The interface-scale mechanism of reaction-induced fracturing during serpentinization

Item DR1: Analytical methods

Microstructures were examined in polished thin sections (~30 µm) using polarized light microscopy. Backscattered electron (BSE) images were acquired in a JEOL JSM 6460LV (Institut für Mineralogie, University of Münster, Germany) and a JEOL 6610-LV scanning electron microscope (SEM; Department of Geosciences, University of Oslo, Norway), respectively. Crystallographic orientation relationships were analyzed by field-emission gun (FEG-) SEM enabling electron backscatter diffraction (EBSD) analysis in a FEI Quanta 200 at 20 kV and equipped with a CD-200 NORDIF EBSD camera (Department of Chemistry, University of Oslo, Norway). Pattern indexing and data processing were executed using the TSL OIM Analysis software. For serpentine polymorph identification (e.g., Groppo et al., 2006; Rinaudo et al., 2003) and detection of brucite (e.g., Dawson et al., 1973), Raman spectra were collected with a high-resolution Jobin-Yvon T6400 Raman spectrometer using the 532-nm line of a 14-mW Nd:YAG laser (Norwegian Center for Raman Spectroscopy, University of Oslo, Norway). The scattered Raman light was analyzed using a 100x objective lens in a 180° backscattering geometry and a charged-coupled device (CCD) detector. After the light passed a 100 µm entrance slit, it was dispersed by a grating of 1,800 grooves per mm.

Item DR2: Physical derivation of spontaneous fracturing assisted by an expanding wedge

The physical derivation of spontaneous cracking due to a volume increasing reaction in a wedge-shaped surface perturbation or incipient fracture (Kornev, 2001) is outlined in detail here.

The mode I stress intensity factor for a crack opened by a semi-infinite rigid wedge of constant thickness h , K_I^w (Barenblatt, 1962; Maiti and Paramguru, 1982), is

$$K_I^w = \frac{Eh}{2\left(1-\nu^2\right)}\sqrt{\frac{2}{\pi\delta}} \tag{1}$$

where E is the Young's modulus, ν is Poisson's ratio and δ is the distance from the end of the wedge to the tip of the crack. When a confining pressure p_0 is applied to the crack, the resulting "closing" stress intensity factor can be found by considering loading on the region δ away from the crack tip and using the general formula (Lawn, 1993)

$$K_I^c = 2\sqrt{\frac{c}{\pi}}\int_{c-\delta}^{c}\frac{-p_0}{\sqrt{c^2-x^2}}\,dx \tag{2}$$

where c is the fracture length. In the limit $\delta << c$, this becomes

$$K_I^c = -\Delta p\sqrt{\frac{8\delta}{\pi}}\,. \tag{3}$$

Due to the additivity of the K-fields, the total stress intensity factor is given by

$$K_I = K_I^w + K_I^c\,. \tag{4}$$

Kornev (2001) used Novozhilov's approach (Novozhilov, 1969) to define a discrete-integral criterion for brittle strength as

$$\frac{1}{kr_e}\int_0^{nr_e}\sigma_y\left(x,0\right)dx = \varphi\sigma_m\,. \tag{5}$$

Here, r_e is the distance between atomic bonds in the material, and n and k are integers where n is the number of atomic distances of the averaging region ahead of the crack tip and k is the number of atomic bonds in this region ($k \le n$, allowing for dislocations). The theoretical strength is σ_m, which can be approximated as (Pugno et al., 2006)

$$\sigma_m \approx \frac{E}{6}\,. \tag{6}$$

The parameter φ ($0 \le \varphi \le 1$) accounts for chemical weakening at the crack tip. The stress σ_y can be found from linear elastic fracture mechanics as a function of coordinate x ahead of the crack tip (Lawn, 1993)

$$\sigma_y\left(x,0\right) = \frac{K_I}{\sqrt{2\pi x}}\,. \tag{7}$$

This gives an expression for the critical stress intensity factor:

$$K_{Ic} = \frac{k\varphi\sigma_m}{n}\sqrt{\frac{\pi n r_e}{2}}\,. \tag{8}$$

Combining the above defines the critical wedge thickness, h_c, which is required for spontaneous crack propagation:

$$h_c = \left(1-\nu^2\right)\left(\frac{\pi k\varphi\sqrt{nr_e}}{6n}\sqrt{\delta} + \frac{8p_0}{E}\delta\right). \tag{9}$$

For a conservative estimate one can set $k/n = \varphi = 1$ and the averaging interval nr_e to be 1 nm. In this case the confining pressure is negligible unless $p_0 = 0.1E$ and the critical wedge thickness (in nm) is approximately $h_c \approx 0.5\sqrt{\delta}$.

