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## Intermediate-depth earthquake faulting by dehydration embrittlement with negative volume change

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Earthquakes are observed to occur in subduction zones to depths of approximately 680 km, even though unassisted brittle failure is inhibited at depths greater than about 50 km, owing to the high pressures and temperatures<sup>1–3</sup>. It is thought that such earthquakes (particularly those at intermediate depths of 50–300 km)

may instead be triggered by embrittlement accompanying dehydration of hydrous minerals, principally serpentine<sup>1–3</sup>. A problem with failure by serpentine dehydration is that the volume change accompanying dehydration becomes negative at pressures of 2–4 GPa (60–120 km depth), above which brittle fracture mechanics predicts that the instability should be quenched<sup>4,5</sup>. Here we show that dehydration of antigorite serpentine under stress results in faults delineated by ultrafine-grained solid reaction products formed during dehydration. This phenomenon was observed under all conditions tested (pressures of 1–6 GPa; temperatures of 650–820 °C), independent of the sign of the volume change of reaction. Although this result contradicts expectations from fracture mechanics, it can be explained by separation of fluid from solid residue before and during faulting, a hypothesis supported by our observations. These observations confirm that dehydration embrittlement is a viable mechanism for nucleating earthquakes independent of depth, as long as there are hydrous minerals breaking down under a differential stress.

A popular hypothesis for overcoming brittle fracture inhibition, especially for earthquakes at intermediate depths (<300 km), is assistance of brittle fracture by generation of a free fluid as a result of dehydration of serpentine or other hydrous minerals<sup>1–3,6–11</sup>. The phenomenon of dehydration embrittlement was discovered almost 40 years ago<sup>1</sup> but has been studied only sporadically since that time<sup>4–8</sup>. In particular, this phenomenon has not been addressed by controlled deformation experiments at pressures greater than 700 MPa, equivalent to only ~20 km depth in Earth. Studies of acoustic emission at elevated pressures<sup>5,8</sup>, however, have implications for deeper earthquakes. The latter studies, although lacking control of differential stress, strain, or strain rate, recorded acoustic emissions at much higher pressures and inferred that faulting had occurred.

The fracture mechanics explanation of how dehydration embrittlement can enable brittle shear failure at elevated pressure is based upon production of a pore pressure as a consequence of a positive volume change,  $\Delta V$ , of the dehydration reaction and consequent decrease in the effective pressure on existing or potential planes of weakness. Thus, as conventionally understood, the theory predicts that if the  $\Delta V$  of the reaction were to become negative, failure would become more difficult and the shearing instability would vanish<sup>4,5</sup>. Because hydrous fluid is much more compressible than solid silicates, the total  $\Delta V$  of dehydration of the common hydrous phases of primary interest (for example, serpentine and chlorite) is progressively reduced as pressure increases and becomes negative at pressures of 2–4 GPa, equivalent to pressures of 60–120 km in Earth. One consequence of this prediction is that earthquakes should not be possible by dehydration embrittlement at greater depths<sup>5</sup>. However, dehydration embrittlement is the only earthquake nucleation mechanism known to be viable for depths less than 300 km (ref. 2). Thus, it is important to determine whether this mechanism can function under conditions where  $\Delta V$  is negative.

We report here the results of deformation experiments at pressures of 1–6 GPa and temperatures of 550–820 °C using an antigorite serpentine from Val Malenco, Italy, for which the phase diagram has been measured<sup>12</sup>. Figure 1a shows the experimental conditions investigated; the slope of the high-temperature limit of antigorite stability (Fig. 1a) is negative above ~2.2 GPa, reflecting negative  $\Delta V$  of reaction above that pressure.

