

Crystal growth history of quartz in the Ordovician Millbrig K-bentonite

W.D. HUFF* AND F.O. INANLI

University of Cincinnati, Cincinnati, OH 45221

(*correspondence: warren.huff@uc.edu)

Crystal size distribution (CSD) analysis has been applied to quartz crystals of the Ordovician Millbrig K-bentonite, which represents one of the largest known fallout ash deposits in the Phanerozoic Era, to establish crystal growth histories and conditions in the magma chamber prior to eruption. Specific CSDs of the quartz crystals of the Millbrig K-bentonite were examined to establish their growth conditions prior to the eruption. On the crystal size distribution plot, all Millbrig samples exhibit concave-down shapes in agreement with previously reported CSDs on large silicic systems [1] but in contrast to more mafic systems characterized by linear CSDs. Crystal growth mechanisms responsible for the concave down CSDs are thought to be surface-controlled crystal growth followed by an episode of textural coarsening. Although all samples follow concave-down shapes, two samples exhibit rather different CSD shapes. These findings appear to fingerprint a separate magma batch with different crystal growth conditions. These ash beds appear to be a product of a series of separate eruptions that represent separate magma layers or batches, each with slightly different crystal growth conditions.

Haynes [2] interpreted the multiple ash layers as either a product of several periods of eruptive activity or the cumulative effect of an evolving magma chamber during a single massive eruptive event. Our data support the model of several periods of eruptive activity that was closely spaced in time. The two of the eight Millbrig samples must have come from an earlier phase eruption and are part of a basal section that have not been preserved in the stratigraphic record and lacks lateral continuity in distal parts of the deposits. Therefore, the multiple ash beds in the Millbrig must have been a product of series of separate eruptions that represent separate magma layers or batches that had different crystal growth conditions.

Although conclusions on crystallization processes and the origin of deposits cannot be drawn from CSD shapes alone, it is shown here that CSDs of a fallout ash deposits can be used to fingerprint separate magma batches, provide valuable information on crystal growth rates as well as nature of the crystal growth mechanisms of quartz crystals.

[1] Bindeman (2003) *Geology* **31**, 367-370. [2] Haynes (1994) *Geol. Soc. Am Spec. Pap.* **290**, 1-80.

Photochemical transformations of carboxylates on TiO₂ and iron(III)(hydr)oxide surfaces

STEPHAN J. HUG AND PAUL BORER

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

Colloidal iron(III)-phases play an important role in the adsorption, transport and transformation of organic and inorganic compounds. In sunlit aqueous phases, light-induced electron transfer in the bulk and on the surface of colloids can lead to photochemical oxidation, reduction and transformation of adsorbed compounds and often to dissolution of ironphases. As illumination of TiO₂ and iron(III)(hydr)oxides with UV-A light can produce oxidizing species, these solids are also of interest for water treatment and degradation of toxic compounds.

To investigate the different phototransformation pathways, we have followed photoreactions of dicarboxylates and of α -hydroxy-dicarboxylates on TiO₂ (a semiconductor known to produce OH-radicals with UV-A light) and on various iron(III)(hydr)oxides (where the photoproduced oxidizing species is not as well-defined) with in-situ ATR-FTIR measurements.

All investigated dicarboxylates adsorbed strongly to TiO₂ and to iron(III)(hydr)oxides up to circumneutral pH. Distinct changes of IR-spectra upon adsorption indicate inner-sphere coordination. On TiO₂, all dicarboxylates were quickly and completely mineralized by UV-A illumination and oxalate was formed before complete mineralization. In contrast, UV-A illumination of lepidocrocite, goethite and hematite did not lead to appreciable degradation of dicarboxylates except oxalate on the same time scale, but to transformation of α -hydroxy-dicarboxylates to oxo-carboxylates, which were further degraded only slowly.

These results suggest different photodegradation pathways. In comparison to TiO₂, OH-radicals seem not to be formed in high yield on iron(III)(hydr)oxides. Instead, photooxidation is more likely induced by direct ligand-to-metal charge transfer on the surface, or by bulk adsorption and migration of valence band holes to the surface and subsequent reaction with surface-coordinated carboxylate groups. The formed oxidants are able to readily oxidize α -hydroxy-carboxylates, but not dicarboxylates except oxalate. If generally valid, this means that iron(III)(hydr)oxides are not efficient photocatalysts for the complete mineralization of organic compounds, but that adsorbed compounds can be photo-transformed to distinct products.