The influence of confining pressure (p_0) and chemical weakening at the crack tip (φ) on the critical wedge thickness (h_c) and distance of the wedge from the crack tip (δ) is found in Figure S1. In addition, the influence of varying the constant C, by using the aforementioned approximation, is shown.

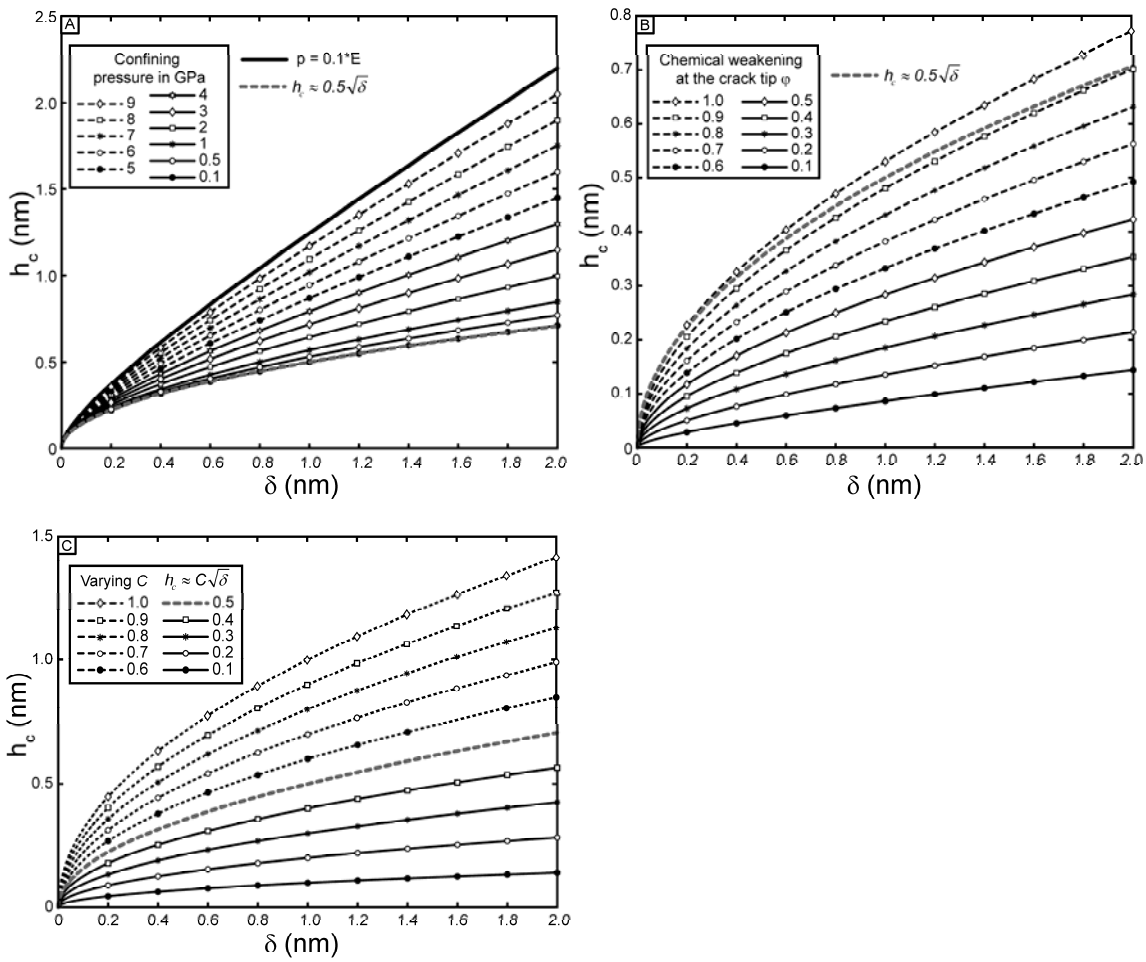

Figure DR1. Critical wedge thickness h_c versus distance from wedge end to the crack tip δ as a function of **(a)** confining pressures and **(b)** chemical weakening at the crack tip φ. The confining pressure is negligible unless $p_0 = 0.1E$ and hence the critical wedge thickness can be approximated by $h_c \approx 0.5\sqrt{\delta}$ (grey dashed-line). **(c)** h_c versus δ as a function of varying C.

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