## Interaction of gypsum with As(V)-bearing aqueous solutions: Surface precipitation of guerinite, sainfeldite, and Ca<sub>2</sub>NaH(AsO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, a synthetic arsenate

## JUAN D. RODRÍGUEZ,<sup>1</sup> AMALIA JIMÉNEZ,<sup>1,\*</sup> MANUEL PRIETO,<sup>1</sup> LAURA TORRE,<sup>2</sup> AND SANTIAGO GARCÍA-GRANDA<sup>2</sup>

<sup>1</sup>Departamento de Geología, University of Oviedo, Jesús Arias de Velasco, Oviedo, Asturias 33005, Spain <sup>2</sup>Departamento de Química Física y Analítica, University of Oviedo, Julian Clavería s/n Oviedo, Asturias 33006, Spain

## ABSTRACT

The interaction of arsenate-bearing aqueous solutions with gypsum at a starting pH of 9 and 25 °C results in surface precipitation of guerinite,  $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$ , sainfeldite,  $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4H_2O$ , and occasionally  $Ca_2Na(HAsO_4)(AsO_4) \cdot 6H_2O$ , a new arsenate. These three solid phases are characterized by the simultaneous presence of  $HAsO_4^{2-}$  and  $AsO_4^{3-}$  groups in their structure, which is explainable since crystallization occurs within a pH range in which both  $HAsO_4^{2-}$  and  $AsO_4^{3-}$  are available in the aqueous solution. The interaction leads to a decrease in the As(V) concentration in the aqueous phase to reach values controlled by the solubility of these solid phases. The study combines several macroscopic experiments, in which changes in the solution chemistry are monitored as a function of time, with the characterization of solid phases by SEM-EDS and XRD. The crystal morphologies of the precipitating phases are interpreted on the basis of their respective structures. The thermodynamic solubility products of both guerinite and the new arsenate have been determined, being  $10^{-31.17\pm0.05}$  and  $10^{-13.83\pm0.03}$ , respectively. The reaction paths followed by the system and the equilibrium endpoints have been modeled using the geochemical code PHREEQC.

**Keywords:** Crystal growth, calcium arsenate, analysis chemical, sainfeldite, phase equilibrium, guerinite, gypsum