American Mineralogist, Volume 100, pages 172–180, 2015

Atomistic simulation on mixing thermodynamics of calcite-smithsonite solid solutions

Xin Liu[1], Xiancai Lu[1,*], Xiandong Liu[1] and Huiqun Zhou[1]

[1]State Key Laboratory for Mineral Deposit Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing Jiangsu, 210026, China

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 × 2 × 1 supercell, the configuration with the lowest energy for the solid solution with a certain composition was determined. The incorporated Zn^{2+} tends to occur at the sites neighboring to another substituted 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 $Ca_{0.5}Zn_{0.5}CO_3$ 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 $ZnCO_3$ 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