Microbially-mediated barite dissolution in anoxic brines

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Hydraulic fracturing for shale gas production yields large quantities of produced water (PW), which is a mixture of injected fracturing fluids and natural brines from the formation. PWs are often highly saline and contain elevated concentrations of Ba [1] [2]. Natural barite ($BaSO_4$) present in the Marcellus Shale is a possible source of Ba. However, abiotic dissolution of barite is shown to be a minor contributor of Ba compared to Ba release from clay minerals [3]. This study aims to evaluate the role of microbial processes on barite dissolution.

Batch laboratory experiments were conducted to compare the rates of abiotic and microbially-mediated dissolution of barite in anoxic brines. Bacterial enrichment cultures were obtained from PW containing elevated Ba from three different gas wells in Tioga Co., PA. All three anaerobic enrichment cultures were dominated by *Halanaerobium* species. Barite crystals, cleaved to expose the (001) surface, were incubated in cultures and controls for over 100 days. Barium release was analyzed by ICP-OES and barite surface dissolution features were evaluated by SEM and AFM.

Barite solubility in the presence of bacteria was shown to be ~5x higher compared to brine controls after 30 days of incubation. Dissolution occurred via formation of etch pits; etch pit morphologies that developed in the presence of bacteria were qualitatively different from the controls, exhibiting morphologies similar to that shown for barite dissolution in the presence of organic chelators [4]. Additionally, our results showed that microbes do not require direct contact with barite surfaces to promote dissolution.

We suggest that organic molecules produced by microbes are promoting dissolution of barite under highly-saline and anaerobic conditions. Identifying these molecules and the mechanism(s) promoting barite dissolution is our current focus. The results of this study have implications for scale treatment, potential environmental pollution, and Ba/Ra geochemistry in shale gas systems.

[1] Rowan *et al*. (2014) AAPG Bulletin. [2] Warner *et al*. (2013) *Environ. Sci. Technol*. **47 (20)**, 11849-11857. [3] Renock *et al*. (2015) in preparation. [4] Putnis *et al*. (2008) *Appl. Geochem*. **23**, 2778-2788.