

## Demixing instability in dense molten $\text{MgSiO}_3$

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The phase diagrams of  $\text{MgSiO}_3$  and  $\text{MgO}$  are studied from first-principles theory for pressures and temperatures up to 600 GPa and 20,000 K. We present evidence for a vast pressure-temperature regime where molten  $\text{MgSiO}_3$  decomposes into liquid  $\text{SiO}_2$  and solid  $\text{MgO}$ . The demixing transition is driven by the crystallization of  $\text{MgO}$  - the reaction only occurs below the high-pressure  $\text{MgO}$  melting curve. The predicted transition pressure at 10,000 K is in close proximity to an anomaly reported in recent laser-driven shock experiments of  $\text{MgSiO}_3$ . We also present new results for the high-pressure melting curve of  $\text{MgO}$  and its B1-B2 solid phase transition, with a triple point at 327 GPa and 11,800 K. Comparison with experimental measurements and explanation of the observed phase boundaries in terms of the computed free energies will be discussed.

## Clumped isotope thermometry of marbles as an indicator of the closure temperatures of calcite and dolomite with respect to solid-state reordering of C–O bonds

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Carbonate clumped isotope thermometry is based on the temperature-dependent preference of rare isotopes  $^{13}\text{C}$  and  $^{18}\text{O}$  to bond with each other within lattices of carbonate minerals (as measured by  $\Delta_{47}$  of  $\text{CO}_2$  extracted by phosphoric acid digestion). In rocks that have experienced burial and/or high temperature histories, this phenomenon may be controlled by solid-state diffusion of C and O within the mineral lattice. Here we examine this issue through clumped isotope measurements of a variety of natural marbles that differ in metamorphic environment, age, cooling rates, grain sizes, and mineralogical and chemical compositions; and compare them to heating experiments conducted at laboratory timescales.

Calcitic marbles increase in  $\Delta_{47}$  (by a range of  $\sim 0.05\text{‰}$ ) with decreasing cooling rates (from  $\sim 100$  to few  $^\circ\text{C}/\text{My}$ ), suggesting that  $^{13}\text{C}$ – $^{18}\text{O}$  reordering during cooling is controlled by solid state diffusion. Also, dolomite marbles are systematically lower in  $\Delta_{47}$  (by at least  $0.06\text{‰}$ ) than calcitic marbles, all other factors being the same. This does not appear to reflect differences between calcite and dolomite in the temperature dependence of clumping or the fractionation on acid digestion; rather, it appears that the blocking temperature with respect to solid-state  $^{13}\text{C}$ – $^{18}\text{O}$  reordering is significantly higher in dolomite ( $\sim 300^\circ\text{C}$ ) than in calcite ( $\sim 150\text{--}200^\circ\text{C}$ ), due to currently unknown chemical and/or structural controls.

These data are relevant for the use of clumped isotope thermometry to study deeply buried sedimentary carbonates and carbonate bearing diagenetic, metamorphic and igneous rocks. Perhaps most importantly, this work suggests that authigenic or early diagenetic dolomite may provide a means of recovering clumped isotope surface temperature records from even deeply buried sedimentary sections and sub-greenschist facies metamorphic rocks.