

Who buffers who? Examples of complex redox processes in petrological subsolidus experiments

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Experiments provide a unique opportunity to explore the effects of individual parameters on complex processes by selectively isolating them. However, this approach also carries the risk of missing crucial coupling mechanisms between processes and often important parameters are overlooked. While some parameters (e.g., temperature, pressure) are straightforward to control, others, such as the redox potential, are more difficult to handle. This contribution will focus on high-pressure and high-temperature experiments, and shows example experiments with sluggish reaction kinetics and unexpected redox behavior.

The release of fluids from serpentinites during subduction is an important process in driving mantle metasomatism and island arc volcanism. The experimentally determined dehydration temperature of serpentine, however, spans a range of more than 100 °C. A potential reason for these results is the (redox) behavior of Fe.

Experiments performed to investigate the behavior of Fe in serpentinites showed reduction of Fe^{3+} to Fe^{2+} as serpentine dehydrates, independent of the composition of the initial serpentine [1, 2]. This contradicts findings from other studies and confirms that although these experiments are nominally closed systems with respect to major elements, they are open to hydrogen diffusion and thus controlled by oxygen fugacity imposed by the experimental assembly. In the very extreme case, the first appearance of anhydrous reaction products tracks hydrogen diffusion in the experimental assembly rather than showing temperature-dependent dehydration. This dilemma can be overcome through the addition of internal redox buffers. The redox state of Fe in lizardite can easily be manipulated. An attempt to control the redox state of Fe in antigorite, however, revealed slow reaction kinetics of antigorite. This caused the buffer to be exhausted without having changed the antigorite composition.

Together, these experiments show that it is essential to carefully investigate the redox state and the processes controlling it. Only then it is possible to correctly interpret experiments and make predictions on large-scale processes, including dehydration and redox reactions in open subduction systems.

References

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- [2] Eberhard, L. et al. (2023). *J. Petrol.*, 64(10), 1–18.
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