Single-grain bulk Hf and *in situ* O isotopes as indicators of crustal recyling in magmas of the northern Arabian-Nubian Shield

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We present new in-situ (SIMS) oxygen isotopic ratios $(\delta^{18}O_{(Zrc)})$ and bulk (MC-ICP-MS) ^{176}Hf / ^{177}Hf (Hf_(Zrc)) for single zircons from a series of basic to felsic plutons (n=12) of post-collisional calc-alkaline (~635-590 Ma) to within-plate alkaline-peralkaline (~607-580 Ma) suites of the northern Arabian-Nubian Shield (Sinai Peninsula, Egypt, and Southern Israel). $\delta^{18}O_{(Zrc)}$ and Hf_(Zrc) measurements systematically were carried out on the same zircon grains, thus providing a robust set of combined $\delta^{18}O_{(Zrc)}$ -Hf_(Zrc) data for these rocks.

In-situ $\delta^{18}O_{(Zrc)}$ values span the range from 3.8 to 14.2‰ (±0.1 to 0.25; 2 σ) and generally compare well with previously determined bulk $\delta^{18}O_{(Zrc)}$ but in some cases identify the presence of different components within the zircon population analyzed here. Coupled with previously determined U-Pb ages, these are inferred to be xenocrysts (~770 Ma and ~900 Ma) characterized by low $\delta^{18}O_{(Zrc)}$ of 3.8-4.4‰ within two plutons of ~630 Ma and $\delta^{18}O_{(Zrc)}$ =5.5-6.6‰.

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m Hf}_{(Zrc)}$ shows a large spread of $\epsilon_{Hf}(t)$ varying between +5.4 and +17.7. T_{DM} model ages span the interval of 650-1200 Ma. Some of these model ages thus correspond to older reservoir ages than the so far accepted ~1000 Ma for this part of the ANS [1]. In general ${
m Hf}_{(Zrc)}$ correlates well with $\delta^{18}O_{(Zrc)}$, with lower but positive zircon $\epsilon_{Hf}(t)$ matching higher $\delta^{18}O_{(Zrc)}$.

Three zircon O-Hf groups are identified: (a) moderately high to high $\delta^{18}O_{(Zrc)}$ with low (but positive) $\epsilon_{Hf}(t)$; (b) mantle-like $\delta^{18}O_{(Zrc)}$ (5.3±0.6‰; 2σ [2]) with intermediate $\epsilon_{Hf}(t)$; (c) very low $\delta^{18}O_{(Zrc)}$ (3.8-4.6‰) with high $\epsilon_{Hf}(t)$.

These groups define three different components involved in the generation of the ANS post-collision calc-alkaline to within-plate alkaline-peralkaline magmatism. Group b reflects partial melting of lower crust material, while juvenile upper felsic crust assimilation is inferred for group a. The peculiar group c includes xenocrysts from two plutons and magmatic zircon from another two plutons and may reflect hydrothermally altered basaltic crust that was subducted and assimilated by some of the ANS magmas. It is interesting to note that the highest $\varepsilon_{Hf}(t)$ in this group correlate with T_{DM} model ages close to the U-Pb ages, thus implying very rapid generation, subduction, and assimilation of the basaltic crust.

References

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Sulfur saturation of Etna Basalt at 200 Mpa: Experimental setup and first results

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The amount and composition of volatile components in magmatic systems affect significantly magma degassing and control the partitioning of volatile components between melt and fluid phase on pressure release.

This study is focused on the solubility of S in natural Etna basalt at high temperatures (up to 1200 °C) and 200 MPa. Here we report the experimental setup for high temperature experiments and first results.

Sulfur is known to be a very aggressive component limiting the application of experimental approaches that use noble metal capsules, especially Pt and AuPd. Therefore, we applied two methods: experiments in gold capsules at 1050°C and in olivine capsules at T>1050°C. The olivine capsules are made of single crystal olivines (natural St. Carlos olivine) inserted into an outer $Au_{80}Pd_{20}$ capsule. Native S, palladium sulphide (PdS) and pyrrhotine (FeS) were used as sulfur sources in the experiments.

The experiments were conducted in internally heated pressure vessels at 200 MPa in a range of redox conditions from relatively reducing at quartz-fayalite-magnetite (QFM) oxygen buffer to oxidizing conditions (~ QFM+4).

The experiments at 1050°C show that S concentration in hydrous (5 wt.% H₂O) basaltic melt at saturation with Sbearing mineral phase (anhydrite at oxidizing conditions and pyrrhotite at reducing conditions) decreases from ~6000 ppm to ~2000 ppm with decreasing fO_2 . This dramatic 3-fold decrease in S content of the basalt is related to the change in S speciation from sulfate (S⁶⁺) to sulfide (S²⁻) with reduction of the system. The transition of S⁶⁺ to S²⁻ occurs in a very narrow range of fO_2 from QFM+2 to QFM+0.5.

Glasses obtained from experiments at 1200°C are in equilibrium with FeS and/or PdFeS phases and content 600 to 2000 ppm sulfur. Furthermore, these glasses are enriched in MgO due to reequilibration with MgO-rich olivine. Water concentrations of H₂O-presaturated basaltic glasses decreased from 5 wt.% to 2.8 wt.%, indicating additional redox reactions inside the capsules, presumably interaction with host olivine. Further improvement of this experimental approach is required to better control the experimental conditions in the capsules.