LETTER: ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT†

Evidence for nanocrystals of vorlanite, a rare uranate mineral, in the Nopal I low-temperature uranium deposit (Sierra Peña Blanca, Mexico)

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ABSTRACT

The occurrence of vorlanite, cubic CaUO4, is reported in the Nopal I uranium deposit (Sierra Peña Blanca, Mexico). This is the first time this rare calcium uranate has been found displaying a cubic morphology, in agreement with its crystal structure. Vorlanite occurs as nanoscale crystals embedded in U-bearing opal, with a Ca/U ratio of ~1. Association with opal suggests that vorlanite formed at Nopal during late-stage U-mobilization under oxidizing conditions and low (<50 °C) temperature. The presence of nanoscale uranate crystals in an environment largely dominated by uranyl silicates indicates that uranates may play a role in uranium scavenging at low temperature. In addition, the occurrence of vorlanite in the crystal shape consistent with its structure provides unique information on its conditions of formation.

Keywords: Vorlanite, cubic CaUO4, uranate, nanoscale crystal, opal, Nopal

INTRODUCTION

Uranium migration in geological formations has major geochemical, economical, and environmental applications (Ragnarsdottir and Charlet 2000). Under oxidizing conditions, soluble hexavalent uranium occurs as uranyl groups complexed by various anions (Langmuir 1978). The fate of uranium in environmental systems is affected by several mechanisms, including precipitation, adsorption onto minerals, amorphous materials or organic matter, and absorption by organisms (e.g., Duff et al. 2002). Colloidal-facilitated transport of actinides may be an additional transport process (Novikov et al. 2006). In silica-saturated waters, uranium trapping mechanisms include adsorption on silica colloids, as shown by Allard et al. (1999) during the oxidative weathering of the Pény (Massif Central, France) uranium deposit, underlining the importance of silicate ligands.

Recently, Schindler et al. (2010) investigated uranium speciation in recent and low-temperature opals from the Nopal I uranium deposit (Sierra Peña Blanca, Mexico) (Calas et al. 2008 and references therein; Angiboust et al. 2012). They found that opal was zoned with respect to Ca and U, retaining an almost constant atomic ratio of 1:1, and suggested a mechanism of trapping Ca-U-particles or aqueous species by colloidal silica.

We present new data on the Ca-U species occurring in the opals from Nopal I, to constrain the chemical conditions that prevailed during uranium transport and further trapping in opal. One thick-section and focused ion beam (FIB) ultrathin sections of one opal sample were investigated, using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectrometry (EDXS). These techniques provided evidence for the presence of vorlanite nanoscale crystals. They are found within U-rich, but amorphous, opal zones retaining a Ca:U ratio of 1:1, which could have played the role of precursor for vorlanite crystallization.

MATERIALS AND METHODS

Samples

Opals at Nopal I fill fractures, pores and cavities in the subsurface (Cesbron et al. 1993; Calas et al. 2008; Schindler et al. 2010). They belong to the amorphous (A) type, as shown by X-ray diffraction (XRD) analyses (Schindler et al. 2010). Opals at Nopal I can overlie kaolinite, hematite, and uranyl minerals and display green or yellow colors. A detailed paragenesis of the uranium-bearing minerals at the Nopal I deposit has been described recently (Fayek et al. 2006; Calas et al. 2008; Angiboust et al. 2012). The sample used in this study consists of yellow opal and comes from an exposed surface of the Nopal I uranium deposit. One thick-section of this sample was prepared to examine the macro- and micro-layering in the sample. Two FIB ultrathin sections were prepared from this thick-section for TEM analysis.

Scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA)

Scanning electron microscopy (SEM) images were obtained using a Zeiss Ultra 55 SEM-FEG UHR (IMPMC, Paris). Semi-quantitative analyses were per-