰ with an average value of 0.45 ‰ ± 0.26 (n=12; 2σ). This is consistent with Δ\(^{17}\)O values measured in black crust from the Parisian Basin (Genot et al., 2020), which are also formed in an environment influenced by anthropogenic and marine emissions. On the other hand, samples from the eastern part of the Mount Etna...
region, which are downwind of the volcanic emissions, show the highest $^{17}$O-anomalies ranging from 0.48 ‰ to 3.87 ‰ with an average value of 2.7 ‰ ± 0.6 (n=11; 2σ).

These results indicate that volcanic emissions influence the oxygen isotopic signature of black crust sulphate. In standard urban areas, SO$_2$ deposited on the substratum is mostly oxidised by O$_2$-TMI and H$_2$O$_2$ to generate the black crust. Yet, under the influence of volcanic emissions, O$_3$ may play the main role in the SO$_2$ oxidation.