

A comparison of mm scale resolution techniques for sediment core analysis

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To study high-frequency variability in the Arabian Monsoon intensity, laminated sediments from the oxygen minimum zone (200-1200m) of the Arabian Sea offer a high-resolution climate archive [1]. The chemical signature which is used to reconstruct past climate can be obtained using several different analysing techniques. In the presented study a 5.3 m long sediment core from the northern Arabian Sea (GeoB12309-5: 24:52.3°N; 62:59.9°E, 960 m water depth), covers the past 4,900 cal yrs BP. The XRF core scanner data show highly varying signals in the upper 1.6 m core depth. Based on these results and radiograph images, samples were taken for LA-ICP-MS and ICP-MS/OES analysis.

The big advantages of analysing a sediment core via XRF core scanning are non-destruction and speed, but only relative variations for chemical elements are obtained and not element concentrations. The LA-ICP-MS methods is quasi non-destructive, you obtain element concentrations but is more time consuming. The most precise, but also most time consuming methods for main and trace element analysis are the ICP-MS/OES techniques after full acid digestion.

Results from all 3 methods show similar chemical patterns at distinct sediment structures (e.g. turbidites) for Ca, Rb and Sr. However, the comparability between the 3 methods is worse for Al, K, Ti, Fe and Zr. The particle size, water content of the sediment and surface roughness highly influences the XRF method, to some extent also the LA-ICP-MS technique. These results suggest that the soft sediment cores including its overall quality and surface conditions limit the ability of the sub-mm scale XRF scanning method to receive reliable data for Ca, Rb and Sr. However, the LA-ICP-MS technique as it was used here shows problems with long term drift, hence making it very difficult to accurately compare the 3 high resolution methods. Due to the relatively large amount of sediment digested, the ICP-MS/OES method delivers the most accurate results which are assumed to best serve as input data for frequency analysis.

[1] Von Rad *et al.* (1999) *Quat. Res.* **51**, 39-53.

Zircon solubility in Na-Si-Al-O-H fluids by *in situ* SR-XRF analysis

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The geochemical budget of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta) in rocks is largely controlled by accessory phases such as zircon or rutile. Thus, the mobility of HFSE during processes in the Earth's crust and mantle is closely linked to solubility and stability of these phases. Fluid composition appears to be the most important parameter because it may drastically affect the complexation of HFSE. Earlier studies ([1],[2]) on rutile report enhanced solubility for aqueous fluids with Na₂Si₃O₇ (NS3) or NaAlSi₃O₈. Complexing of Ti with alkalis and silica (siloxan groups) dissolved in the fluid has been suggested as an important mechanism to explain these high solubilities. A similar mechanism for enhanced solubility can be expected for the zircon-hafnon series.

Synthetic zircon was equilibrated with fluids containing Na₂Si₃O₇, Na₂Si₃O₇ + 5 wt% Al₂O₃, or NaAlSi₃O₈ at *T* up to 750 °C and *P* up to 1.5 GPa using hydrothermal diamond-anvil cells. The Zr content of the fluids was determined *in situ* at *P* and *T* by confocal synchrotron radiation μ XRF analysis at beamline L, HASYLAB. At *P* of 450–950 MPa and *T* of 500–750°C, Zr concentrations range from 20 to 90 ppm in H₂O + 10 wt% NS3 fluids. In H₂O + 18 wt% NS3 solutions, they increase to 200 to 500 ppm and drop to 100–150 ppm upon addition of Al. The highest concentrations of up to 1000 ppm were measured in fluids containing 30 wt% NS3. At constant NS3 content, the Zr concentration generally decreases with *P* and increases with *T*. One experiment with zircon *and* hafnon was done to measure Zr-Hf fractionation. At a NS3 content of 27 wt%, a molar Hf/Zr ratio of 2.7 was determined, which indicates significant Hf-Zr fractionation in these fluids. For a fluid with 6 wt% NaAlSi₃O₈ at ~1.45 GPa and 600°C, the XRF signal was at the detection limit, i.e. ~1 ppm Zr or below. These solubility data are qualitatively consistent with those on rutile ([1],[2]) and indicate strong differences in Zr speciation with *P*, *T*, and fluid composition. They represent another example for which efficient complexation of HFSE by siloxan-like units in the fluid is indicated (see also ref. [3]).

[1] Manning *et al.* (2008) *Earth Planet. Sci. Lett.* **272**, 730-737. [2] Antignano & Manning (2008) *Chem. Geol.* **255**, 283-293. [3] Dubrail *et al.* (2011) *MinMag*, this volume.