

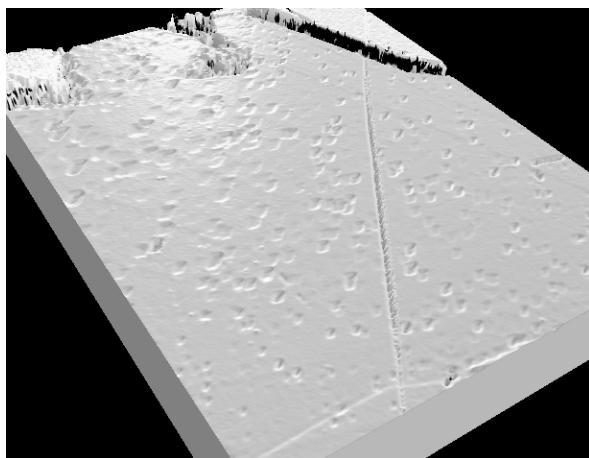
## Near-equilibrium albite dissolution kinetics

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Extensions of BCF theory indicate that if undersaturation does not exceed a critical value (i.e.,  $\Delta G \geq \Delta G_{\text{crit}}$ ), hollow cores of screw dislocations with large Burgers vectors will not open to form macroscopic etch pits [1]. This analysis has been expanded to a general framework of crystal dissolution that explains the oft-observed nonlinear decrease in crystal dissolution rate as equilibrium is approached [2]. These relationships, when applied to albite dissolution (Fig. 1), also imply the existence of two distinct near-equilibrium reaction mechanisms with large differences in specific rate: a *fast* mechanism in which etch pits serve both as areas of accelerated bulk removal and as step-generators (stepwaves) as well, and a *slow* mechanism in which step-generation is inactive [3, 4]. However, both  $\Delta G$  and  $\Delta G_{\text{crit}}$  are functions of temperature. We have thus used novel experimental and analytical techniques to explore these potential mechanisms, and here present preliminary results under near equilibrium conditions < 100°C.



**Figure 1:** Albite cleavage surface after dissolution, pH 9.

- [1] Cabrera *et al.* (1954) *Phys. Rev.* **96**, 1153. [2] Lasaga & Luttge (2001) *Science* **291**, 2400–2404. [3] Beig & Luttge (2006) *GCA* **70**, 1402–1420 [4] Luttge (2006) *J. Electron. Spectrosc. Relat. Phenom.* **150**, 248–259.

## Origins of hematite, magnetite and siderite in banded iron formations

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Geological, geochemical and mineralogical investigations by previous investigators and our group suggest that Lake Superior-type BIFs have accumulated in large, nearly completely-closed basins, much like the modern Black and Red Seas. The basins possibly developed by rifting of a thick continental crust and hosted Fe<sup>2+</sup>-rich brine pools. TEM and other data suggest the primary Fe<sup>3+</sup>-bearing compounds were colloidal ferric hydroxide particles ( $T < \sim 60^\circ\text{C}$ ), which were subsequently transformed to hematite during diagenesis. Nucleation of silica and ferric hydroxides occurred episodically, but simultaneously throughout the basin, probably at the interface between the Fe<sup>2+</sup>-rich brine and overlying O<sub>2</sub>-rich seawater, to form basin-wide continuous microbands.

Algoma-type BIFs, occurring in submarine volcanic terranes, possess many characteristics of black-smoker-type VMS deposits, including foot-wall alteration. The Marble Bar Jasper/Chert unit (MBC) in the Pilbara Craton, Western Australia is a 3.46 Ga low-grade Algoma-type BIF. Hematite in the MBC mostly occurs as a nano-sized (~100 - 600 nm) particle with varying morphology and habit. TEM and SEM observations suggest the hematite particles formed directly as single crystals of hematite at  $T > 60^\circ\text{C}$ , during the rapid mixing of high-temperature ( $> 150^\circ\text{C}$ ) Fe<sup>2+</sup>-rich submarine hydrothermal fluids with O<sub>2</sub>- and CO<sub>2</sub>-rich seawater near the vents at depths > 400 m. Hematite in the MBC is frequently enclosed in magnetite (Fe<sub>3</sub>O<sub>4</sub>) and siderite (FeCO<sub>3</sub>) crystals, indicating that the hematite formed earlier than these minerals. The magnetite most likely formed during the early diagenesis of hematite- and silica-rich sediments by reaction between hematite and Fe<sup>2+</sup>-rich hydrothermal solutions:  $\text{Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 2\text{H}^+$ . The siderite also formed during diagenesis of the chemical sediments by reaction between hydrothermal Fe<sup>2+</sup> and CO<sub>2</sub> (and HCO<sub>3</sub><sup>-</sup>)-rich pore fluids; the CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> were derived from a CO<sub>2</sub>-rich Archean atmosphere and the decay of organic matter in the chemical sediments. These and various other mineralogical and geochemical data of the MBC suggest that the oceans and atmosphere were already oxygenated 3.46 Ga ago.