Supplementary Information for
Volatile-consuming reactions fracture rocks and self-accelerate fluid flow in the lithosphere

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This PDF file includes:

- Supplementary text
- Figures S1 to S4
- Tables S1
Supplementary Information Text

Experimental results. P-MgO experiment FTP06 showed a significant decrease in flow rate, from 3.0 to ~0.1 mL/min, during the first 100 min of fluid injection (Supplementary Information Fig. S2). Inlet fluid pressure was almost constant ($P_{in}^f = 5$ MPa); outlet pressure showed minor fluctuations for the first 40 min, with a gradual decrease to a constant ~4 MPa after 100 min. Sample permeability decreased rapidly from $3 \times 10^{-15}$ to $5 \times 10^{-17}$ m$^2$ during the first 100 min (Figs. 2a and S2b). In contrast, IP-MgO experiment FTD10 showed almost undetectable flow for the first 330 min (<0.001 mL/min), except for some minor pulsed-flow up to 0.003 mL/min (Fig. S2). After 340 min, the flow rate gradually increased and reached a maximum of 0.5 mL/min at 577 min. Outlet fluid pressure was <0.1 MPa until 340 min, after which it gradually increased, suggesting fluid arrival at the outlet at 340 min. The measured increase in outlet fluid pressure at 515–525 min is equivalent to vapor saturation pressure (~1.4 MPa) at 200°C, and subsequently it reached ~3 MPa, which is the pressure regulated by the back-pressure valve. The obtained permeability was <2 $\times$ 10$^{-19}$ m$^2$ until 340 min, and gradually increased up to 1.5 $\times$ 10$^{-18}$ m$^2$, representing a permeability increase of up to ~3 orders of magnitude. All other experiments for impermeable starting materials showed a consistent permeability increase, albeit initiated at different stages in the experiments (Fig. 2b). MP-MgO experiment FTMP02 showed a significant decrease in permeability, from $1 \times 10^{-17}$ to <10$^{-19}$ m$^2$ during the first 3.5 min, followed by a rapid increase, from $1 \times 10^{-18}$ to $1 \times 10^{-16}$ m$^2$ during 12–16 min, then fluctuated between $8 \times 10^{-18}$ and $6 \times 10^{-17}$ m$^2$ for the remainder of the experiment. The other experiments showed similar and consistent behaviour, with a rapid decrease and subsequent increase in permeability (Fig. 2a). To our knowledge, these are the first experimental results that show permeability enhancement during volume-increasing fluid–rock reactions under confining pressure.
Fig. S1. Schematic illustration of the hydrothermal flow-through experiment set-up. a, Overview of the experiment set-up. b, Enlarged view of the sample assembly. $Q$, $T$, $P_{\text{in}}$, $P_{\text{out}}$, and $P_c$ indicate flow rate, temperature, inlet fluid pressure, outlet fluid pressure, and confining pressure, respectively. DW refers to the distilled water used as pore fluid and confining fluid.
Fig. S2. Results of hydrothermal flow-through experiments showing flow rate, confining pressure, inlet/outlet fluid pressure and permeability as a function of reaction time. a–b, Permeable MgO starting materials. c–e, Moderately permeable MgO starting materials. d–h, Impermeable MgO starting materials. FTxxx are experiment numbers (Extended Data Table 1).
Fig. S3. Backscattered electron images of the starting materials. a, Permeable MgO starting material (P-MgO). b, Moderately permeable MgO starting material (MP-MgO). c, Impermeable MgO starting material (IP-MgO). Note that pores are interconnected in P-MgO samples, whereas they are isolated in IP-MgO samples. Whitish interstitial phase in c is zirconium oxide (ZrO). Per: periclase.
Fig. S4. Pseudo-coloured backscattered electron (BSE) images of IP-MgO run products (FTP10). a, view of whole thinsection. b, closeup of an area with hierarchical fragmentation. Note the polygonal shape of remaining periclase surrounded by brucite veins in a and b.
Table S1. Experimental conditions and results, including reaction extent and volume change of the run product. All experiments were conducted under confining pressure of 20 MPa at 200°C. MB, mass balance; TG, thermogravimetry; XCT, X-ray computed tomography.

|                         | Permeable MgO | Moderately permeable MgO | Impermeable MgO |
|-------------------------|---------------|--------------------------|-----------------|
|                         | FTP08         | FTP06                    | FTMP05          |
| Initial grain size [µm]| 56 (12–176)   | 79 (8–242)*              | 50 (11–157)*    |
| Initial connected porosity [%]| 19.4    | 19.4                     | 11.5            |
| Initial unconnected porosity [%]| 3.9     | 4.0                      | 4.6             |
| Inlet pressure [MPa] | 5.0           | 4.9–5.0                  | 5.0             |
| Outlet pressure [MPa] | 0.1–1.0       | 3.8–4.4                  | 0.2             |
| Fluid flux [mL/min]   | 0.34–6.9     | 0.08–3.2                 | 0.01–0.45       |
| Experimental duration [min] | 4.7     | 237                      | 3.3             |
| Initial permeability** [m²] | 3–7×10⁻¹⁵ | 3–5×10⁻¹⁵                | 3–5×10⁻¹⁷      |
| Final permeability [m²] | 5.1×10⁻¹⁷   | 5.6×10⁻¹⁷                | 1.1×10⁻¹⁸      |
| Volume change [%]   | ΔV/V₀         | 92                       | 122             |
| Reaction extent MB [%]| 64           | 107                      | 13              |
| Reaction extent TG [%]| 76           | 99                       | 17              |
| Reaction extent XCT [%]| 78          | 98                       | 3               |

*: average (minimum and maximum) grain size determined from SEM images.
**: measured in advance at room temperature by independent experimental run for each type of MgO starting materials.
D.L.: detection limit.