The effect of carbonate on barite growth at elevated temperatures studied with Raman spectroscopy

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Barite ($BaSO_4$) occurs in a wide variety of geologic environments from the early Archean to the present (Hanor 2000). Due to its low solubility in water ($K\text{sp} = 10^{-9.96}$ at 20 ºC), barite precipitation and dissolution control the geochemical distribution of barium in surface waters as well as in crustal fluids. Mixing of Ba-rich hydrothermal fluids with sulfate-rich meteoric or ocean fluids produces supersaturated solutions and results in a rapid precipitation (Hanor 1994). Crystal growth from solution is a complex process comprising of several steps from bulk diffusion to the final incorporation of the growth unit (Astilleros et al. 2006).

To characterize the influence of temperature and the possible incorporation of carbonate into the structure, Raman spectroscopic analyses were performed. For this purpose, natural barite crystals were cleaved along the (001) surface and placed within a batch reactor (volume ~1000 ml). The reactor was filled with a solution supersaturated with respect to barite (Ω_{barite} = 12.3, $\Omega_{\text{witherite}}$ = 0.03) and containing 0.03 mMol sodium carbonate at 50 ºC (carbonate speciation $a(CO_3^{2-})$ = 0.1×10 5 Mol, $a(HCO_3^{-})$ = 2.8×10–5 Mol). For Raman measurements, the crystals were removed from the solution after 240 hours.

Raman spectra were taken with a confocal micro-Raman spectrometer (HORIBA; XploRa-Raman-System) in order to clarify whether the growing barite crystal incorporates significant amounts of carbonate. For excitation we used the second harmonic generation (532 nm, P_{max} = 15 mW) of a Nd-YAG laser, focused with a 100× long- distance objective (Olympus) and a beam diameter of 0.7 µm. All spectra were analyzed using FITYK curve fitting and data processing software (Wojdyr 2010).

The Raman spectra of the barite samples were dominated by an intense ν_1 band (symmetric stretching) of SO_4 tetrahedra at 989 cm^{-1} (Fig. 1). The other characteristic bands, ν_2, ν_3 and ν_4 reported in literature (Sánchez-Pastor et al. 2011) were also present (Fig. 1). The ν_2 vibration (in-plane bending) generated bands in the 400–500 cm^{-1} region, the ν_4 vibration (out-of-plane bending) generated bands in the 600–700 cm^{-1} region, and the ν_3 vibration (asymmetric stretching) generated bands in the 1080–1200 cm^{-1} region. Figure 1 shows these regions for a pristine barite (barite_pure, grey data) and a crystal that was treated with the growth solution at 50 ºC (barite_C, black data). In both cases, the Raman bands are approximately in the same positions. However, it should be noted that the Raman spectra of crystals are anisotropic. That is, the band positions and relative band intensities may vary slightly depending on the crystal lattice orientation. Figure 2 shows the band component analysis of a section of the Raman spectra with the ν_3 band for pristine barite (barite_pure, grey data) and treated barite (barite_C, black data). For comparison the Raman spectrum of a natural witherite aggregate has been superimposed. The peaks at 1084 cm^{-1}, 1106 cm^{-1}, 1140 cm^{-1} and 1168 cm^{-1} are characteristic for Raman spectra of pure barite and are present in both barite spectra. The Raman spectrum of the treated barite shows an additional peak at 1059 cm^{-1}. This peak was exclusively observed at barite samples which grew in carbonate containing solution and corresponds to the ν_1 internal mode (symmetric stretching) of carbonate in witherite. Therefore, the peak is conclusive for the presence of carbonate groups incorporated within the barite lattice. On the basis of this finding we speculate that the different effects of carbonate are not only caused by (temporarily) chemisorbed complexes but also by incorporation of carbonate into the barite structure.

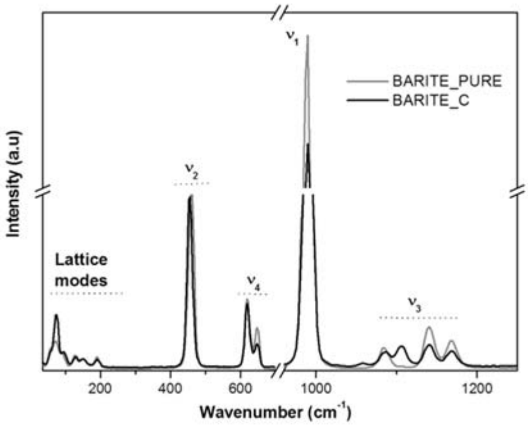

Fig.1. *Raman spectra of pristine barite (barite_pure) and barite crystals which grew in carbonate containing solutions (barite_C).*

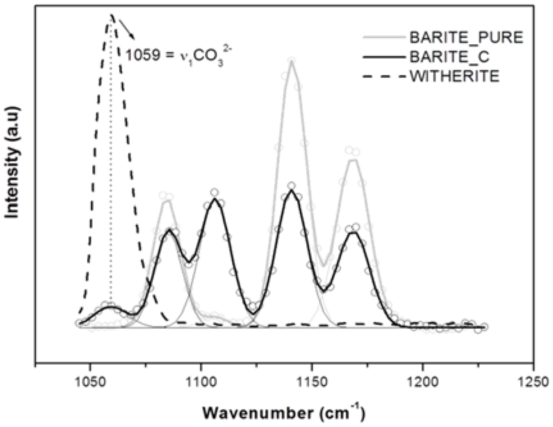

Fig.2. *Fitted Raman spectra (FITYK) of pristine barite (barite_pure) and barite crystals which grew in carbonate containing solutions (barite_C).*

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