

## Nanoscale epitaxial growth of PbSO<sub>4</sub> on the celestite (001) face: Implications for mineral reactivity

C.M. PINA\* AND A. RICO-GARCÍA

Department of Crystallography and Mineralogy, Complutense University, 28040 Madrid, Spain  
(\*correspondence: cmpina@geo.ucm.es)

Epitaxial growth can strongly modify the reactivity of mineral surfaces in aqueous environments. In some cases, the growth of just a few epitaxial monolayers is enough to seal mineral surfaces and prevent further interaction with the surrounding aqueous solutions. As previously demonstrated, such an epitaxial sealing of mineral surfaces can drastically reduce their efficiency to remove toxic metals from water (e.g. removal of cadmium by dissolution-crystallisation on calcite (104) surfaces [1,2]). On the other hand, the formation of metastable monolayers with composition and/or structure different than the substrate can inhibit continuous multilayer growth and impede the formation of mineral phases like dolomite [3].

Here we present *in situ* Atomic Force Microscopy (AFM) observations of the epitaxial growth of PbSO<sub>4</sub> (anglesite) monolayers on the celestite (001) face at room temperature. Apart from its possible environmental implications, this experimental system has been revealed as an interesting model example to study the nanoscale controlling factors of epitaxial growth from aqueous solutions. Our AFM observations demonstrate that PbSO<sub>4</sub> monolayers can grow in structural continuity with the celestite (001) face. However, continuous multilayer growth is inhibited for supersaturations with respect to PbSO<sub>4</sub> ( $\beta_{\text{anglesite}} = a(\text{Pb}^{2+}) \cdot a(\text{SO}_4^{2-}) / K_{sp, \text{anglesite}}$ ) lower than ~1.9. Such an inhibition is due to the in-plane strain generated in the PbSO<sub>4</sub> monolayers when they grow on a substrate with slightly different lattice parameters. The minimum supersaturation required to observe continuous PbSO<sub>4</sub> multilayer growth on the celestite (001) face allowed us to calculate a total in-plane strain energy of ~ 11 mJm<sup>-2</sup>. On the basis of the results of our AFM experiments, both the reactivity of celestite in Pb-bearing solutions and the growth behaviour of Pb<sub>x</sub>Sr<sub>1-x</sub>SO<sub>4</sub> solid solutions with a wide compositional range are discussed.

[1] Prieto, Cubillas & Fernández-González (2003) *Geochim. Cosmochim. Acta* **67**, 3859-3869. [2] Pérez-Garrido, Fernández-Díaz, Pina & Prieto (2007) *Surf. Sci.* **601**, 5499-5509. [3] Higgins & Hu (2005) *Geochim. Cosmochim. Acta* **69**, 2085-2094.

## An atomistic perspective of the incorporation of noble gases and other trace elements into magmatic crystals

C. PINILLA<sup>1,2\*</sup>, S.A. DAVIS<sup>1</sup>, T.B. SCOTT<sup>3</sup>, N.L. ALLAN<sup>1</sup> AND J.D. BLUNDY<sup>2</sup>

<sup>1</sup>School of Chemistry, Uni. of Bristol, Bristol, BS8 1TS, UK  
(\* c.pinilla@bristol.ac.uk)

<sup>2</sup>CETSEI, Dep. of Earth Sciences, Uni. of Bristol, UK

<sup>3</sup>Interface Analysis Centre. Uni. Bristol, BS2 8BS, UK

Trace elements are widely used to unravel magmatic processes and constrain the chemical differentiation of the Earth. Central to this enterprise is understanding the controls on trace element fractionation between solid and liquid phases and thus the energetics of incorporating trace elements into crystals. In this contribution we focus on the incorporation of noble gases into crystals, with implications for the degassing processes in the Earth and the atmosphere.

Most geochemical models for the behaviour of noble gases make the explicit assumption that they are completely incompatible in minerals such that during any process involving solid and liquid phases the noble gas partitions exclusively into the melt. However, a recent study [1] has concluded that noble gases are highly soluble in the solid phases of minerals which are major constituents of the Earth's mantle and suggesting a different depletion mechanism. These conclusions were based on a set of experiments in which various minerals of vary different composition and structure were exposed to Ar at different temperatures and pressures. The results show high concentrations of Ar close to the mineral surface, diminishing rapidly over a depth of 50-100 nm. The authors interpret the data to show that Ar solubility is much higher than previously thought, while its diffusivity through the crystal lattice is very slow. Here we present results of computer simulations, which show that noble gases are far less compatible in bulk minerals than recently suggested. *ab-initio* and MM methods are used to study the incorporation of noble gas atoms in forsterite both in the bulk and interfaces. Results from the simulations and from transmission electron microscopy (TEM) suggest a different picture and provide the basis for a revised understanding of how noble gases and, more generally, trace elements are accommodated in minerals and how they behave during melting or crystallisation. Our conclusions highlight the importance of interfaces and grain boundaries and are applicable to a much wider range of trace elements.

[1] Watson, *et. al.* (2007) *Nature* **449**, 299-304.