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Dehydration reactions and stress

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Dehydration reactions usually involve the loss of fluid. This implies that there are gradients in fluid pressure and that therefore in general fluid pressure is not equal to confining. This is true whether the reaction begins at shallow levels, where a connected pore network may be at hydrostatic pressure, or whether the reaction begins deep in an entirely solid starting material, where pore pressure gradients will eventually form as permeability develops. On the grain scale, the difference between pore and lithostatic pressure implies that the grains are actually under deviatoric stress. Grain/fluid surfaces are under pore fluid pressure but grain/grain contacts will be carrying greater stress; this is also true under large-scale deviatoric stress.

How does the stress state affect the thermodynamics of reaction? Using gypsum as a cipher for more general phases which may dehydrate, we are investigating this question in laboratory experiments. In addition we aim to model the behaviour - for this we need the theory of non-hydrostatic thermodynamics. This tells us that the chemical potential is controlled by the local normal stress at an interface or surface. T-F Wong and co-workers produced models where the pore fluid pressure controls equilibrium, implying no chemical communication with the more highly stressed solid/solid grain boundaries. This may be an appropriate approximation on short timescales (minutes to hours in their experiments). In contrast de Meer and Spiers made gypsum to undergo pressure solution over 30 days at room temperature. Pressure solution is driven by chemical potential differences involving solid/solid grain contacts. The latter experiments, though, involved no phase change. Our aim is to include the thermodynamics of solid/solid and solid/fluid boundaries in a model which is intended to embrace previous work as well as explain the behaviour in our own new dehydration experiments. We will report on the progress of the numerical and experimental aspects of

this project.