

SUPPORTING INFORMATION

The role of interfaces in controlling Pb²⁺ removal by calcium carbonate minerals

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4
5
6
7
8
9
10

item	figure	text	page
1		Adsorption in the system CaCO ₃ -Pb-H ₂ O	SIp3
2	TEM-SAED analysis of a reacted CAL grain (Figure SI1)		SIp4
3	Reciprocal lattice view of a reacted ARG grain (Figure SI2)		SIp5
4	Relationship between ICDP and mineral replacement (Figure SI3)	The distribution of inorganic carbon during the early reaction stages	SIp6

The adsorption in the system $\text{CaCO}_3\text{-Pb-H}_2\text{O}$

The contribution of adsorption on the observed uptake of Pb by CAL and ARG is ignored in the manuscript because negligible. When applied to our system, mass balances provide a validation for this assumption. The maximum adsorption capacity can be calculated from the total surface area of the samples (BET, see methods) and the cation density of the representative surfaces of ARG and CAL (Figure 7). We considered a monoatomic layer of Pb ions bound to the oxygen of carbonate units on the surface of the substrate. Our calculations demonstrate that the maximum adsorption capacity corresponds to less than 5% of the total amount of Pb atoms uptaken after 10 days of batch recrystallization with CAL. Experiments with ARG showed a lower uptake, thus the maximum adsorption capacity corresponds to a higher percentage of the total Pb uptaken (15%). Even for ARG, the hypothetical maximum contribution of adsorption to the observed Pb uptake is remarkably lower than the contribution due to dissolution-precipitation (more than five times bigger).

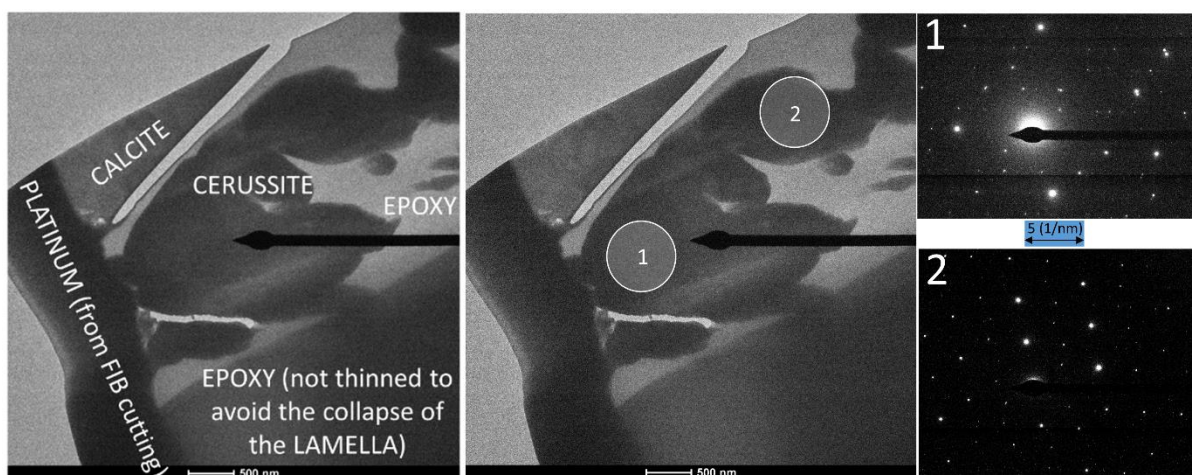


Figure SII.1. Three lamellas were made with CAL samples reacted for 10 days with Pb^{2+} but none allowed to observe any tight CAL-CER interface. One of these lamellas is shown: from the TEM image is evident the incongruent growth of CER on CAL. Electron diffraction also confirmed the different orientation of CER crystals grown onto CAL surfaces by showing different geometries for the diffraction pattern of CER along the reaction front.

