Acessing the surface area of natural nanoparticles

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Information on the reactive surface area of natural samples is essential for the application of surface complexation models (SCM). The PO_4-CO_3 interaction on iron oxide is used to quantify the reactive surface area of soil particles. In the approach, phosphate is used to act as probe ion in natural samples brought at well-chosen solution conditions enforced by a 0.5 M $NaHCO_3$ extract solution. This matrix suppresses the influence of Ca^{2+} ions, desorbs organic matter (further stimulated by adding active carbon), and fixes the pH and ionic strength, leading to dominance of the PO_4-CO_3 interaction. Samples were equilibrated for solid/solution ratios between 1/6 and 1/300.

The CO_3-PO_4 interaction is calibrated by studying it for goethite, using the CD model [1] with an Extended Stern (ES) double layer option. The CD values are independently obtained from MO/DFT optimized geometries of iron-carbonate and -phosphate complexes and are additionally corrected for dipole orientation effects [2]. The surface speciation derived from the data analysis of the CO_3-PO_4 interaction on goethite agrees with ATR-FTIR spectroscopy.

Application to data of natural samples shows SA values from ~1000-10.000m^2/kg soil. The SA correlates to the organic mater (OM) content of the samples, which is due to the correlation of OM with the Fe oxide fraction, suggesting that the natural oxide particles are embedded in an OM matrix. Scaling of SA on the experimental soil oxide contents shows high values for the specific surface area (~200-900 m^2/g extracted oxide), pointing to the presence of nanometer-sized particles (~1-5 nm).

References

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In situ Hf and O isotopic data from Archean zircons of SW Greenland

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We have obtained new, coupled U-Pb, O and Hf isotopic data from Archean TTG suites in Southwest Greenland in order to explore mechanisms for Archean tonalite genesis and crust formation. The dataset comprises analyses of >250 zircon spots from 11 rocks ranging in age from 3.85 Ga to 2.55 Ga, including the most ancient tonalites of the Itsaq Gneiss Complex through to late Archean granitoids of the Qôrqut Granite Complex. All grains were characterized by CL, reflected and transmitted light imaging prior to analysis. U-Pb ages were determined using either SHRIMP RG or SHRIMP II; $^{18}O/^{16}O$ ratios were measured on the same zircon spots using SHRIMP II in multi-collector configuration; $^{176}Hf/^{177}Hf$ data was subsequently acquired by LA-MC-ICPMS (ANU Neptune).

Zircons from the oldest, ca. 3.85 Ga, tonalites record $\delta^{18}O$ compostions within 1‰ of mantle values ($\delta^{18}O$ mantle = 5.3 ± 0.3 [e.g. 1]) and initial ε_{Hf} values largely within ±1 epsilon unit of chondritic composition (calculated using $\lambda^{176}Lu = 1.867x10^{-11}yr^{-1}$). These narrow, mantle-like, O–Hf fields contrast markedly with results from studies of Phanerozoic suites [2, 3], which show diverse Hf-O isotopic arrays, displaced from mantle compositions.

Hf isotopic compositions of zircons from the youngest sample analysed, the 2.55 Ga Qôrqut Granite Complex (initial $\varepsilon_{Hf} \approx -25$), are in agreement with earlier Pb isotopic studies [4] suggesting the origin of the Complex by the remelting of >3.7 Ga crust. The O isotope data from this suite however lie 1-2‰ below mantle compositions, again in contrast with results for Phanerozoic suites.

A striking feature of the overall dataset is the absence of high (>7‰) $\delta^{18}O$ values highlighting the lack of recycled supracrustal material in the genesis of the TTG. Of particular note is the prevalence of low $\delta^{18}O$ values, with 4 out of 11 samples, with ages from 3.7 to 2.55 Ga, having compositions 1-3‰ below mantle values. Low $\delta^{18}O$ values are a relatively rare feature in granitic suites (e.g. [1]) and typically result from hydrothermal alteration by surface waters, in some cases enhanced by glaciation. The presence of low $\delta^{18}O$ in these mid-crustal level Archean granitoids is unexpected and may reflect different surface conditions and hence fluid compositions in the Archean.

References

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