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From minerals to Middle Ages stained glasses: the role of Co^{2+} speciation in the blue color

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Cobalt coordination plays a major role in the coloration of minerals and glasses. We present a spectroscopic study of Co^{2+} speciation in minerals and glasses, using optical absorption and X-ray absorption spectroscopy.

Crystalline references, with 6-, 5- and 4-coordinated Co^{2+} have been investigated. Octahedral Co^{2+} was investigated in calcite, olivine, sulphate and $Co_2B_2O_5$, chosen for the important color variations provided by the presence of this element. The latter offers an original linkage of octahedra in a ribbon-like structure. Its purple color arises from the distortion of the octahedral sites and the EXAFS analysis confirms the long-distance correlations arising from this original structure. We compared Co-doped spinels of various degree of inversion to investigate the effect of the superposition of the contribution of tetrahedral and octahedral Co^{2+}. Optical spectroscopy only reveals the strong absorption of tetrahedral Co^{2+} but Co K-edge XANES confirms the presence of Co^{2+} in both tetrahedral and octahedral sites, a confirmation that only the former is an efficient coloring form. In $Co_3(PO_4)_2$, both 6 – and 5-coordinated Co^{2+} coexist, providing information on the spectroscopic properties of 5-coordinated Co^{2+}.

Co^{2+}-bearing alkali borate glasses present a wide range of colors, due to a Co^{2+} coordination change as a function of the alkali content of the glass. However, this color change is more complex than a simple transformation from octahedral to tetrahedral coordinated Co^{2+}: a major fraction of Co^{2+} appears as "silent" species, and may occur in symmetric, non octahedral sites. In silicate glasses, such silent species explain the strong variations in the apparent molar absorption coefficient of tetrahedral Co^{2+}: indeed, despite silicate glasses exhibit a similar blue color, the intensity of this coloration varies with the glass composition. We will present the application of this study to the origin of the blue coloration of stained glasses, from the French Middle Age period (12-13th centuries) and more recent glasses (16th century and modern glasses used for their replacement). The presence of several glass modifiers in the glass composition and the coexistence of different transition elements explain the strong variation observed in the optical properties of these glasses.