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## A new hypothesis for the slow feldspar dissolution in groundwater aquifers

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We measured an *in situ* plagioclase dissolution rate of 10<sup>-</sup> <sup>16..3</sup> mol (feldspar)  $m^{-2}$  sec<sup>-1</sup> and a K-feldspar dissolution rate of  $10^{-17.7}$  mol  $m^{-2}$  sec<sup>-1</sup> along up to 80 km long flow paths within the confined Navajo sandstone aquifer of the Black Mesa of Arizona, with residence times up to 35 Ky. These rates are among the slowest feldspar dissolution rates reported. However, evaluation of previously published water chemistry from other areas suggests these slow feldspar reaction rates are typical of regional aquifers. The well constrained physical and chemical conditions of the Navajo aquifer, coupled with detailed FEG-SEM and HRTEM analysis of the compositions and textures of the primary and secondary phases, allowed the evaluation of most commonly proposed mechanisms for limiting feldspar dissolution rates, all of which are found to be inadequate to explain the observations. Rather, it is proposed that clay precipitation kinetics is the rate limiting step in controlling overall feldspar reaction rates in regional aquifer systems.



Reaction-path models to illustrates the mechansim of this hypothesis. Feldspar effective dissolution rate constant  $k^{*_1} = k_1S$ , where S stands for surface area. Model 1,  $k^{*_1} = 10^{-10.3}$  mol s<sup>-1</sup> m<sup>-2</sup>,  $k^{*}_{clay} >> k^{*_1}$ ; 2.  $k^{*}_{clay} = k^{*_1}$ ; 3.  $k^{*_1} = k^{*}_{kaol}$ , and  $k^{*}_{mus} = k^{*_1} \times 10^{-4}$ ; 4.  $k^{*}_{kaol} = k^{*_1} \times 10^{-2}$ , but  $k^{*}_{mus} = k^{*_1} \times 10^{-4}$ ; 5.  $k^{*_1} = k^{*}_{kaol}$ , and  $k^{*}_{mus} = k^{*_1} \times 10^{-6}$ .

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## Kinetic and thermodynamic controls on the precipitation and morphology of barite (BaSO<sub>4</sub>)

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The precipitation and subsequent build up of barite (barium sulphate) inside extraction tubing presents a costly problem for off-shore oil wells that use seawater to mobilize oil during hydrocarbon recovery. An experimental programme was designed to study barite formation under environmentally relevant conditions with control of several system variables during the precipitation reaction. Synthetic sea-water and formation-water brines containing sodium sulphate and barium chloride, respectively, were mixed to induce BaSO<sub>4</sub> precipitation. Experiments were carried out in sealed batch reactors up to temperatures of 90° C. Barite formation as a function of ionic strength (0.01-0.5 mol), the addition of calcium, strontium, and magnesium (1-7 mMol), PPCA and PVS scale inhibitors (~50 ppm) was investigated whilst monitoring EC and pH using in-situ logging equipment. Data concerning growth rates (EC and ICP-AES), pH, crystal morphology (ESEM) and identified crystal phases (XRD) were obtained. ICP-AES and EC data from the experiments revealed the influence of the scale inhibitor (SI) in controlling precipitation rate constants for these experiments, see Fig. 1, along with the influence of foreign divalent cations on inhibition efficiency and precipitation rate.



Fig. 1. Log k' values for varying ionic strengths, with and without a PPCA scale inhibitor (SI).

ESEM analysis of precipitates showed a shift in habit from the typical tabular morphology produced in low supersaturation experiments to less-faceted anhedral crystals produced in the experiments performed in the presence of SIs. Additional flow-cell experiments are planned in an effort to measure intrinsic rate constants.