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VIBRATIONAL STUDY ON CARBON DIOXIDE SIEVED INTO THE SODALITE β-CAGE OF LAPIS LAZULI

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In 1999 a study of the GCI reports about a small and sharp absorption band at 2340 cm^{-1} in samples of ultramarine blue from several Italian paintings of the XV and XVI centuries. Derrick and co-worker noted that the absorption band at 2340 cm^{-1} occurred only in natural ultramarine from Afghanistan and tentatively assigned it to the sulfur species S_6^+. Despite the interest of this finding, the small band at 2340 cm^{-1} has not been further considered by other authors dealing with vibrational properties of lapis lazuli. In this paper we present a spectroscopic investigation of natural ultramarine pigments aimed to furthering our understanding on the origin of this absorption band at 2340 cm^{-1}. Non-invasive reflectance mid-FTIR measurements have been carried out on more than 15 ultramarine minerals belonging to the historical mineral collection of the Museum of Natural History, University of Florence, revealing that the absorption at 2340 cm^{-1} is present in all the samples from Afghanistan and generally with minor intensity also in sample from Siberia. The band 2340 shows a satellite peak at 2275 cm^{-1} with a relative intensity of about 2%. The value of d shift (65 cm^{-1}) and the relative intensity of the two bands allow them to be correlated to the presence of CO_2 that is responsible of the absorption at 2340 as $^{12}CO_2$ and at 2275 as $^{13}CO_2$. The thermal behavior of powdered natural ultramarine from Afghanistan, has been studied by FTIR, XRD, UV-*vis* and Raman from 300°C to 850 °C. Data show that CO_2 and the S_3^- chromophore behave in the same way during the heating experiment, being released only at T > 650°C when the sodalite β-cage starts to be distorted as effect of the temperature.

All these data demonstrate that CO_2, as the S_3^- chromophore, is encapsulated within the sodalite β-cage of natural ultramarine blue, originating the sharp signal at 2340 cm^{-1} visible by non-invasive mid-FTIR on blue areas of several Renaissance paintings.