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Figure 6: Articulated white fossil *Lebachacanthus,* as shown at GEOSKOP.

Metamorphosed Permian vertebrate fossils: geochemistry and mineralogy of “white” sharks

Preliminary results

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The Saar-Nahe Basin (SNB) is an intra-mountainous basin in SW Germany, that was formed during the Variscan orogeny and has accommodated a freshwater lake-system during the Late Carboniferous/Early Permian. Intense syn- and post-sedimentary magmatic activity has affected the basin (von Seckendorff et al., 2004).
From the Remigiusberg Formation at Remigiusberg quarry (Fig. 1), vertebrate fossils in exceptional white-coloured preservation have been recovered, among them the oldest amniote fossil of Germany (Voigt et al., 2014).
Due to close proximity to an andesitic sill, the Kuselit, fossil remains have likely been affected by hydrothermal/contact metamorphism, causing the special type of preservation. Here we analysed teeth from the extinct freshwater shark *Lebachacanthus*, to assess geochemical and mineralogical aspects of this particular diagenetic setting.

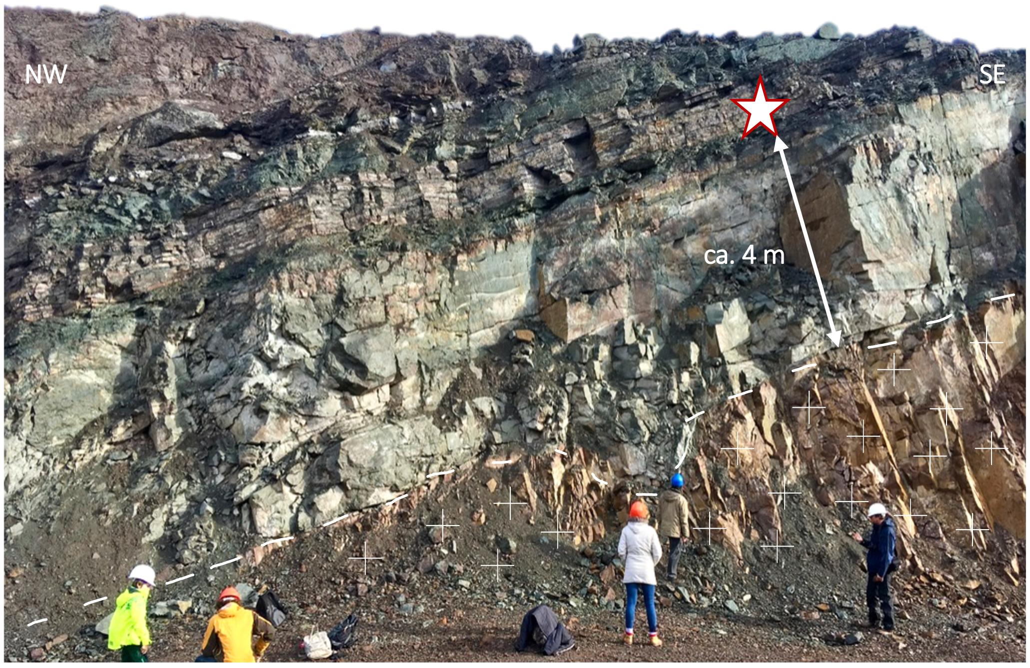

Figure 1: Quarry wall exposing the Kuselit intrusion (marked with +) into Lower Permian siliciclastic/calcareous lake sediments at the Remigiusberg quarry within the SNB, SW Germany. The near-concordant contact of the sill and sediments is indicated by a dashed line. The stratigraphic position of white fossils within the sedimentary sequence is highlighted by a star.

Figure 2: Photomicrographs of cross-sections of white *Lebachacanthus* shark teeth from the Remigiusberg quarry. Note that LA-ICP-MS spots and lines are visible.

Fossil white-coloured shark teeth from the Remigiusberg quarry (Fig. 2, Fig. 6), display intense alteration due to high temperature hydrothermal/contact metamorphism, clearly distinguishable from that of contemporaneous black-coloured shark teeth diagenetically altered at low temperature in black shale facies (Fig. 5).
Element and isotope data indicate different diagenetic histories for black and white teeth. Elements associated with hydrothermal fluid activity such as U, Cu, Fe, Zn and Al are enriched in white teeth. Other elements, such as Sr, Ba and Y are depleted. REE patterns are similar, however, REE concentrations are lower in white teeth.
In situ LA-ICP-MS U-Pb dating yielded none-depositional ages for shark teeth of both preservation types due to open-system behaviour of the U-Pb system and high U mobility.
Stable isotopes (^{13}C, ^{18}O) point to different types and intensities of diagenetic alteration for black and white teeth. Nevertheless, all shark teeth are preserved as carbonated fluorapatite, however, with clearly elevated crystallite dimensions in the white teeth (Fig. 4).

