Role of carboxylates released by microorganisms and roots of alpine pioneer plants in mobilising phosphorus and metal cations during early soil formation

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In the framework of an interdisciplinary study on initial soil formation along a deglaciation chronosequence, we examined the role of carboxylates in mobilising P and metal cations, in particular at the early stages of soil development, where no or only little soil organic matter has built up.

At selected sites with 6, 70 and 128 year old soils, soil solution was collected in-situ using micro suction cups, differentiating between the rhizosphere of specific plants and bulk soil. At the youngest site, carboxylates were enhanced in all rhizospheres exhibiting plant specific patterns, while phosphate and metal concentrations were increased in rhizospheres at all soil ages. Overall and independent of soil age, soil type and sampling date, net mobilisation of P and metals correlated with the net production of carboxylates, with malate, tartrate, oxalate and citrate playing specific roles.

A comparison with laboratory experiments on P mobilisation by plants and on granite dissolution by bacterial and fungal isolates, suggests that both bacteria and fungi are important for initial nutrient mobilisation. Bacteria, releasing mainly oxalate, are efficient in mobilising metals, while fungi, releasing mainly citrate and malate, are able to mobilise both phosphate and metals [1,2]. Once first plants appear, they seem to strongly increase nutrient release from minerals in their rhizosphere with root exudation of carboxylates probably playing a two-fold role. On one hand it stimulates microbial activity, on the other hand contributes directly to weathering, in particular by means of ligands that are not produced by microorganisms such as tartrate.

[1] Frey, Rieder, Brunner, Plötze, Koetzsch, Lapanje, Brandl & Furrer (2010), Appl. Env. Microbiol. 76, 4788-4796. [2] Brunner, Plötze, Rieder, Zumsteg, Furrer & Frey (2011), Geobiology 9, 266-279.

Carbonate, not carbonatite, at Villamayor volcano (Calatrava Volcanic District, Central Spain)

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The Villamayor Volcano (~9 Ma) represents the oldest volcanic activity in the Calatrava Volcanic field, Central Spain. The products of this activity have been classified in literature as leucitites despite a minor presence of modal leucite (<5 vol. %), the low K_2O content (<4.3 wt) and the low K_2O/Na_2O ratio (<1.8). The lava flows of this small volcano are strongly porphyritic with the presence of subhedral to euhedral olivine phenocrysts. A recent paper (Humphreys *et al*.., 2010) classify these rocks as leucitites and considers the olivine phenocrysts as mantle debris. The carbonate inclusion is considered to represent the relict of Ca-carbonatitic magma crystallizing calcite and, in one single case, aragonite. We challenge the Humphreys *et al*. (2010) hypothesis for several reasons:

1) The olivine crystals cannot be considered mantle xenocrysts because of their low Forsterite content (72-89 mol% Fo) and euhedral to subhedral shape..

2) The rare mica associated with carbonate within hollow olivine has relatively low Mg# (73-84 vs. 89-95).

3) The carbonate present in the Villamayor mantle sources, in equilibrium with the leucititic magma cannot be Mg-free as the Ca-carbonate (calcite and aragonite) found within the hollow olivine crystals. The calculated leucitite composition (obtained subtracting 30% olivine, considered xenocrysts by Humphreys *et al*.., 2010) is MgO-poor (0.52 wt%). This is not compatible with a mantle melt.

4) The SrO content of the carbonate inclusions is generally low (generally <0.20 wt) and never exceeding 0.54 wt%, values, compatible with sedimentary carbonates.

We propose a sedimentary source for the carbonate inclusions. In our model sedimentary carbonate is scraped off the country rocks and partially digested by the ultrabasic melt. When in contact with the carbonate xenocrysts the olivine growth is stopped, producing the typical hollow body euhedral shape of the Villamayor olivine.

[1] Ref: Humphreys *et al*.. (2010) Geology, 38, 911-914.

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