Origin of heterogenite (CoOOH) as illustrated by rare earth element fractionation

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The Katanga Copperbelt (DR Congo) hosts around half of the world's known reserve of mineable cobalt. Heterogenite (CoOOH) is the most abundant oxidized cobalt mineral in this belt. It was ultimately derived from the oxidation of carrolite ($CuCo_2S_4$), during a Pliocene weathering event. The latter led to heterogenite concentration in the near-surface, as "cobalt cap" [1]. However, the detailed processes leading to the formation of heterogenite are not yet well constrained. Here, these processes are investiguated through the study of REE distribution, which is an underexplored but powerful tool to understand the formation of oxyhydroxides [2]. Indeed, since these elements behave as a coherent group, REE fractionation can be used as tracer of processes. In this way, studied heterogenite REE patterns display two major types: (i) the first type is Middle REE enriched, with negative cerium anomaly and relatively low REE content; (ii) the second one is Light REE enriched, without cerium anomaly and with higher REE content.

Weathering processes leading to heterogenite mineralisation mainly consist of water-rock equilibrium. At high Co activity, heterogenite precipitates at near-neutral pH as well as manganese oxide (i.e., pyrolusite). REE are mainly fractionated in between these two solid phases: heterogenite REE patterns are clearly the opposite ones of manganese oxides. As cobalt activity decreases, heterogenite stability field shifts to alkaline pH. In these conditions, REE speciation is mainly driven by carbonate complexation, resulting in the formation of the heterogenite type with a LREE enriched REE pattern.

Both REE signatures are consistent with the formation of heterogenite in a two-step *per descensum* model, in which this mineral (i) forms as residual deposits - similar to laterite - in association with Mn oxide, in the immediate near-surface environment, and (ii) is deposited from a carbonate-bearing fluid, due country rock dissolution, in deeper part of the oxidation profile.

[1] Decrée *et al.*. (2010), *Mineralium Deposita* 45, 621-629. [2] Pourret & Davranche (2013), *Journal of Colloid and Interface Science* 395, 18-23.

Crustal versus source processes on the Northeast volcanic rift zone of Tenerife, Canary Islands

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The Miocene-Pliocene Northeast Rift Zone (NERZ) on Tenerife is a well exposed example of a major ocean island volcanic rift. We present elemental and O-Sr-Nd-Pb isotope data for dykes of the NERZ with the aim of unravelling the petrological evolution of the rift and ultimately defining the mantle source contributions.

Fractional crystallisation is found to be the principal control on major and trace element variability in the dykes. Differing degrees of low temperature alteration and assimilation of hydrothermally altered island edifice and/or sediments elevated the primary $\delta^{18}O$ and the Sr isotope composition of many of the dykes, but had little to no discernible effect on Pb isotopes. Minor degrees of sediment contamination, however, may be reflected in the Pb isotope composition of a few samples that plot to slightly higher $^{207}Pb/^{204}Pb$ values.

Once the data are screened for alteration and shallow level contamination, the underlying isotope variations of the NERZ reflect a mixture essentially of Depleted Mid-Ocean Ridge-type Mantle (DMM) and young High-μ (HIMU, where $\mu = {}^{238}U/^{204}Pb$)-type mantle components. Furthermore, the Pb isotope data of the NERZ rocks ($^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ range from 19.591-19.838 and 15.603-15.635, respectively) support a model of initiation and growth of the rift from the Central Shield volcano (Roque del Conde), consistent with latest geochronology results [1]. The similar isotope signature of the NERZ to both the Miocene Central Shield volcano and the Pliocene Las Cañadas central edifice suggests that the central part of Tenerife Island was derived from a mantle source of semi-constant composition through the Miocene to the Pliocene. This can be explained by the presence of a discrete "blob" of HIMU material, ≤ 100 km in vertical extent, occupying the melting zone beneath central Tenerife throughout this period. The most recent central magmatism on Tenerife appears to reflect greater entrainment of DMM material, perhaps due to waning of the blob with time.

[1] Carracedo *et al.*. (2011) *Bull. Geol. Soc. America,* **123,** 562-584.

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