A new approach to the study of calcite dissolution utilising localised electrochemical proton generation

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Method

An ultramicroelectrode (UME) is used to generate protons in the vicinity of calcite to create highly localised, controlled and measurable acid challenges [1]. The time and flux of protons produced by the UME are quantifiable and reproducible. The process can be carried out in the presence of organic acid anions [2] to produce the corresponding weak acid. The high resolution technique of white light interferometry (WLI) is used to image calcite topography and provide information on the etch pits produced. A Matlab program has been designed to quantify the dimensions of dissolution pits, as well as providing profile pits for quantitative analysis. These data are inputted into a finite element model that mimics the experiment and reveals local surface fluxes and concentrations. In this way, considerable quantitative insight into the dissolution process is obtained.

Results

The method reveals spatial variation in dissolution sites and surface concentrations. The localised electrochemical technique is shown to successfully etch calcite samples, providing new insights on the kinetics of the process. The method could be widely applied to other minerals that undergo pH-dependant reactions.

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Linkages between recharge rates, flowpaths, and metabolic pathways for methanogenesis in Powder River Basin coalbeds, WY (USA)

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The Powder River Basin in northeastern Wyoming is the second largest producer of coal bed methane (CBM) in the United States. Methane was generated by microorganisms in the low rank (subbituminous) coals via two metabolic pathways, acetate fermentation and carbon dioxide reduction, which can be distinguished using C and H isotopes of CO_2, CH_4, and H_2O, and DNA studies. The relative importance of these pathways is primarily dependent on the bioavailability of organic matter, presence of nutrients, salinity, and microbial community structure. Previous studies by Flores et al. (2008) in the Powder River Basin observed the dominance of acetoclastic methanogenesis in select areas near the basin margins where coal zones were burned (clinker deposits). Methane generated by CO_2 reduction is dominant at depth throughout the basin. We hypothesize that the spatial and depth distribution of CO_2 versus acetate-utilizing methanogens in the Powder River Basin is related to groundwater recharge rates, residence times, and influx of sulfate through clinker deposits at the basin margin. To test this hypothesis, we collected and analyzed groundwaters and natural gas from 36 wells, along two transects across the basin that were parallel to regional hydraulic gradients. $\delta^{18}O$ and δD values of coal waters decrease with distance along flowpaths, from values within the range of modern mean annual precipitation (-15 to –18 per mil) in the recharge areas to values as low as –20 per mil downgradient, providing a qualitative indicator of residence time that will be confirmed by carbon-14 and tritium age dating. Sulfur isotope results show that pyrite oxidation in recharge areas is the source of SO_4 to coalbeds. Interestingly, CBM wells with isotopic signatures of acetate fermentation contain high sulfate concentrations (12 mg/L), positive $\delta^{34}S$ values (up to 101 per mil), and low $\delta^{13}C$-DIC values (>-10 per mil) indicative of sulfate reduction, whereas wells with methane generated via CO_2 reduction contain no detectable SO_4. Determining controls on metabolic pathways and rates of methanogenesis is important for pilot studies of *in situ* stimulation.