Barite dissolution rates measured with different methods

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Barite ($BaSO_4$) is a model substance for study of crystal dissolution. Cleavage on barite's {001} surface is perfect and can yield an atomically flat surface, making it ideal for atomic force microscopy (AFM) studies. Barite crystals are easily grown in the laboratory, eliminating the need for mechanical grinding, and making them ideal for powder experiments. The chemical structure of barite is a simple two-component system consisting of Ba^{2+} and SO_4^{2-} ions. Dissolution of this [AB] structure is significantly easier to conceptualize than other mineral systems. Barite is thus well suited for computer simulations, and lacks much of the complexity with which similar two component systems, e.g., carbonates, must contend. Therefore, barite is a perfect mineral for comparison of different experimental and analytical techniques.

Overall bulk dissolution rates are composed of various components, e.g., development of deep and shallow etch pits, as well as lateral step movement. These processes contribute to the overall rate, and must be measured using different techniques at different scales to understand their respective contributions. For example, Figure 1 shows the overall removal of material from stepwaves (29 nm) as well as localized development of deep etch pits (40 nm), and shallow, linearly coalescing etch pits (trenches, 7 nm). These processes contribute to the overall ("bulk") dissolution of 1.86×10^{-8} moles $m^{-2}\,sec^{-1}$.

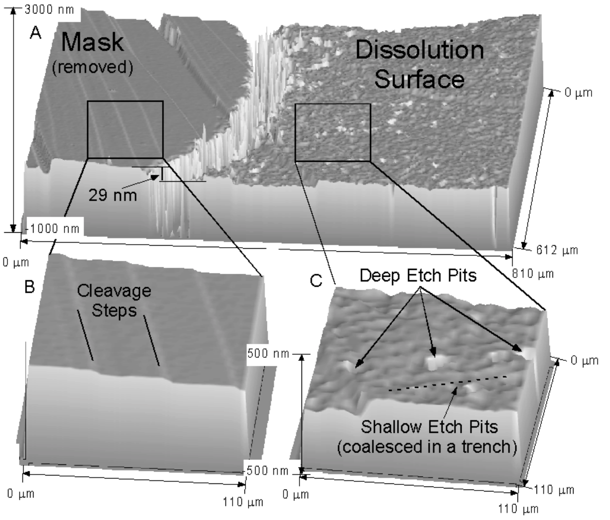

Figure 1. Barite {001} vertical scanning interferometry (VSI) data, 4 hours, 0.05 M EDTA, pH~12, 25ºC

We present rate data measured using VSI and provide comparisons to published rates from AFM and powder experiments. Our goal is to identify the causes of discrepancies between rates measured by various techniques.

Effect of agricultural activities on the mineralogy of soil clays

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Soils from different locations in Texas were studied by Potter *et al.* (1999) for their soil organic carbon (SOC) content and its relation to agricultural practices. More than 100 years of continuous agricultural activity has reduced SOC by more than 50% compared with untilled prairie soils. Although return to grass reverses this effect, the carbon sequestration rate is then very slow. Agricultural practices may also modify the soil clay mineralogy, and these "modified" clays could play an important role during SOC mineralization or sequestration. Our objective was to study the effects of agricultural practices on soil clays.

The cultivated (AGRI) and prairie (PRAI) soils selected for the present study are vertisols, previously studied for SOC by Potter *et al.* (1999). These soils, located near Temple (Texas), are classified as Houston Black clay (Udic Haplusterts), with large dioctahedral clay contents. Selected cores of AGRI and PRAI were split into depth segments, air dried, crushed to pass a 2-mm sieve, and suspended in water. The SOC was decomposed with H_2O_2 (30%) in the presence of a NaOAc buffer (pH5). The 0.1-0.25 µm fractions were studied by X-ray diffraction (XRD; mineralogy, charge, swelling) and Fourier transform infrared spectroscopy (FTIR; OH stretching and bending modes) after various treatments.

FTIR and XRD results indicate that dioctahedral smectites dominate the clay mineralogy of both AGRI and PRAI. NEWMOD simulations of the XRD patterns after Ca-exchange and glycolation suggest that the smectites are randomly interstratified illite/smectite with ~50% expandable layers. FTIR data established the aluminous character of the clays (intense Al_2OH bending band), and substitution of Fe^{3+} and Mg for Al was also observed (low-intensity Fe_2OH and AlMgOH bending modes). Low amounts of kaolinite and micaceous phases are present in both AGRI and PRAI, with a slightly greater micaceous component in AGRI. XRD data after K-exchange and treatment at 110°C overnight show slightly more high-charge smectite layers in AGRI than in PRAI (more irreversibly collapsed layers). Results after Li-exchange and treatment at 300°C (Greene-Kelly test) indicate that the smectite layers are predominantly beidellitic in both AGRI and PRAI, although there are slightly more montmorillonitic layers in PRAI. It is clear that agricultural practices induced only minor modifications of the clays, probably due to the low charge of the smectite layers and the short period of time involved.

Potter, K.N., Torbert, H.A., Johnson, H.B. and Tischler, C.R. (1999) *Soil Science* **10**. 718-725.