Cobalt incorporation in calcite: thermochemistry of (Ca,Co)CO$_3$ solid solutions from density functional theory simulations

Jorge González-López (1), Sergio E. Ruiz-Hernández (2), Ángeles Fernández-González (1), Amalia Jiménez (1), Nora H. de Leeuw (2), and Ricardo Grau-Crespo (3)

(1) Departament of Geology, University of Oviedo,Calle Arias de Velasco s/n, Oviedo 33005, Spain (jgonzalez@geol.uniovi.es), (2) Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK, (3) Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

The incorporation of cobalt in mixed metal carbonates is a possible route to the immobilization of this toxic element in the environment. However, the thermodynamics of (Ca,Co)CO$_3$ solid solutions are still unclear due to conflicting data from experiment and from the observation of natural ocurrences. Atomistic computer simulations, which allow the evaluation of thermodynamic properties without the interference of unknown kinetic factors, have been increasingly used in recent years for the investigation of the thermodynamics of mixing and impurity incorporation in carbonate. We report here the results of a computer simulation study of the mixing of calcite (CaCO$_3$) and spherocobaltite (CoCO$_3$), using density functional theory calculations.

Our simulations suggest that previously proposed thermodynamic models, based only on observed compositions, significantly overestimate the solubility between the two solids and therefore underestimate the extension of the miscibility gap under ambient conditions. The enthalpy of mixing of the disordered solid solution is strongly positive and moderately asymmetric: calcium incorporation in spherocobaltite is more endothermic than cobalt incorporation in calcite. Ordering of the impurities in (0001) layers is energetically favourable with respect to the disordered solid solution at low temperatures and intermediate compositions, but the ordered phase is still unstable to demixing. The solvus and spinodal lines in the phase diagram using a sub-regular solution model has been also calculated, and conclude that many Ca$_{1-x}$Co$_x$CO$_3$ mineral solid solutions (with observed compositions of up to x=0.027, and above x=0.93) are metastable with respect to phase separation. The strong non-ideality of this solid solution has an important effect on the solid solution / aqueous solution thermodynamic partitioning: the equilibrium level of substitutional impurities in the endmember solids is always low, regardless of the composition of the aqueous solution. Thus, even in equilibrium with a very Co-rich aqueous solution, calcite is predicted to have a very low level of cobalt impurities, which is unfortunate as it means that Co/Ca substitution in calcite is not an effective way to immobilize Co(II) cations in solution. On the other hand, our results also mean that if spherocobaltite could be formed (which is admittedly difficult due to competition from other cobalt-bearing phases), almost perfect immobilization of the Co^{2+} ions would be achieved as there would be negligible Ca^{2+}/Co^{2+} ion exchange with aqueous solutions.