

## Geochemical variability of the mantle beneath São Tomé Island (Cameroon Volcanic Line)

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São Tomé is an intraplate oceanic island belonging to the Cameroon Volcanic Line (CVL), a 1600 km long alkaline volcanic chain that straddles continental and oceanic lithosphere. This line doesn't fit in the age distribution pattern of the classical plume model, and has been object of intense debate regarding its source of magmatism. Here we look at São Tomé elemental geochemistry in light of the main volcanic cycles that we established: the Mizambú Volcanic Complex (CMZ: 6 -8 Ma), the Ribeira Afonso Volcanic Complex (CRA: 2.5 - 5 Ma) and the São Tomé Volcanic Complex (CST: < 1.5 Ma). Major and trace element geochemistry support the alkaline, sub-saturated character of the basalt - phonolite suite. Primitive basalts (Mg#>57; Ni>170 ppm) REE and incompatible element patterns, are typical of OIB, with strong enrichment of LREE relative to HREE [(La/Yb)<sub>N</sub> = 16.01 - 31.95], K negative anomaly, and Nb, Ta enrichment relatively to LILE (e.g. Ba/Nb = 8.55 ± 1.25 vs. 9.79<sub>chm</sub>), and other HFSE such as Th and U (e.g. Th/Ta = 1.22 ± 0.12 and Nb/U = 49.65 ± 5.23 vs. 2.07<sub>chm</sub> and 34<sub>chm</sub>), features normally related to the contribution of a HIMU component in the mantle source. Both patterns show an increasing enrichment towards the younger complex (CST) suggesting decrease in partial melting degree with age. Accordingly, calculated melting degree (17 % in CMZ to 8 % in CST), temperature (CMZ = 1571 °C, CRA = 1431 °C, CST = 1396 °C) and pressure /depth (CMZ - 36/112, CRA - 30/93, CST - 27/84 in kbar/km) of magmatic extraction show decreasing through time. These features reflect inter-complex source chemical variations and melting processes. However they do not explain intra-complex variations found in some incompatible elements ratio, larger in CST than in the other volcanic complexes. These intra-complex variations can be justified by sampling of mantle source horizontal heterogeneities, that seem to increase with decreasing age. This study identified mantle heterogeneities and variations in the chemical temporal evolution of the island compatible with a upward moving melting front, which does not necessary imply the presence of a mantle plume beneath S. Tomé Island. It also emphasizes the necessity of further investigation supported by isotope data for each volcanic cycle.

## Impact of sulfide oxidation on continental chemical weathering budgets and global carbon cycle

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Riverine transport of chemical weathering products is one of the most efficient mechanisms of mass transfer at the Earth surface. It is a key process in global biogeochemical cycles, especially in the surface carbon cycle. Chemical weathering reactions neutralize atmospheric CO<sub>2</sub>, the main weathering agent on Earth at present, to produce alkalinity and cations that are then transported to the oceans and eventually buried as carbonate for hundreds Ma. However, involvement of other weathering agents (e.g. sulfuric acid, hydrochloric acid, nitric acid) in weathering systems may affect both alkalinity and weathering budgets as there is no atmospheric CO<sub>2</sub> consumed [1]. Sulfuric acid is of particular interest since it is naturally produced by volcanoes and oxidation of sulfide minerals. Unfortunately, the contribution of sulfuric acid to weathering budgets remains poorly quantified. Identification of riverine sulfate sources is still challenging and the coupled use of δ<sup>34</sup>S and δ<sup>18</sup>O of dissolved sulphate or the use of δ<sup>13</sup>C of DIC in well constrained systems have proved to be powerful tools [1-3]. Results from a few river systems (Mackenzie basin, Ganges-Brahmaputra basin, Southwest China and Taiwan) suggest that the global ocean delivery of sulfide-derived sulfate and associated chemical weathering fluxes are significantly underestimated. Indeed, calculated fluxes of sulfide oxidation at those sites already account for 55-75% of the global estimate of sulfide-derived sulfate. Associated chemical weathering budgets show that more than 60% of the DIC discharged to the ocean from those sites is ancient sedimentary carbon from carbonate and not atmospheric carbon. Subsequent carbonate precipitation in the oceans of these weathering products might thus release more CO<sub>2</sub> in the atmosphere-ocean system than that consumed by continental weathering. Controls on sulphide oxidation rates will be discussed.

[1] Calmels *et al.* (2007) *Geology* **35**, 1003-1006. [2] Galy & France-Lanord (1999) *Chem. Geol.* **159**, 31-60. [3] Li *et al.* (2008) *EPSL* **270**, 189-199