Figure 1b–f shows microstructures of the starting material and results of annealing without deformation outside antigorite stability. The layering, strong foliation and proportions of antigorite and relict olivine shown are typical of our starting material. Figure 1f shows breakdown of antigorite along boundaries with relict olivine and healed cracks of several orientations outlined by fluid inclusions; such inclusion trails are rare in the starting material,

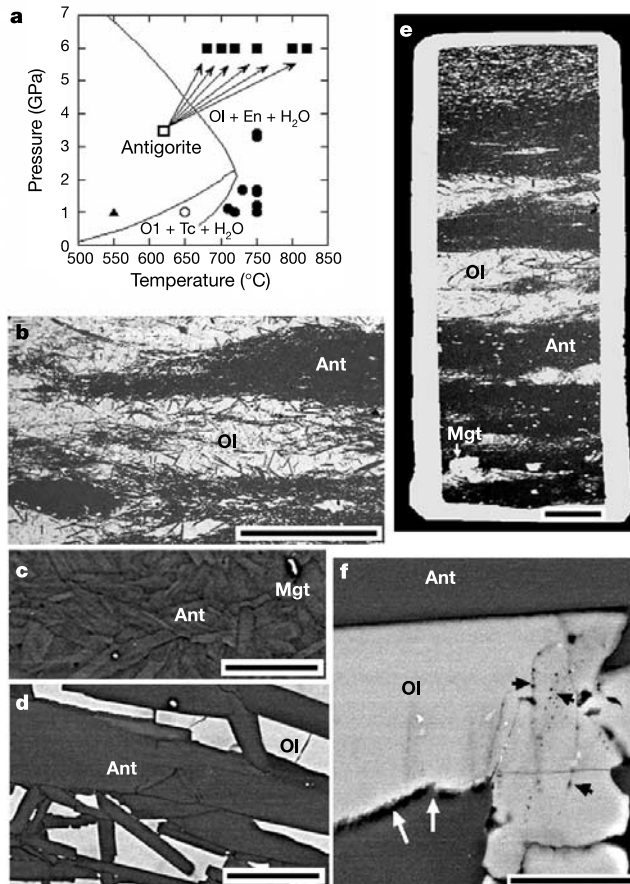
hence clearly were produced during the experiment. Similar healed cracks are abundant and strongly oriented in deformed specimens (see below).

One specimen was deformed within the stability field of antigorite (triangle in Fig. 1a). This specimen was extremely strong ( $\sigma_1 - \sigma_3 = 1.5$  GPa) and failed by conventional brittle fracture; no sign of dehydration products was found within the specimen after deformation ( $\sigma_1$  is maximum compressive stress;  $\sigma_3$  is minimum compressive stress). All other specimens deformed in the Griggs apparatus failed at significantly lower stresses (for example, 0.8–0.9 GPa at  $\sigma_3 = 1$  GPa), exhibiting multiple faults. Except in complicated multi-fault regions, faults are aligned  $\sim 25$ – $40^\circ$  to the maximum applied stress,  $\sigma_1$ . Figure 2a–c shows fault displacements demonstrated by offsets of specimen surfaces, regions of relict olivine, and across films of Ni incorporated as described in Methods. Figure 2d–f shows details of the breakdown of antigorite adjacent to relict olivine where progression of the reaction can be

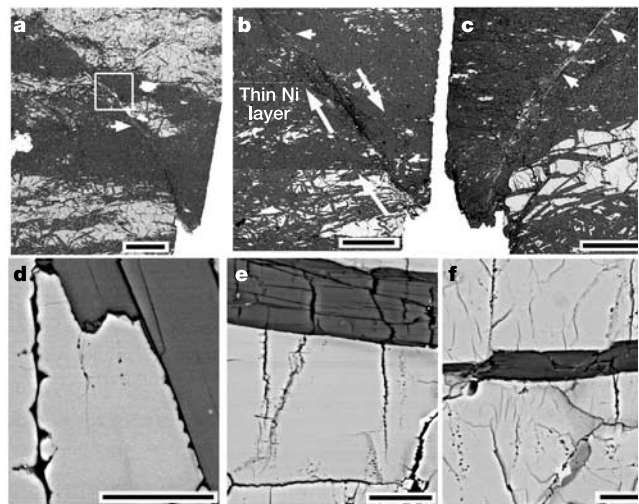
seen much more clearly than in the antigorite matrix. Many grain boundaries are open and show cusps along them, reflecting dissolution of olivine by the fluid released during antigorite decomposition. Open Mode I cracks parallel to  $\sigma_1$  (top–bottom in photographs) are abundant, as are healed cracks outlined by fluid inclusion trails. Open cracks display cusps with smaller cracks, commonly healed, emanating from them.