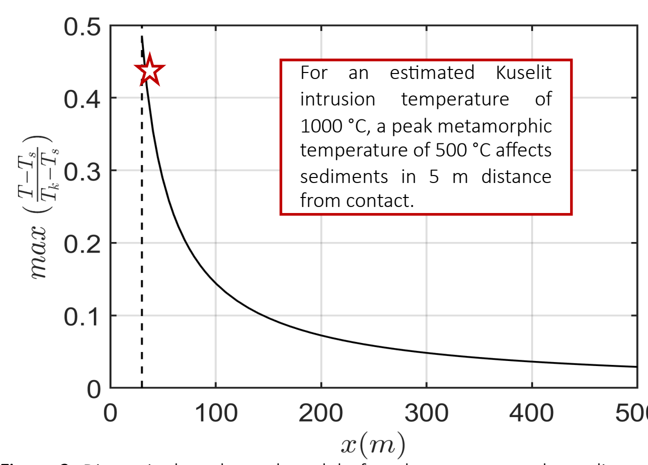

Figure 3: Dimensionless thermal model of peak temperature depending on the distance to sill's centre. Peak metamorphic temperature T is given in relation to intrusion temperature T_K and corrected against background temperature T_S. Typical parameters for crustal lithologies have been chosen. The half width of the sill was taken as 30 m, the rock density was taken equal to 2400 kg m^{-3} and the specific heat capacity was 1000 J K^{-1} kg^{-1}. At estimated Kuselit (i.e. andesite) intrusion temperature of 1000 °C and T_S of 100 °C, the fossils will experience a peak temperature of around 500 °C. The position of the fossils with respect to the sill centre is indicated by a star.

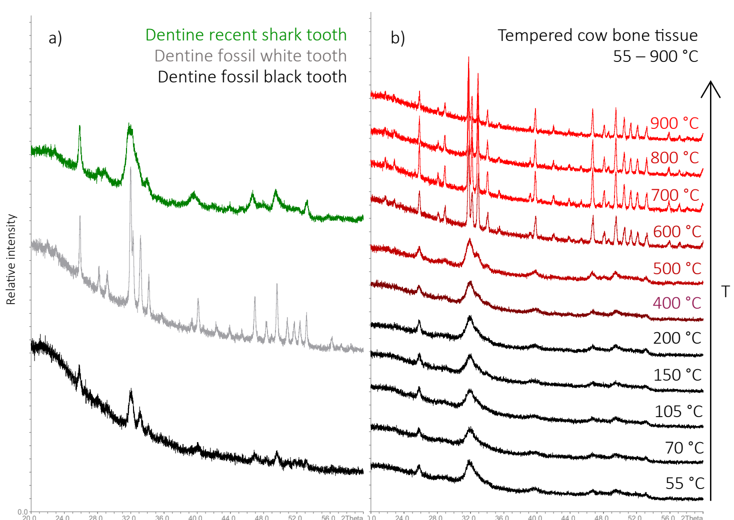

Figure 4: X-ray diffraction patterns of a) shark tooth dentine from fossil black (SZ1, black line) and white (WZ1, grey line) *Lebachacanthus,* as well as a recent shark (green line) for comparison, and b) cow bone, tempered in air at 55 to 900 °C. A higher crystallinity is reflected by lower FWHM of reflexes.

In experimentally tempered cow bone, which structurally resembles tooth dentine, bioapatite crystallinity, indicated by the sharpness of XRD reflexes (Fig. 4), increases strongly above 500 °C due to sintering and loss of organic compounds (e.g. Munro et al., 2007). The significant difference in black and white fossil shark teeth crystallinity is believed to reflect likewise intensely elevated temperature affecting white fossil shark teeth (Fig. 4). Following that, a preliminary peak temperature of ≥ 500 °C was reconstructed for the Remigiusberg setting, which is in good agreement with thermal conditions calculated from a simple thermal model (Fig. 3).
High temperature, and possibly hydrothermal fluid overprint, likely disintegrated and removed organic matter from the teeth, which probably led to increased apatite crystallinity and the white colour.
Fossil bioapatite crystallinity may serve as a proxy for reconstructing diagenetic thermal history, especially for high temperatures. However, to reach more accurate temperature estimates for sedimentary basins based on bioapatite crystallinity of fossils, more experimental constraints are needed to better represent geological conditions.

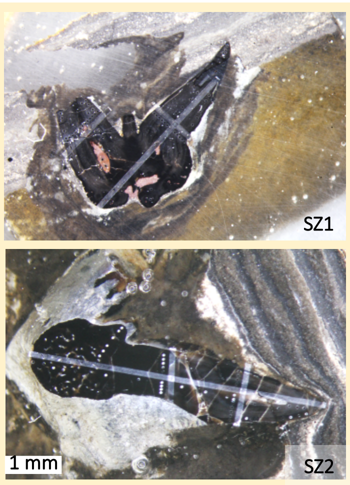

Figure 5: Black shark teeth of *Lebachacanthus* from a synchronous black shale formation within the SNB, for comparison. Note that LA-ICP-MS spots and lines are visible.

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