Modeling of copper and cobalt fractionation in soils: A useful tool to predict edaphic factors influence upon Cu and Co accumulation in two metallophytes

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In Katanga (Dem. Rep of Congo), an original and unique metallophyte flora takes place on extremely copper and cobalt rich soils, deriving from Cu and Co outcrops. Among the present species, some are able to accumulate extremely high concentrations of Cu and Co in shoot, which are considered as Cu and Co hyperaccumulators. Still non-explained high variations of Cu and Co concentrations in shoot have been highlighted within this copper and cobalt flora. A good comprehension of the Cu and Co accumulation would go through a characterization of the Cu and Co speciation and bioavailability in soil. The objectives of the present study are to (i) examine variations of Cu and Co speciation in soils and Cu and Co concentrations in plants, (ii) determine which edaphic factors influence the Cu and Co accumulation in plants, and (iii) highlight the Cu and Co bioavailable fraction.

Two species have been selected as biological model: *Anisopappus chinensis* and *Crepidorhopalon tenuis*. Plant samples and soil samples (n=146) have been collected in seven pedogeochemicaly contrasted sites. Concentrations of Cu and Co in plants have been measured using ICP-MS and speciation modeling (WHAM 6.0) was performed to estimate Cu and Co speciation in soils. Huge variations in the Cu and Co fractionation in soils, as well as huge variations in the Cu and Co concentration in plants have been highlighted among and within the different sites and populations. Copper is mostly bind to organic matter (OM) and Fe oxides. Oppositely, Co occurs as ionic species and has strong affinity for Mn oxides. Copper accumulation variations are mostly explained by Cu adsorbed onto Mn oxides whereas Co accumulation variations are mostly explained by Co ionic species and Co adsorbed by OM. Bioavailable Cu and Co concentrations seem to correspond not only to the Cu and Co ionic species content but also part of linked Mn oxides and OM, for Cu and Co, respectively. Eventually, this latter fraction can be mobilized and / or absorbed by plants.

Why do some andesite stratovolcanoes evolve to erupt rhyolite and/or rhyodacite and others do not?

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If rhyolite/rhyodacite liquid commonly forms as an interstitial melt in crystal-rich andesite/dacite magmas in sub-volcanic chambers in the upper crust, an outstanding question is why segregation and eruption of the interstitial liquid occurs in some cases but not others. An example of this variation is seen among five andesite volcanoes along the western Mexican volcanic arc, spanning >150 km of arc length; three have explosively erupted rhyodacite and/or rhyolite (Volcáns Ceboruco, Tepetiltic and San Juan) and two have not (Volcáns Sanganguey and Tequila). Hypotheses for why some andesite volcanoes erupt rhyolite/rhyodacite and others do not include: (1) the effect of mafic magma recharge, which drives the differentiating magma back to more evolved compositions and prevents the formation and extraction of interstitial rhyolitic melt; (2) segregation of interstitial melt from a crystallizing magma requires compaction and thus crystal-rich (50-70%) conditions (e.g., Dufek and Bachmann, 2010) and/or gas filter-pressing (e.g., Sisson and Grove, 1999), and the time interval in which the magma spends under these optimal conditions for melt segregation may be variable, thus limiting the ubiquity of this process; and (3) extraction of interstitial melt may be most efficient during partial melting (vs. crystallization) because of the increase in volume associated with the crystal-liquid phase change, which causes the interstitial melt to be over-pressurized (vs. under-pressurized); however, this requires an influx of hot new magma into a sub-solidus system to transfer the heat and volatiles necessary to drive partial melting of adjacent wallrock. In this study, we use a combined geochemical and $^{40}Ar/^{39}Ar$ geochronology study to test which of the three models best explains the eruptive history of Volcán Tepetiltic, an andesitic stratovolcano (~42 km^3) that explosively erupted zoned crystal-poor rhyodacite-rhyolite (4-8 km^3) after a 180 k.y. hiatus in volcanic activity from the central vent. The explosive eruption was synchronous with an episode of basaltic andesite volcanism (~9 km^3) from three vents along the flanks Volcan Tepetiltic. Thus all three mechanisms can be tested against each other.

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DOI:10.1180/minmag.2013.077.5.12