Faults all contain ultrafine-grained aggregates ( $\leq 300$  nm) of solid dehydration products that consist primarily of olivine, as shown by energy-dispersive spectroscopy (EDS) analysis and bright contrast. Although the  $\Delta V$  of reaction is strongly positive at 1.0 GPa, moderately positive at 1.7 GPa and distinctly negative at 3.3 and 6 GPa, all specimens showed the same ‘wispy’ pattern of solid reaction products preserved within and along the faults.

Figure 3a (pressure  $P = 1.7$  GPa) shows a fault that branches near the centre of the image. The branch to the right ends near the top of the image (arrowheads), with the wispy dehydration products changing orientation to approximately normal to macroscopic  $\sigma_1$  (top–bottom), defining surfaces akin to stylolites<sup>13</sup> or anticracks<sup>14</sup> (surfaces across which contraction has occurred and volume has been lost). The right-lateral shear on this fault system is such that the triangular region near the branch (arrow) is in compression and displays a high density of dehydration product lenses. It is well known that faults at Earth’s surface commonly show *en echelon* fault segments, with ‘pull-aparts’ between them<sup>15</sup>. The inset of Fig. 3a shows an analogous feature that is very common in our experiments in which, rather than a ‘pull-apart’, a ‘push-together’ is formed between *en echelon* fault segments arranged such that the region between their overlapping tips has experienced contraction rather than extension. The region of the ‘push-together’ has an abundance of dehydration products defining anticrack lenses that have accommodated shortening in response to the enhanced compression. Figure 3b ( $P = 6$  GPa) shows a series of such ‘push-togethers’ (also shown diagrammatically in Fig. 3c for clarity), again showing



**Figure 1** Experimental conditions and starting material for deformation experiments. **a**, Phase diagram for antigorite<sup>12</sup> and experimental conditions. Ol, olivine; En, enstatite; Tc, talc. Open symbols, hydrostatic experiments. Filled circles, deformation experiments in modified Griggs apparatus (strain rate  $2 \times 10^{-4} \text{ s}^{-1}$ ). Filled squares, experiments in Walker-type multianvil apparatus; arrows indicate  $P/T$  paths during rapid pumping, yielding strain rates approximating those in the Griggs apparatus. All deformation experiments displayed faults and evidence of antigorite breakdown except the experiment within antigorite stability (filled triangle). **b–d**, Microstructure of starting material: antigorite (Ant), relict olivine (Ol), and minor magnetite (Mgt). **e, f**, Specimen pressurized to 1.0 GPa and annealed for 1 h at 650 °C (open circle in **a**). Pt capsule (white) and specimen are undeformed. **f**, Minor antigorite breakdown (arrows) yields fluid inclusion trails (arrowheads) on healed cracks of several orientations. Scale bars: 1 mm (**b, e**); 10  $\mu\text{m}$  (**c, d, f**).



