

Different coloured vitreous phases in obsidian

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Different coloured glass matrices obsidian are the object of the study. Their compositions and phase analyses of implemented nanocrystals were determined by Transmission Electron Microscopy (TEM). The analyses were carried out with an STEM Philips CM 200.

The Büyük Yayla obsidian (Eastern Pontides, Turkey) shows various bands, coloured black, red, and partially colourless. Moreover, a sharp black displacement (up to 1 cm) passes through the obsidian due to a still unknown shear process, displacing the several layers. Note, the different bands do not show a macroscopic 'schlieren-like' texture close to the displacement front.

The results of TEM-EDX analyses are given in the following table.

Oxide [wt-%]	red glass matrix	colourless glass matrix	black glass matrix	glass close to the displacement trace
Na ₂ O	4.5	1.6	5.2	5.8
MgO	0.1	0.2	0.2	0
Al ₂ O ₃	13.4	13.1	12.9	13.1
SiO ₂	76.0	74.9	74.4	75.0
K ₂ O	4.7	8.4	5.3	4.6
CaO	1	0.9	1	1.1
TiO ₂	0	0	0.2	0
MnO	0	0	0.1	0
Fe ₂ O ₃ (Fe-tot)	0.4	0.9	0.6	0.5

Table 1: Chemical composition of different coloured glass matrices of the Büyük Yayla obsidian

Surprisingly the highest Fe-amount was detected in the colourless vitreous matrix. Hence, the iron soluted in the glass is not responsible for the different colours of the glass. The detected 0.3 – 0.5 wt-% of hematite- and magnetite-nanocrystals colour the vitreous matrices.

Calcium and magnesium isotopes in biogenic calcite

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As shown recently [1], the isotopic fractionation of calcium is strongly correlated with the partitioning of Sr in inorganically precipitated calcite, wherein the main control on both proxies is the precipitation rate. In a follow up study [2], the inorganic correlation between $\Delta^{44/40}\text{Ca}$ and D_{Sr} has been verified for planktic foraminifera. We extend this approach to coccolithophores, including *Emiliana huxleyi* and *Coccolithus braarudii*, grown under controlled laboratory conditions. The slope of the regression between $\Delta^{44/40}\text{Ca}$ (‰) and $\log D_{\text{Sr}}$ in coccolithophores (-1.8 ± 0.9 , [3]) is within error of that in inorganically precipitated calcite (-1.9 ± 0.3 , [1]), whereas there is a large offset between the inorganic and coccolithophorid regressions due to the higher Sr content in the latter.

Comparing the fractionation of magnesium isotopes versus the Mg content in the calcitic skeletons of the Alcyonarian soft coral *Rhythisma fulvum*, benthic foraminifer *Amphistegina* sp., coccolithophores *Emiliana huxleyi* and *Coccolithus braarudii*, echinoid *Echinocyamus pusillus*, red alga *Corallina officinalis*, brachiopod *Terebratula* sp. and sponge *Acanthochaetetes wellsi* [4, 5, 6] we find that species with high Mg content (>10 mol% MgCO_3) have a higher degree of fractionation ($\Delta^{26/24}\text{Mg} < -2$ ‰) compared to low Mg species (<5 mol% MgCO_3 ; $\Delta^{26/24}\text{Mg} > -2$ ‰). Planktic foraminifera and the blue mussel *Mytilus edulis* [5, 6] are exceptions with low Mg content but a high degree of fractionation ($\Delta^{26/24}\text{Mg} < -3.5$ ‰).

These results will be discussed in a comparative manner in terms of our understanding of the pathways of biomineralization in different calcifiers.

[1] Tang *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 3733–3745. [2] Kısakürek *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 427–443. [3] Müller *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 2088–2102. [4] Eisenhauer *et al.* (2009) *Elements* **5**, 365–368. [5] Hippler *et al.* (2009) *Geochim. Cosmochim. Acta* **73**, 6134–6146. [6] Wombacher *et al.* (2006) *Geophys. Res. Abstr.* **8**, 06353.