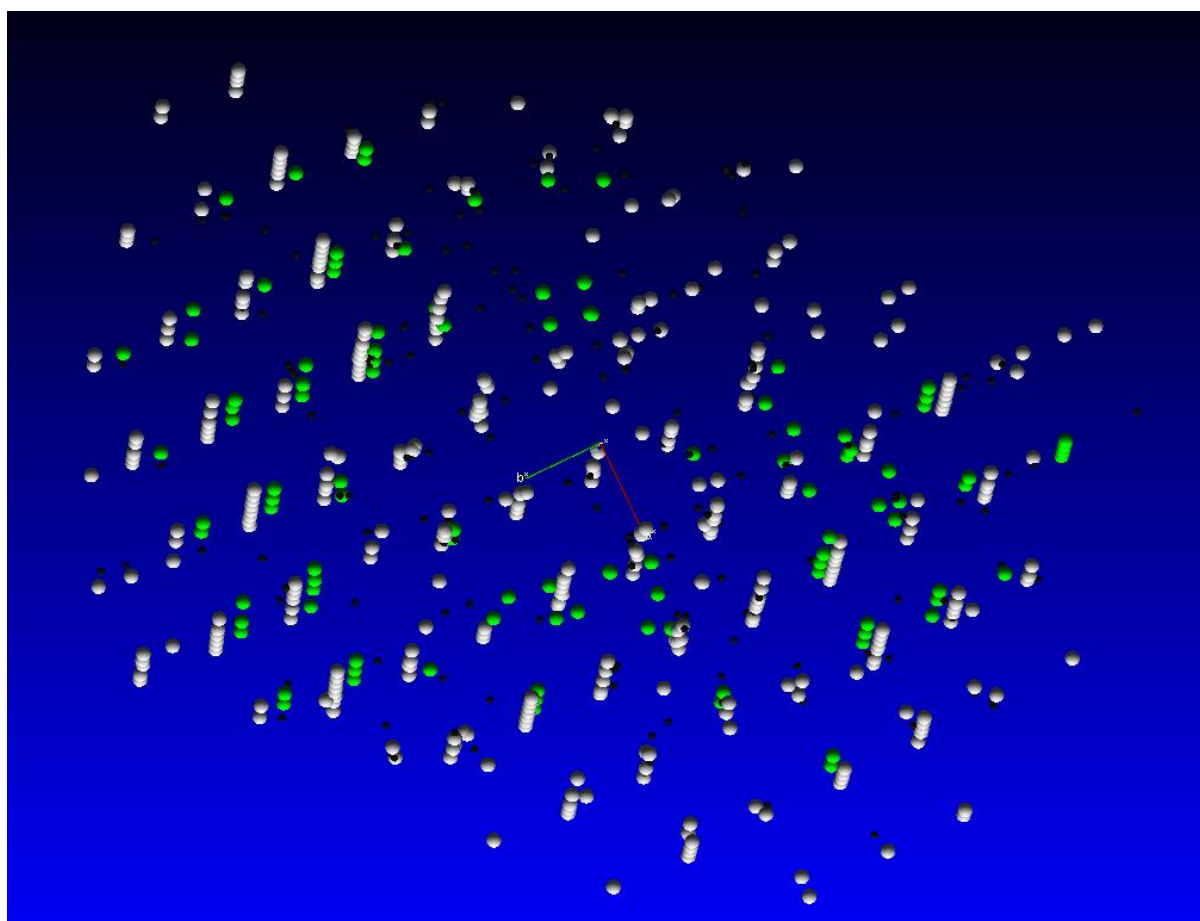
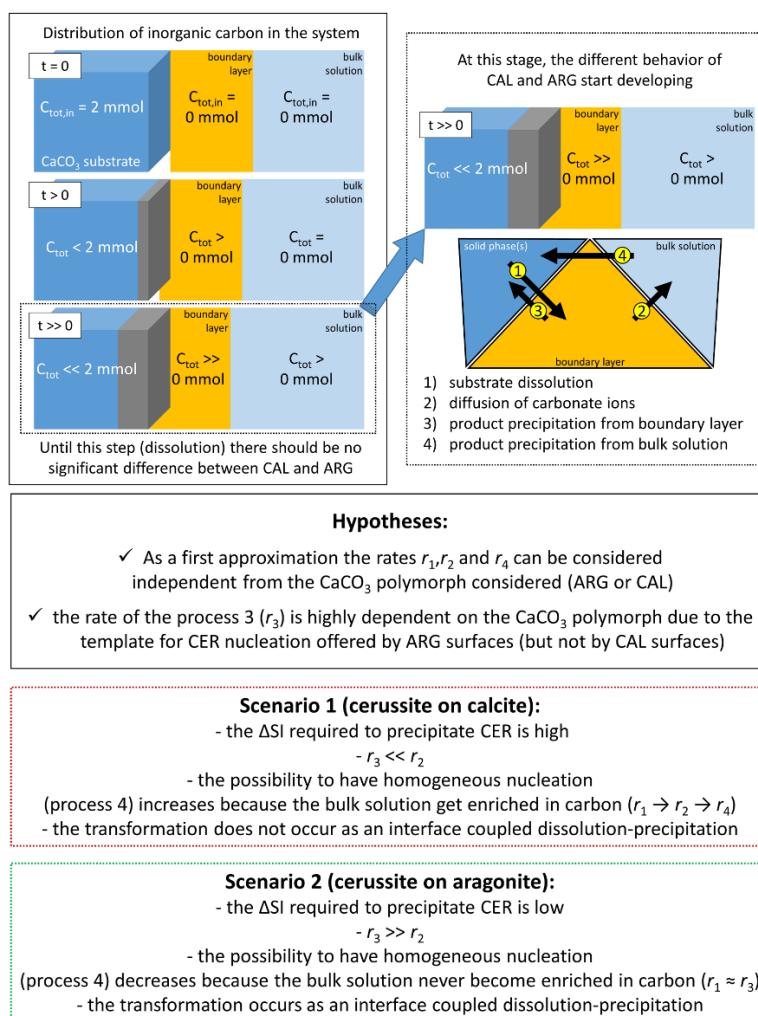