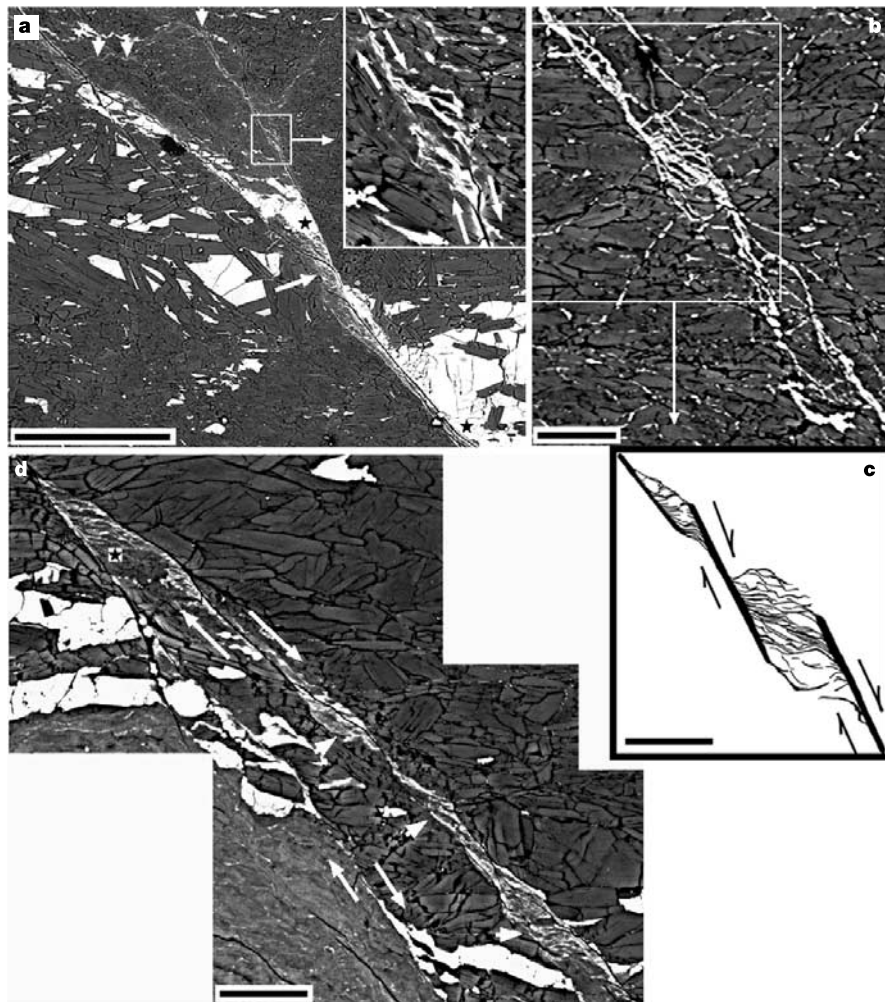
**Figure 2** Microstructures of faulted specimens. **a**, Fault offsetting layers richer and poorer in relict olivine (1.7 GPa, 750 °C;  $\Delta V > 0$ ); square shows location of Fig. 3a. **b**, Fault displacing Ni films (arrows) (1.0 GPa, 720 °C;  $\Delta V > 0$ ). **c**, Similar to **a** but 3.3 GPa, 750 °C;  $\Delta V < 0$ . Dehydration products along faults in **a–c** indicated by arrowheads. **d–f**, Open Mode I cracks ( $\sigma_1$  is top–bottom in image) with multiple cusps showing dissolution of olivine and fluid inclusion trails outlining healed Mode I cracks. Minor irregular cracking during decompression after experiment also visible. **d**, 1.7 GPa, 750 °C;  $\Delta V > 0$ . **e**, 1.7 GPa, 730 °C;  $\Delta V > 0$ . **f**, 6 GPa, 750 °C;  $\Delta V < 0$ . Scale bars: 200  $\mu\text{m}$  (**a–c**); 10  $\mu\text{m}$  (**d**); 20  $\mu\text{m}$  (**e, f**).

that the dehydration products decorate surfaces of maximum compression. Figure 3d ( $P = 1.0$  GPa) shows another fault trace that displays the same features as described in Fig. 3a–c. In this case, branching of the fault zone is seen at the top left corner of the image, with compression (anticrack) lenses in the squeezed wedge at the branch point (star), and several ‘push-togethers’, marked by arrowheads, are strung out along the fault trace. These panels also show that the extent of reaction outside fault zones is distinctly less than within them, suggesting that the fault zones have self-organized and propagated from points where the reaction initiated.

