

Cathodoluminescence of quartz as a reflection of the evolution of the Teplice Caldera

KATEŘINA ŠVECOVÁ¹,
KAREL BREITER² JAROMÍR LEICHMANN¹

¹Department of Geological Sciences, Masaryk University,
Kotlářská 2, CZ-61137 Brno, Czech Republic
(175727@mail.muni.cz) (leichman@sci.muni.cz)

²Institute of Geology AS CR, v. v. i., Rozvojová 269CZ-165
00 Praha 6, Czech Republic (breiter@gli.cas.cz)

The late-Variscan Altenberg-Teplice Caldera (ATC) is situated in the Eastern Krušné Hory Mts./Erzgebirge on both sides of the Czech-German border. The studied borehole Mi-4, situated in the western part of the ATC, crossed all volcanic units of the caldera fill in the thickness of 950m.

According to Breiter *et al.* [1], the ATC consists of five volcanic phases. Two oldest units composed of the basal rhyolites (BR) and overlying dacites (DC) are calc-alkaline in character and may probably represent a product of high-degree melting of a immature material of the lower crust. Three younger units of Teplice rhyolite (TR1-3) are high-K calc-alkaline in character, significantly enriched in Rb, Th and HREE. This younger part of the ATC should be interpreted as a product of low-degree high-temperature melting of much more evolved crustal material.

The inner structure of quartz crystals was studied using cathode luminescence with hot-cathode (HC 2) and scanning luminescence (microprobe CAMECA SX100). Quartz grains from the ATC show intensive zoning in both modes of observations. The oldest unit, BR is characteristic with nearly violet luminescence with weak zoning. In many cases these are just fragments of much larger grains and there are carbonate veins going through the quartz. In DC unit have quartz grains dark blue luminescence and no zoning. Quartz grains in three younger units TR1-3 have blue luminescence in hot CL with dark center and lighter margins. Significantly more intensive zonation appears in scanning luminescence. Very tiny zones symmetrically rim the core, dissolution of individual zones could be often documented. Some grains appears as fragments only. Majority of grains were corroded during their evolution. This has resulted in sometimes very bizarre shapes of grains. Quartz grains from the uppermost extrusive unit, rhyolite lava (TR3) are mostly rounded (2 mm diam.), often with granophyric overgrowth.

[1] Breiter, K. Novák, J. K. Chlupáčová, M. (2001) Chemical Evolution of Volcanic Rocks in the Altenberg-Teplice Caldera. *Geolines* **13**, 17–22.

Surface complexation evidence that amino acids prefer special sites on oxide surfaces

D.A. SVERJENSKY^{1*}, R.M. HAZEN², D. AZZOLINI¹,
N. LEE¹ AND K. KLOCHKO²

¹Johns Hopkins University, Baltimore, MD 21218 USA
(*correspondence: sver@jhu.edu)

²Geophysical Laboratory, Carnegie Institution of Washington,
Washington, DC 20015 USA

Adsorption data for a variety of amino acids on rutile, amorphous titanium dioxide and hydrous ferric oxide covering wide ranges of pH, ionic strength and surface loading have been analyzed with the extended triple-layer model (ETLM), ATR-FTIR spectroscopic studies and quantum chemical approaches [1-4]. The results provide a consistent picture of the surface speciation of amino acids on oxides. The ETLM analysis requires a surface site density of 3.0 sites/nm². Each amino acid adsorbs in at least two ways to oxide surfaces: at low surface loadings, a species 'lying down' on the surface; at high surface loadings, a species 'standing up' on the surface. We focus here on glutamic acid (H₂Glu) and dihydroxyphenylalanine (DOPA or H₃DP) on rutile. At the highest loadings, about 0.47 sites/nm² are occupied by the 'standing up' Glu attached through the distal carboxylate to a surface functional group >TiO (OH²⁺). The attachment consists of one inner-sphere bond and one H-bond. The amount of Glu adsorbed corresponds to about 16% of the total site density. However, this type of attachment cannot take place on the ideal (110) face of rutile which overwhelmingly predominates on our rutile sample in SEM pictures. The reason is that groups such as >Ti (OH)₂ or >Ti (OH)O are not present on the ideal (110) face. They are present on (111) or (101), suggesting that at least 16% of the (110) surface in our sample consists of (111) or (101) structures that contain the special functional groups that Glu prefers. A similar conclusion applies to DOPA. At high loadings, DOPA attaches to two Ti as (>TiOH²⁺)>TiHDP- with one inner-sphere bond and one H-bond from the two phenolic groups on the DOPA the separation of which (2.78 Å) almost exactly matches the two >TiOH groups (2.77 Å), but only when these are exposed on the (101) plane. Overall, the ETLM analysis indicates that both Glu and DOPA at high loadings prefer special functional groups that are not available on the ideal (110) plane, implying that most amino acid adsorption is on steps on (110) surfaces of rutile and similar structures on other oxides. HRTEM studies are underway to test this suggestion.

[1] Jonsson *et al.* (2009) *Langmuir* **25**, 12127–12135.
[2] Parikh *et al.* (2011) *Langmuir* **27**, 1778–1787. [3] Bahri *et al.* (2011) *Env. Sci. Technol.* DOI: 10.1021/es1042832.
[4] Sverjensky *et al.* (2008) *Env. Sci. Technol.* **42**, 6034–6039.