

## The replacement of gypsum by $\text{CaCO}_3$ polymorphs: Reaction steps and formation of pseudomorphs

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On the Earth's surface, the replacement of evaporitic calcium sulphates (anhydrite and gypsum) by  $\text{CaCO}_3$  is a common phenomenon that can lead to the formation of large deposits of diagenetic carbonates. In spite of the geological and industrial implications of this phenomenon, very few experimental studies have been conducted to investigate the microscopic mechanisms involved in this replacement process. Here we present an experimental study of the interaction between gypsum and carbonate-bearing aqueous solutions. This interaction leads to the replacement of gypsum single crystals ( $\sim 3 \text{ mm}^3$ ) by an aggregate of  $\text{CaCO}_3$  crystals. Scanning Electron Microscopy (SEM) and glancing incidence X-ray diffraction (GIXRD) were used to monitor the development of the replacement process. The replacement takes place through a number of solvent-mediated transformations, which involves the dissolution of gypsum and the sequential formation and dissolution of different  $\text{CaCO}_3$  polymorphs. Although the actual sequence of reactions depends on the initial concentration of carbonate, amorphous calcium carbonate (ACC) is always the first phase that forms and can be considered a precursor for the formation of more stable crystalline  $\text{CaCO}_3$  polymorphs. Moreover, the initial concentration of carbonate also controls the kinetics of the replacement and the degree of faithfulness of the pseudomorphs. The phase formation sequence and the textural characteristics of the replacement are interpreted on the basis of the evolution of physicochemical parameters, like the supersaturation with respect to the different  $\text{CaCO}_3$  polymorphs and the  $[\text{SO}_4^{2-}]/[\text{CO}_3^{2-}]$  ratio in the aqueous solution.

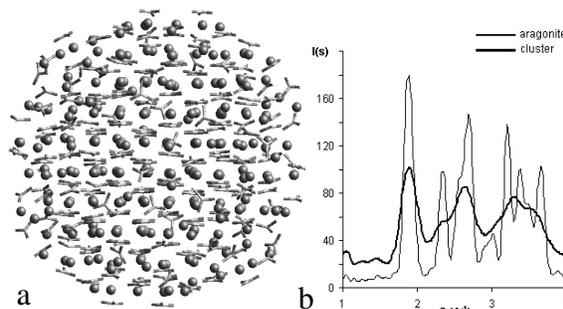
## From crystals to clusters: A molecular simulation study of $\text{CaCO}_3$ configurations

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Equilibrium relationships involving solids are based in bulk thermodynamic properties that concern ideal crystals of infinite size. However, real processes towards equilibrium imply development of finite molecular-scale entities. The configuration of these early-stage clusters and the estimation of their excess energies with respect to the ideal crystal is key to understand the macroscopic behaviour of a given system. Here, starting from the ideal atomic positions in calcite, aragonite, or vaterite, the relaxation in vacuum of finite clusters of  $\text{CaCO}_3$  has been explored. With the aim of determining the influence of the cluster size on its energy and on its geometrical configuration, a series of  $\text{CaCO}_3$  clusters have been simulated and their lattice energies calculated. The cluster geometry has been fully optimized at constant pressure and its energy has been determined using GULP. A wide variety of clusters ranging from 1 to 2000 formulae has been considered for each (calcite, aragonite, or vaterite) starting structure. GULP calculations have been carried out using the pair potentials set derived by Rhol *et al.* (2003). In a number of cases the final configuration has been checked with good agreement using the DFT code SIESTA (Soler *et al.*, 2002). Although these simulations represent not fully realistic scenarios, some results are relevant from the point of view of the polymorphic precipitation of  $\text{CaCO}_3$ . A fundamental question like the size that must have a cluster to be considered calcite, aragonite, or vaterite is addressed from the diffraction patterns of the relaxed clusters.



**Figure 1:** relaxed aragonite cluster with 250 formulae (a) and calculated diffraction patterns (b).

### References

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