Mineral synthesis using the coupled dissolution-reprecipitation route

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Replacement reactions ('pseudomorphism') are common in nature, occurring under a large range of conditions (e.g., replacement of pentlandite by violarite in the supergene zone of ore deposits; leucite by analcime under hydrothermal conditions). Replacement reactions of this kind are often assumed to proceed by solid-state diffusion of the metal ions through the mineral. However, Putnis and co-authors have recently suggested that many mineral replacements are the product of coupled dissolution and reprecipitation (CDR) reactions: the replaced mineral is fully dissolved into a fluid, and this dissolution is tightly coupled with the precipitation of the replacing phase across the reaction front. The kinetics and chemistry of the CDR route are fundamentally different from solid-state diffusion: (i) reaction kinetics is not simply temperature dependant, but also depends upon the solution chemistry (e.g., pH, fO_2(g), metal and ligand concentrations). The kinetics of reaction is also dependant upon the transport properties of the fluid and the texture of the starting material, because the fluid needs to access the reaction front. (ii) As the fluid is transporting metals and other elements to and from the reaction front, the chemistry of the product can be different from that of the precursor, and the volume of reaction cannot be estimated simply by comparing the molar volumes of the product and precursor. The product usually displays high porosity, even if the product has higher molar volume than the precursor.

Two thiospinels, violarite $(Ni,Fe)_3S_4$ and linnaeite Co_3S_4 were synthesized using pentlandite $(Fe,Ni)_9S_8$ and cobaltpentlandite Co_9S_8 as precursors. The Fe/Ni ratio of violarite can be adjusted by varying the reaction conditions, e.g., temperature (125-145 ºC), pH (2.90, 3.90, 5.00), and precursor stoichiometry ($(Fe_xNi_{1-x})_9S_8$, x=0.4, 0.5, 0.55, 0.6). Synthesis times range from 5 to 20 days, compared to the traditional dry synthesis route for violarite that requires three months annealing to obtain a product of only 72 ± 5 wt % purity. This synthesis route is ideal for preparing compounds with low thermal stabilities (< 500 ºC).

We also studied the effect of pH on the transformation of leucite $KAlSi_2O_6$ to analcime $NaAlSi_2O_6 \bullet H_2O$, showing that the reaction mechanism and the texture of the product change when pH goes from acidic and near neutral to strongly basic.

[1] Putnis, A. (2002) *Min. Mag.* **66**, 689-708.

Sampling an active continental paleo-margin: A LA-ICP-MS U-Pb zircon study from the Adrar des Iforas (Mali)

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The Tuareg Shield results from the amalgamation, during the Pan-African orogeny, of more than twenty terranes comprising Neoproterozoic juvenile oceanic terranes and reworked or well-preserved Archean and Paleoproterozoic crustal blocks. All these amalgamated terranes are limited by trans-continental N–S shear-zones. Their main relative movements resulted from a northern transpressional tectonic escape due to their squeezing between the West African craton (WAC) to the west and the East Saharan craton to the east. This configuration hampers tectonic correlations through the shield, but gives rise to major issues including the way along which amalgamation of the terranes occurred, their respective tectonometamorphic evolution and their origin. In order to help unravel the tectonometamorphic evolution of the westernmost part of the shield, we performed LA-ICPMS U-Pb zircon geochronology on samples from key lithologies collected through the Adrar des Iforas area (Mali). Samples were selected in order to represent a Neoproterozoic Andean-type active margin developed during subduction of the WAC beneath the Iforas terrane of the Tuareg Shield. In the Central Iforas Belt, arc-related calc-alkaline magmatism occurred as early as 716±6 Ma and was coeval with the 710-730 Ma old Tilemsi intraoceanic arc. Subduction-related magmatism persisted until 634±8 Ma and possibly down to 623±6 Ma, the age of the Tafeliant metadacite. Calc-alkaline batholiths were emplaced into a pre-Panafrican gneissic basement containing Paleoproterozoic units (such as the Tafeliant syenitic gneiss dated at 1966±9 Ma) and Archean components (inheritance in granitoids at *c.* 2.4-2.5 Ga and up to 2.8 Ga). Emplacement of syn-kinematic granitic plutons, associated to collision with the WAC, occurred at 604±5 Ma, whereas late-kinematic emplacement of the central batholith is dated at 599±3 Ma. East of the Adrar fault, the basement of the Eastern Iforas Belt contains Paleoproterozoic granitoids (Tin Essako orthogneiss dated at 2020±5 Ma), which were intruded by pre-kinematic granitoids such as the 630±6 Ma Tamaradant metadiorite. This suggests a possible synchronism of ante-collisional events on either sides of the Iforas Granulitic Unit.