

## Geochemical partitioning and mineral speciation of Zn in naturally metal-enriched soils of SW Spain

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Some soils of the Sierra de Aracena (SW Spain) have been naturally highly enriched in Zn, and other metals, by intensive supergene alteration of sulphide-bearing parent rocks. The soils are mineralogically composed of illite, vermiculite, kaolinite, quartz, feldspars with minor hematite, and have a near neutral reaction (pH: 6.6-6.9).

Results from the BCR sequential extraction procedure modified by using focused ultrasound [1] showed that the vast majority of Zn was present in the residual immobile fraction of soils (F4, Table 1). The exchangeable fraction of Zn, assessed by single extraction with MgCl<sub>2</sub> and NH<sub>4</sub>AcO, was found to be virtually negligible (< 1%). A SEM-EDS analysis hinted that Zn is hosted mainly in the crystal lattice of vermiculite (up to 0.37 pfu).

These findings conclusively indicated that potential mobility of Zn should remain low under the present soil conditions.

Samples	FH-4a	FH-5a
Total concentration in soil	7680	5540
<i>Sequential extraction (in triplicate)</i>		
<b>F1</b> (HOAc 0.11 M, 7 min)	195±4	295±11
<b>F2</b> (NH <sub>2</sub> OH.HCl 0.1 M, pH 2, 7 min)	572±23	610±21
<b>F3</b> (H <sub>2</sub> O <sub>2</sub> 8.8 M, 2 min, 85° C + NH <sub>4</sub> AcO 1M, pH 2, 6 min)	254±30	265±19
<b>F4</b> (HF+HNO <sub>3</sub> +HCl digestion)	7032±75	4797±93
Total (Σ F1+F2+F3+F4)	8053	5967
<i>Single extractions (in triplicate)</i>		
MgCl <sub>2</sub> 1 M, 1 h	26.4±2.3	59.6±5.3
NH <sub>4</sub> AcO 1M, 1 h	11.5±0.5	21.4±1.2

**Table 1:** Concentrations of Zn in soil samples and extract solutions, as determined by ICP-OES. All values are reported in mg kg<sup>-1</sup>

[1] Pérez-Cid *et al.* (1998) *Anal Chim Acta* **360**, 35-41

## An experimental study on the role of the tetrahedral SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup> anions in the CaCO<sub>3</sub> polymorphism

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Crystallization in the CaCO<sub>3</sub>-H<sub>2</sub>O system is major topic, in a wide variety of disciplines, from geology and geochemistry to biomineralization and industrial crystallization. Although calcite is its most stable polymorph under Earth's surface conditions, CaCO<sub>3</sub> can precipitate as three different crystalline forms: vaterite, aragonite and calcite. Moreover, a number of hydrated and amorphous phases with different water contents can also precipitate. The nucleation and growth of metastable CaCO<sub>3</sub> polymorphs is commonly related to the predominance of kinetic factors over thermodynamic properties. The presence of different foreign ions in the fluid during CaCO<sub>3</sub> crystallization can also promote the formation of metastable phases. The possible incorporation of foreign ions into the structure of the different polymorphs would change their energetic properties and because the free energy of CaCO<sub>3</sub> polymorphs is relatively close, any modification of their energetic properties could determine stability crossovers that would affect the polymorph selection at nucleation and the development of transformations between polymorphs. Therefore, when foreign ions are present in the crystallization medium, both kinetic and thermodynamic factors have to be considered to understand the formation of CaCO<sub>3</sub>. Recent studies have shown that tetrahedral anions like sulfate, chromate or selenate are among the most influential in the crystallization of CaCO<sub>3</sub>, contributing to the stabilization of amorphous calcium carbonate in biogenic systems [1] or vaterite [2] in inorganic systems. We present here experimental results that illustrate the influence of some tetrahedral anions on the crystallization of CaCO<sub>3</sub> from aqueous solutions. These results include examples of unexpected polymorph formation and transformation pathways that carry the pass by of polymorphs.

[1] Gal A., Weiner S. & Addadi L. (2010), *J. Am Chem. Soc.* **132**, 13208-13211. [2] Fernández-Díaz L., Fernández-González A. & Prieto M. (2010), *Geochim. Cosmochim. Acta* **74** 6064-6076.