In situ monitoring of reaction band formation using synchrotron radiation

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Diffusion reaction couple experiments are an essential tool in order to understand corona microstructures and underlying processes in metamorphosed and igneous natural rocks. By employing a heating attachment and synchrotron radiation we monitored the initial and transient stages of an *in situ* reaction rim formation at the nanoscale. Additionally, by miniaturising the experimental setup using thin films we could lower the temperatures and test durations that are usually applied in diffusion couple experiments.

As a model system the reaction between corundum (Al_2O_3) and periclase (MgO) that forms spinel ($MgAl_2O_4$) was chosen. The diffusion couples consisted of single crystal substrates of either (0001) oriented corundum with an amorphous MgO thin film on top or (111) oriented periclase which reacted with an Al_2O_3 thin film. Thin films were produced by laser ablation, and their thickness was always less than 300 nm. Experimental temperatures were varied from 700 to 1000 °C, and test durations ranged from 5 minutes to 3 hours. The texture of the *in-situ* grown spinel, i.e. the crystallographic relationship between substrate and thin film, was subsequently analysed using a four-circle diffractometer to obtain pole figures. As complementary methods to the X-ray diffraction techniques transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed.

At 700 and 800 °C no spinel formation could be observed, but the reaction layers crystallise oriented on the substrate. Spinel formation occurs at a moderate rate at 900 °C, and is rapid at 1000 °C. The time series conducted at 1000 °C points to an interface-controlled reaction regime, i.e. the thickness of spinel grows linearly with time. Microstructures within the spinel, as revealed by TEM, suggest 'counter-diffusion of the cations' as the diffusion mechanism. Diffraction spectra and pole figures show that the spinel crystallises and grows epitactically on and into the substrates.

Delayed response in sedimentary discharge from the Himalaya to the ocean at Milankovitch periods

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The neodymium isotopic composition of marine sediments (ε_{Nd}) is often used as a proxy for past climate changes in paleoceanography studies. However, in some parts of the world ocean, the origin of ε_{Nd} variations in seawater over the last Glacial/Interglacial cycles remains unclear. This is particularly true in the Indian Ocean because of its connections with the Atlantic and the Pacific Ocean waters, and because of the huge Himalayan sedimentary discharge that brings low ε_{Nd} into the ocean. The ε_{Nd} variations could result of changes in the global oceanic circulation or be due to changes in the continental input controlled by continental rainfalls. Here we present a simple technique to discriminate these two interpretations at a given site, based on the correlation of $\delta^{18}O$ and ε_{Nd} seawater signals. We show in-phase records at site SK129-CR2 [1] (Arabian Sea) and out-of phase records at site ODP-758 [2] (Bay of Bengal), suggesting that the two sites have recorded different phenomena through time. Arabian Site fluctuations were interpreted as changes of the thermohaline circulation and Bay of Bengal Site fluctuations as changes on the Himalayan input. As Himalayan rivers input is linked to the Earth's climate variability, we filtered the time series of $\delta^{18}O$ and ε_{Nd} at Site ODP 758 around the three periods related to the three main orbital parameters. We show that the time lag between $\delta^{18}O$ and ε_{Nd}, increases from 1000 to 2000 and then to 7000 years for the 23 ky, 41 ky, and 100 ky filtered signals. To explain the delays between temperature changes recorded by $\delta^{18}O$ and ε_{Nd}, two models were proposed: diffusive [3] and erosion [4] models of Himalayans. For the first time, we demonstrate that a geochemical dataset can record and thus constrain the time lag in the erosional response of an active mountain belt to climate change.

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