

## Oxygen diffusion "fast-paths" in titanite single crystals

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Natural titanites are far from perfect ideal crystals. In addition to point defects, which affect oxygen lattice diffusion, there might be line- or planar defects along which fast diffusion could occur. While experimentally measuring oxygen lattice diffusion in titanites, we found that almost all of the oxygen diffusion profiles for natural titanites departed from the complementary error function solution expected for simple lattice diffusion, instead having a "tail" reaching deeper into the samples. For both dry and hydrothermal experiments,  $^{18}\text{O}$  was used as the diffusant. In dry experiments, the source material was  $^{18}\text{O}$ -enriched  $\text{SiO}_2$  powder, while  $^{18}\text{O}$ -enriched water was used for the hydrothermal experiments. Diffusive uptake profiles of  $^{18}\text{O}$  were measured in all cases by nuclear reaction analysis (NRA) using the  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$  reaction.

The diffusion "tails" can be explained by either parallel planar defect or one-dimensional "pipe" models. In our experiments, different sizes of "tails" (with varying  $^{18}\text{O}$  concentrations) were observed. Under the same temperature and pressure conditions, the sizes of tails were affected by two factors: the diffusion duration and the defect density. For the same experiment duration, the higher the defect density, the larger the "tail"; for the same defect densities, the longer the diffusion duration, the larger the "tail".

The oxygen diffusion rates in the fast-paths were obtained by traditional graphical analysis methods, using the Whipple-Le Claire equation (for 2-D defects) assuming that the width of the fast path is 1nm. Two Arrhenius relations were obtained for the fast-path diffusion, one for experiments under dry conditions, the other for hydrothermal conditions:

$$D_{\text{dry}} = 4.03 \times 10^{-2} (\text{m}^2/\text{sec}) \exp(-313 \pm 22) (\text{kJ}/\text{mol}) / RT$$

$$D_{\text{wet}} = 3.48 \times 10^{-7} (\text{m}^2/\text{sec}) \exp(-219 \pm 39) (\text{kJ}/\text{mol}) / RT$$

AFM imaging of HF etched titanite surfaces suggest that the diffusion fast-paths might be either parallel planar defects or parallel pipe defects.

In addition to the lattice diffusivity, the presence and 3-D distribution of any fast paths—and the diffusivity in these paths—is important to the bulk closure properties of single crystals. For titanites, AFM imaging showed that the fast-paths may not be interconnected at a length-scale comparable with the crystal dimension, so they may not have a dramatic effect on bulk closure properties.

## Effects on a basaltic surface of an impact-derived hot fluid bed (Kirbet-el-Umbachi, Syria)

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Evidence for widespread dispersion of impact ejecta micro-debris at ca. 4-kyr-BP was recently investigated from archives in lands and seas. Regional diversity of surface effects linked to the ejecta fallout that range from moderate heating to localized melting raised questions about the nature and composition of the impact cloud when reaching the soil surface. The most extensive melting caused by the ejecta fallout has been reported as a unique bone-rich basaltic breccia over ten square metres at Kirbet-el-Umbachi (Syrian desert). The aims of the present study are to elucidate composition of the ejecta, its interaction with the host materials, and its significance in terms of impact-related processes. This is achieved by *in situ* analytical characterization based on high resolution SEM, WDS microprobe, and Raman spectrometry. The basaltic breccia displays a complex imbrication of anomalous petrographic facies that are distinctive from the local basalts. The unique suite of carbonaceous polymorphs (nano-sized diamonds, graphitic carbon, PAH species and amorphous carbon) in the recrystallised materials trace the carbonaceous component of the 4-kyr BP impact ejecta. Heterogeneous tear-dropped clasts that are embedded in the recrystallised basalts consist of Ca-rich silicate glass with heterogeneities indicating silicate-carbonate immiscibility, diaplectic quartz, barium sulphate, and diverse re-crystallized phases (silico-phosphate, Ca-phosphates, silicates). They trace solidified debris from the ejecta melt that derived from partial melting of carbonates, silicates, phosphates and soluble salts. Occurrence of a cm-thick crust with abundant domains of heated to melted bone fragments and a flow acicular facies is explained to result from high temperature (1200-1400°C) interaction between  $\text{CO}_2$ -rich hot intrusive fluids and materials present at the surface: animals, basalts, and calcareous soils. Heating and selective melting over a few square meters would trace the exceptional pulverisation of a large mass of hot liquid melt with solid debris, in contrast to the widespread spray of hot fine debris in other regions.