In summary, dehydration of antigorite under stress at pressures of 1–6 GPa leads to faulting under all conditions tested. Moreover, we document the presence of abundant healed cracks marked by fluid inclusion trails on surfaces of least normal stress (parallel to  $\sigma_1$ ) and lenses of solid reaction products located preferentially on surfaces of highest normal stress (normal to  $\sigma_1$ ), showing that the fluid and solid products of antigorite breakdown become separated during faulting. Thus, free fluid of density lower than antigorite was

available at all pressures to generate abundant Mode I cracks and lead to shear failure<sup>2</sup>. Faulting apparently in conflict with fracture mechanics theory is explained by separation of fluid (lower density than antigorite—positive  $\Delta V$ ) and solid reaction products (higher density than antigorite—negative  $\Delta V$ ) during deformation. Each component is concentrated on appropriate surfaces to help accommodate the local strain field.

Returning to consideration of Fig. 3, we note that during growth of a fault (or growth of a slip patch on an existing fault), at any point in that growth the stress distribution resulting from its displacement field is as sketched in Fig. 4a. As the slipping patch grows, there is continuing renewal of such stressed regions, with the compressive zones sketched in Fig. 4b, c. Thus, such a fault patch evolving in a system in which an on-going reaction produces a fluid/solid slurry is ideally situated to focus the reaction in local regions of enhanced compression, leading to concentration of the denser solids on planes of high normal stress as microanticracks and expelling the less-dense fluid into the fault zone where it reduces friction and lubricates the fault surface. The result of such a scenario would be

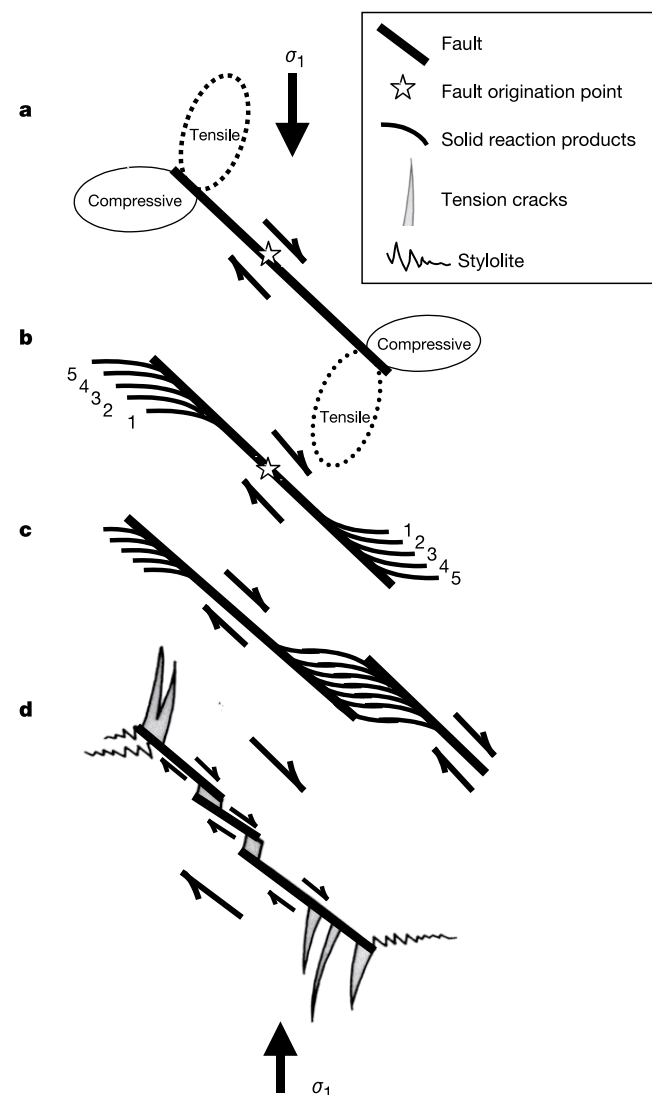


**Figure 3** Fault microstructures. **a**, Detail of Fig. 2a. Fault shows minor branch that dies out near top of image, outlined by ‘wisps’ of solid reaction products at high angles to  $\sigma_1$  (arrowheads). Convergence near branch point (arrow) is under compression and exhibits a concentration of ‘wisps’. Stars show fault displacement of a severed magnetite blob. Inset shows multiple anticrack ‘wisps’ in ‘push-together’ between overlapping ends of *en echelon* microfaults (1.7 GPa;  $\Delta V > 0$ ). **b**, Topologically identical series of ‘push-togethers’ between *en echelon* fault segments at 6 GPa ( $\Delta V < 0$ ). **c**, Schematic

