Structure of the calcite (104)-Water interface: direct comparison of x-ray reflectivity data with computational results

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Understanding the calcite-water interface structure is important because of its abundance in natural systems, relatively high reactivity (e.g., rates of growth and dissolution), and ability to incorporate trace impurities. Previous studies have probed the structure of the calcite-water interface by X-ray reflectivity (XR) [1] and computational approaches [2]. These different approaches have led to a qualitatively similar picture of the molecular-scale structure at this interface, including displacements of the surface lattice and organization of the fluid water adjacent to the surface, but without a full quantitative agreement in the derived structures. It is unclear if these differences are significant (i.e., if there is a conflict between the XR measurement and the simulation) or whether the apparent discrepancy between the XR data and the simulation reflect a deficiency in the model used to described the XR data (e.g., due to a potential non-uniqueness of the model).

Substanial improvements in XR reflectivity data quality due to advances in detectors over the past ~10 years suggest that a reassessment of this system may be warranted. New XR measurements of the calcite-water interface were made at the Advanced Photon Source following previously described procedures [1] and care was taken to avoid X-ray-induced perturbations to the interfacial structure. The XR results show clear modulations of the specular reflectivity signal, which are associated with the presence of a small but significant oscillatory relaxation profile of the calcite surface layers, which has not been previously observed. Also observed is an organized interfacial water layer, similar to previous results.

A further test of these new results is to compare these XR data *directly* to computational results without any intevening model-dependent assumptions using a recent conceptual advance [3]. Comparison with a molecular-dynamics simulation shows that the simulated structure provides a qualitative description of the XR data, but with a poorer quality of agreement than that obtained using the model-dependent fitting approach.

[1] P. Fenter et al., *Geochimica et Cosmochimica Acta* **64**, 1221-1228 (2000).
[2] Kerisit and Parker (2004) *J. Am. Chem. Soc.* **126**, 10152-10161.
[3] P. Fenter et al., *J. Synchrotron Radiation*, **18**, 257-265 (2011).

Oxidation of black shales as a source of Re-Os ratios in epigenetic pyrite: A case study from MacMillan Pass, Yukon, Canada

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High Os in late Devonian, shale hosted epigenetic pyrite

The Devonian - Mississippian Earn Group in the Selwyn Basin contains a number of sediment-hosted barite sequences which outcrop in the Mackenzie Mountains, NWT and Yukon. The Hess occurrence (middle Devonian) contains epigenetic pyrite with textures suggesting that it was formed post-lithification, but predating barium mineral formation.

Re-Os isotopic composition of Hess pyrite give values of 16.51 to 93.8 for ^{187}Re/^{188}Os, and 0.8253 to 1.6001 for ^{187}Os/^{188}Os respectively. Most calculated initial ^{187}Os/^{188}Os ratios (at 390 Ma) range from 0.6 to 0.9, substantially higher than that of the ^{187}Os/^{188}Os value for seawater at the Frasnian-Fammenian boundary (0.42) [1].

Oxidation of organic matter as a source of Os

We suggest, therefore, the fluid that precipitated pyrite had acquired substantial radiogenic Os before pyrite formation. It is likely that organic matter in the underlying lower Earn Group shales was the source for the high Os and low Re values in the fluid. Oxidizing fluids migrating through the stratigraphy would be necessary in order to degrade the organic matter in the host shale and solubilize Os.

If we assume the Os is derived from the host shales, then modeling the data suggests that it would take 25 to 75 Myr to generate the high initial ^{187}Os/^{188}Os ratios observed. This supports an epigenetic source for the pyrite and suggests that the Re-Os isotopic system is a powerful tool in understanding the evolution of black shales and shale-hosted mineralization.

[1] Selby & Creaser (2005), *Geology*, **v. 33**, 545-548.