RAMAN SPECTROSCOPY AND MICROPROBE INVESTIGATION OF THE INCORPORATION OF Cr (VI) IN CaCO₃. A. M. Gigler¹, N. Sánchez-Pastor², J. A. Cruz², and L. Fernández-Díaz². CeNS and Department for Earth and Environmental Sciences, Ludwig-Maximilians-Universität. 80333, Munich (Germany), Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. 28040, Madrid (Spain).

Introduction. Due to its high mobility and toxic effects even in low concentrations, hexavalent chromium (Cr (VI)) is known as one of the most common environmental contaminants resulting from its widespread use in industrial applications. Cr (VI) compounds are used mainly because of their acidic properties and their ability to form intensely colored and insoluble salts.

Experimental. The crystallization experiments were performed in a double diffusion system [1]. Different concentrations of Na₂CrO₄ (0.1, 0.15, and 0.2 M) were added to the sodium silicate solution during the gel preparation. Two months after the nucleation, crystals comprising a representative range of morphologies with different intensities in yellow color were hand-picked from the gel. Their morphology was studied by scanning electron microscopy and the Cr concentration of the crystals and the development of zoning were analyzed by electron microprobe. A confocal Raman microscope was used to identify the CaCO₃ polymorphs and to investigate the zoning in the crystals.

Results and discussion. All spectra revealed the characteristic peak of calcite at 1085 cm⁻¹ which is caused by the symmetric stretching vibration of the carbonate group. Furthermore, we observed peaks at 280 cm⁻¹ and 711 cm⁻¹ corresponding to the translational and rotational lattice mode vibrations and to the internal translational modes of in-plane bending of the carbonate ions, respectively. In Figure 1, a close up of the v₂ region (peaks between 700 and 1100 cm⁻¹) of these samples together with the main vibrational modes for chromatite as a reference is shown. The chromatite spectrum was obtained from a natural sample. In addition to the calcite bands mentioned above, some weak Raman bands appear between 850 and 925 cm⁻¹. As mentioned by Urmos et al. [2], the v₂ band at 875 cm⁻¹ is not allowed in the Raman spectra of crystals with calcite structure. However, this vibrational mode at 875 cm⁻¹ is the most intense in chromatite and could be assigned to the v₁ symmetric stretching vibration of CrO₄. Some additional weak bands are also present. Frost and Weiner described the Raman spectra of the CrO stretching region of some chromate-bearing minerals [3] in this region the band position varies from 825 to 972 cm⁻¹ depending on the mineral. We found three main bands at 855, 875, and 975 cm⁻¹. The first two agree well with those enunciated by Frost and Weiner and subsequently, the new bands represent the incorporation of Cr (VI) into the calcite structure as chromate groups. Furthermore, Wang et al. conducted a Raman spectroscopic study to distinguish the chromate species on Cr-MCM-41 synthesized by a direct hydrothermal synthesis method [4] In this work, the band at 980 cm⁻¹ was assigned to the Cr-O vibration stretching of the dehydrogenated monochromate species (CrO₄²⁻). Thus, the third more intense band found in our spectra can be also correlated with the presence of Cr (VI) in the structure. These hypotheses are supported by the fact of the different intensities of the new bands. As can be observed in Figure 1, the intensity of the new peaks can be correlated to the content of Cr (VI) in the gel medium.

To investigate the possible zoning of the calcite crystals, a yellow crystal from the experiments with higher Cr concentration (0.2 M) was analyzed in detail by Raman and microprobe mapping. The electron microprobe showed that the inner part is Cr rich, while pure calcite is present in the outer regions. Moreover, a Raman profile was obtained from the same crystal and the analysis is perfectly correlated with the microprobe analysis.

Conclusions. i. Our results confirm the suitability of Raman spectroscopy to characterize the incorporation of impurities in carbonate phases and, ii. The incorporation of Cr is evidenced by the appearance of new vibrational bands in the calcite spectrum, which are consistent with the substitution of carbonate groups by chromate groups.

Figure 1. Close up of the v₂ region with the main vibrational modes for chromatite superimposed.

References.