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Quantifying the influence of non-hydrostatic stress on polymorph equilibria

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Thermodynamic modeling in active tectonic settings typically makes the assumption that stress is equal in all directions. This allows for the application of classical equilibrium thermodynamics. In contrast, geodynamic modeling indicates that differential, or non-hydrostatic, stresses are widespread. Non-hydrostatic equilibrium thermodynamics have been developed by past workers [1], but their application to geological systems has generated controversy in recent years [2-5]. Therefore, we seek to clarify how stress influences the chemical potential of non-hydrostatically stressed elastic solids. To quantify this, we consider the effects of stress variation on the equilibrium between the single-component polymorph pairs of kyanite/sillimanite, quartz/coesite, calcite/aragonite, and diamond/graphite.

The stress on each interface of a solid can be decomposed into components normal to the interface and parallel to the interface. In our work, we determine the shift in the temperature of equilibrium on fixed interfaces between polymorph pairs as a function of both interface-normal and interface-parallel stress variation. We find that the influence of normal stress variation on the equilibrium temperature of polymorphs is approximately two orders of magnitude greater than interface-parallel stress variation. Thus, at a fixed temperature, normal stress determines the chemical potential of a given interface to first order. Consequently, high-pressure polymorphs will preferentially form normal to the maximum stress, while low-pressure polymorphs, normal to the minimum stress.

Nonetheless, interface-parallel stress variations can meaningfully affect the stability of phases that are at or near equilibrium. We demonstrate the surprising result that for a given polymorph pair, a decrease in interface-parallel stresses can make a high-pressure polymorph more stable relative to a low-pressure polymorph on the given interface.

The effects of non-hydrostatic stress on mineral assemblages are most likely to be seen in dry systems. Many reactions in metamorphic systems are fluid-mediated, and fluids cannot sustain non-hydrostatic stress. Consequently, in systems with interconnected, fluid-filled porosity, mineral assemblages will tend to form at a pressure approximately equal to the fluid pressure. In contrast, in dry systems all reactions occur directly between solids which can sustain non-hydrostatic stress. This facilitates the application of non-hydrostatic thermodynamics. Consequently, dry rocks containing polymorphs such as such as quartzites, marbles, and peridotites represent ideal lithologies for the testing and application of these concepts. By influencing the chemical potential of solid interfaces, non-hydrostatic stress alters the thermodynamic driving force and subsequent kinetics of polymorphic reactions. This likely results in preferential orientations of polymorphs which could influence seismic anisotropy and potentially generate seismicity.

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