drawing of part of fault zone in **b**; heavier lines are fault segments and lighter lines are traces of the solid reaction products. **d**, Similar microstructures at 1.0 GPa ( $\Delta V > 0$ ); ‘push-togethers’ (arrowheads) and a converging zone (star) are again decorated by solid reaction products oriented normal to the orientation of the local  $\sigma_1$  (top–bottom). Open cracks in the fault zones are decompression features. Scale bars: 100  $\mu\text{m}$  (**a**); 20  $\mu\text{m}$  (**b–d**).

microstructures like those shown in Fig. 3. Remarkably similar structures (except showing 'pull-aparts') have been shown in small natural faults<sup>13,14</sup> (Fig. 4d), and 'push-togethers' have been seen previously between the tips of *en echelon* faults produced by transformation-induced faulting in Mg<sub>2</sub>GeO<sub>4</sub> during the olivine-spinel transformation<sup>16</sup>.

These results show that dehydration embrittlement as a mechanism for initiation of earthquakes is not restricted to conditions where the total volume change of reaction is positive ( $\Delta V > 0$ ). It is clear that in our experiments the self-organization of the shear failure process includes separation of fluid from solid reaction products, thereby extending the potential operation of pore-pressure-induced faulting to all conditions where the density of the fluid



**Figure 4** Hypothetical evolution of observed fault microstructure. **a**, Stress distribution at tips of growing fault. **b**, Potential microstructure developed along a newly formed microfault in which solid components ( $\Delta V < 0$ ) are preserved periodically (sequential positions marked 1–5) and fluid components ( $\Delta V > 0$ ) are not preserved (perhaps pumped into the evolving fault zone). Note that solid reaction products are oriented normal to local  $\sigma_1$ . **c**, *En echelon* array of microfaults with characteristics illustrated in **b**. **d**, Sketched natural fault in limestone (modified after Fig. 3 of ref. 13) showing both tension cracks (filled with calcite) and compression stylolites. Note that *en echelon* stepping is the reverse sense from our high-pressure faults, yielding 'pull-aparts' (also filled with calcite).

generated is less than that of the solid phase from which the fluid is derived. That would surely include all conditions obtaining in Earth's upper mantle except perhaps at simultaneously high pressures and temperatures where solubility of rock components in fluid becomes very high<sup>17</sup>, potentially yielding melts more dense than the rock from which they are derived<sup>18</sup>.

Arguments that dehydration embrittlement can explain all intermediate-depth earthquakes (and perhaps deep earthquakes as well) have become common in recent years, both from the standpoint of seismology<sup>19</sup> and petrology<sup>9,11,20</sup>. Our results are supportive of this concept if the requisite dehydration reaction is occurring. On the other hand, serious questions have been raised about the ability of this mechanism to explain the lower plane of earthquakes in double seismic zones because the presence of hydrous phases would be required to depths of 40 km or more immediately beneath oceanic trenches. One potential resolution of this quandary is that deep penetration of H<sub>2</sub>O perhaps occurs on major faults of the oceanic lithosphere, leading to hydrous alteration along them to the required depths<sup>19,21</sup>. However, a recent study of the Vanuatu subduction zone<sup>22</sup> shows that new faults are generated during subduction, an observation that would require more extensive hydrous alteration than solely along pre-existing faults. Reference 20 suggests up dip flow of fluid along the dehydration reaction boundary, a mechanism that might be plausible, but to produce earthquakes directly below the trench, the fluid would have to continue to flow beyond the point where any subduction-related hydration could have reached that depth. The growing sophistication of seismic studies of subduction zones holds great promise for measuring the distribution of hydrous phases<sup>23</sup>.

