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Characterization of sulfur-containing calcite in a travertine carbonate rock

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Since the first documentation by Reeder and Wenk (1979), a number of studies reported weak extra reflections in rhombohedral carbonates in electron diffraction (ED) and referred to them as *c*-reflections.It was suggested that *c*-reflections are formed by the ordering of impurity cations such as Mg^{2+}, Fe^{2+} and , Mn^{2+} substituting Ca^{2+} (e.g. Reeder, 1981). Recently we have also found weak extra reflections similar to *c*-reflections in the ED patterns of calcite precipitated in a hot-spring (La Duke) near Yellow Stone National Park. The Selected-area ED pattern along the [001] direction indicated that the extra reflections appear holding the three-fold symmetry of calcite. Those weak reflections were found halfway between principal reflections. However, X-ray microanalysis indicated that the amount of impurity cations such as Mg^{2+} is very small and sulfur (S) is the major impurity element. S/Ca atomic ratio is about 3%. The cell parameters of the La Duke sample were determined by synchrotron X-ray powder diffraction (wavelength = 0.7749 angstrom) and Rietveld refinement. It showed that the *a*-length (4.9757 angstrom) slightly decreased and the *c*-length (17.0998 angstrom) slightly increased compared to the pure calcite (*a* = 4.9906 angstrom, *c* = 17.0621 angstrom), or the *c/a* axial length(3.437) of La Duke calcite is longer than that of pure calcite (3.419). The TG-DTA analysis was performed to find whether the sulfur exists in the calcite crystal or as organic matter. The anhydrite ($CaSO_4$) was detected at 600 degrees C and the *c*-length has recovered to that of pure calcite, suggesting that sulfur are incorporated in the calcite as a solid solution. XPS analysis was used to determine the chemical species of sulfur. Since the sulfur 2p3/2peak of La Duke is located at 168.35 eV, the sulfur is involved in the ions of sulfate (SO_4^{2-}).The crystal structure of La Duke calcite has been investigated using a four-circle X-ray diffractometer (Mo, wavelength = 0.71075 angstrom). Weak electron density around the oxygen was found, which may be related to the SO_4^{2-}.

Keywords: calcite, electron diffraction, sulfur, superstructure, travertine