Figure SI2. Reciprocal lattice view of the ARG grain after 10 days of interaction with a solution containing Pb^{2+} . Reflections corresponding to aragonite are depicted in grey. Green reflections correspond to those that could be harvested and indexed with cerussite unit cell. A reciprocal lattice view similar to this cannot be obtained for CAL because CER signals were not oriented and perfect Debye rings were observed (Figure 3a).

1 The physical-chemical interpretation of the interface coupled dissolution-precipitation

2 This paragraph describes briefly the relationship existing between ICDP and mineral
 3 replacement. The possibility to have a product phase with the same morphology of the substrate
 4 relies on the fact that the dissolved ions should immediately reprecipitate as components of the
 5 product phase. When dissolved ions reprecipitate from the boundary layer at a much faster rate
 6 than diffusion to bulk solution, the process is an ICDP and the transformation reaction is a
 7 mineral replacement (i.e. a specific subcategory of the solvent-mediated transformations, see
 8 introduction).



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10 Figure SI3. Evolution of the distribution of inorganic carbon in the system. After the beginning
 11 of the dissolution, some inorganic carbon is transferred from the substrate to the boundary

1 layer. At this stage, the possibility that precipitation will occur in the boundary layer has an
2 inverse relationship with the energetic barrier required to nucleate the product on the substrate.
3 When the substrate offers a template for the nucleation of the product (i.e. ARG case), the
4 activation energy for the process 3 is small. Most of the carbonate ions, delivered by ARG
5 dissolution to the boundary layer, will reprecipitate as CER without reaching the bulk solution.
6 Thus, the possibility to have homogeneous nucleation in the bulk solution is minimum. The
7 occurrence of precipitation directly in the boundary layer (i.e. ICDP) is a prerequisite for the
8 development of a mineral replacement reaction. If there is not template effect, the activation
9 barrier of the process 3 is relatively high (at least higher than the ARG case) and the process 2
10 is more effective in transferring the carbonate ions to the bulk solution. In this case, a significant
11 amount of carbonate ions reaches the bulk solution. This could allow the homogenous
12 nucleation of the product (cf. Figure 8).

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