Lastly, recent laboratory experiments have demonstrated that generation of less than 1% fluid, if appropriately distributed, can be sufficient to enable faulting<sup>24</sup>. As a consequence, it is possible that dehydration of even minor hydrous phases such as clinohumite in peridotite or phengite in eclogite could trigger earthquakes as deep as 400 km (ref. 25). Moreover, discovery of seismic reflectors that move<sup>26</sup> in fault zones of the continental crust clearly demonstrates fluid saturation in such fault zones. Therefore, hydrous alteration of crustal minerals must be widespread at seismogenic depths in continents, and dehydration of clays or other hydrous minerals just before (or in the early stages of) crustal faulting could also contribute significantly to initiation or enhancement of shallow earthquakes. □

**Methods**

Several studies of antigorite stability have yielded varying results that are attributed to variations in structure and Al content<sup>27</sup>. For the results presented here, that uncertainty is not a problem for two reasons: (1) our results are dependent only on the running of the dehydration reaction, not the specific location of phase boundaries; (2) our starting material is the same as that used in ref. 12, hence we know the positions of the phase boundaries (Fig. 1a).

Experiments at pressures  $\leq 3.4$  GPa were conducted in a modified Griggs apparatus with sample assemblies illustrated previously<sup>24,28</sup>. Samples were right circular cylinders, 3.1 mm diameter and 8.4 mm long, encapsulated in Pt with oxygen fugacity buffered at Ni/NiO. CsCl, an extremely weak solid, was used as pressure medium to minimize friction of the apparatus. In order to document small fault offsets, some experiments were composed of stacks of 20–25 disks with Ni evaporated on one surface of each disk. Pressure was increased to 40 MPa at room temperature with further pressurization at 300 °C. The temperature was then increased to the desired temperature, annealed for 0–60 min, and deformed at a strain rate of  $2 \times 10^{-4} \text{ s}^{-1}$ . Samples were quenched to room temperature in seconds following deformation. Each experiment contained thermocouples at both the top and bottom of the specimen; the temperature difference between them was generally less than  $\sim 10^\circ\text{C}$ . Experiments at pressures of 3.5–6 GPa were conducted using a Walker-type multianvil device with a single thermocouple in the centre of the specimen. The multianvil is designed to generate hydrostatic stresses. However, with Al<sub>2</sub>O<sub>3</sub> pistons at the ends of fully-dense specimens, rapid pumping can generate the necessary differential stress to produce faulting<sup>29</sup>. Therefore, samples were initially pressurized cold to 3.5 GPa and temperature raised to 620 °C followed by rapid simultaneous increase in pressure and temperature along the arrows shown in Fig. 1a over 5–9 min. No measurement of stress is possible in specimens deformed in the multianvil but, as shown in Figs 2 and 3, microstructures of faulted specimens were indistinguishable from those in the Griggs rig. Some specimens were made up of stacked disks of starting material on which Ni

films were evaporated on the disk surfaces, yielding well-defined internal markers of fault offsets. All deformed specimens were observed by optical and scanning electron microscopy (SEM); all half-tone figures are back-scattered electron images taken at 20 kV acceleration voltage with a Philips XL-30 SEM with a field emission gun.

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## The decline and fate of an iron-induced subarctic phytoplankton bloom

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Iron supply has a key role in stimulating phytoplankton blooms in high-nitrate low-chlorophyll oceanic waters<sup>1–5</sup>. However, the fate of the carbon fixed by these blooms, and how efficiently it is exported into the ocean’s interior, remains largely unknown<sup>1–5</sup>. Here we report on the decline and fate of an iron-stimulated diatom bloom in the Gulf of Alaska. The bloom terminated on day 18, following the depletion of iron and then silicic acid, after which mixed-layer particulate organic carbon (POC) concentrations declined over six days. Increased particulate silica export via sinking diatoms was recorded in sediment traps at depths between 50 and 125 m from day 21, yet increased POC export was not evident until day 24. Only a small proportion of the