

VATERITE STABILITY IN THE PRESENCE OF Cr (VI). J.A. Cruz¹, N. Sánchez-Pastor¹, A. M. Gigler², and L. Fernández-Díaz¹. ¹Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. 28040, Madrid (Spain), ²CeNS and Department for Earth and Environmental Sciences, Ludwig-Maximilians-Universität. 80333, Munich (Germany).

Calcium carbonate phases are relevant in numerous scientific disciplines due to their abundance in both inorganic and biotic media and for a wide range of industrial applications. Many studies demonstrate that vaterite is thermodynamically unstable with respect to the aragonite and calcite. However, Navrotsky pointed out that calcite, aragonite, and vaterite are close enough in free energy such that small changes in their surface properties and/or concentration of impurities can determine stability crossovers.[1] It has been shown experimentally that vaterite can become temporarily stabilized when it forms in the presence of different ions [2, 3].

This investigation was focused on the effect of Cr (VI) stabilizing the polymorph vaterite. The crystallization of vaterite was carried out using a double diffusion system [4] which consisted of two vertical branches separated by a column of silica hydrogel. The vertical branches were filled with 0.5 M CaCl₂ and 0.5 M Na₂CO₃ solutions, and different amounts of a Na₂CrO₄ solution were added to the silica gel during its preparation (0.1, 0.15, and 0.2 M). The vaterite aggregates were recovered from the gel after 30 days and were studied by scanning electron microscope and Raman spectroscopy. Figure 1 shows examples of vaterite aggregates grown in silica gel bearing Cr (VI) concentrations ranging from 0.1 M (a) to 0.2 M (c), where their characteristic morphology can be observed.

The Raman spectra collected from those aggregates formed in gels containing ≥ 0.15 M Cr(VI) (Figure 1b and 1c) show the typical vaterite triplet at 1074, 1081, and 1094 cm⁻¹ and an additional line at 750 cm⁻¹. Further translational and rotational lattice modes can be observed between 100 and 300 cm⁻¹ consistent with vaterite [5]. However, in contrast to the external morphology of the aggregate shown in Figure 1a, its Raman spectrum shows peaks at 1085 cm⁻¹, 208 cm⁻¹ and 711 cm⁻¹, all of them characteristic of calcite [6]. A closer examination of this sample (see the inset of Figure 1a) shows that it is, in fact, a vaterite pseudomorph that consists of small calcite rhombohedra. The facts that: i. Cr-free experiments did not yield any other CaCO₃ polymorph than calcite and ii. Vaterite transformed into calcite when the concentration of Cr (VI) in the growth medium was lower than 0.15 M, indicate that the presence of Cr (VI) promotes the formation of vaterite. However, only high Cr (VI) concentrations in the growth medium can prevent its transformation into calcite after a relatively short time.

References:

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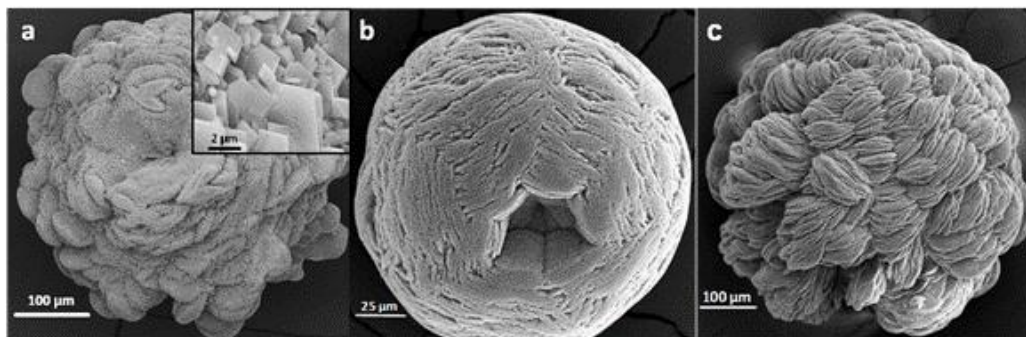


Figure 1. SEM micrographs of aggregates extracted from experiments with: (a) 0.1 M, the close up reveals small calcite crystals, (b) 0.15 M and (c) 0.2 M chromate concentration.