

## **Atomistic simulation on mixing thermodynamics of calcite-smithsonite solid solutions**

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### **ABSTRACT**

By using atomistic simulation and configurational statistics techniques, the thermodynamics of mixing for calcite-smithsonite solid solutions have been investigated. By employing a  $2 \times 2 \times 1$  supercell, the configuration with the lowest energy for the solid solution with a certain composition was determined. The incorporated  $\text{Zn}^{2+}$  tends to occur at the sites neighboring to another substituted  $\text{Zn}^{2+}$  within the (0001) layer, but the substituted layers are preferentially segregated by calcite layers, and vice versa. The supercells with compositions around the two end-members stand positive enthalpies at any temperatures, whereas those supercells with composition of about  $\text{Ca}_{0.5}\text{Zn}_{0.5}\text{CO}_3$  prominently exhibit negative values in various temperatures of reality (e.g., <1000 K). The free energies are prominently negative at high temperatures (>1500 K) for the whole range of compositions, only those around both end-members have positive values at some low temperatures (<1200 K). In the derived phase relations of this solid solution system, the potential incorporation content of  $\text{ZnCO}_3$  into calcite is only 0–2.5% mole fraction (i.e., Zn content of 0–1.6 wt%) in most geochemistry equilibrium processes, and vice versa.

**Keywords:** Calcite-smithsonite, solid solution, mixing thermodynamics, atomistic simulation