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Spectroscopic and physicochemical study of the color grain-size effect in lazurite-type minerals

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Abstract

X-ray photoelectron spectroscopy, micro-Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray powder diffraction, thermal analysis, and scanning electron microscopy were used to study the nature of color grain-size effect (CGSE) in samples of lazurite-type minerals (LTM) from deposits near Lake Baikal (Russia). A neotype of the mineral with the ratio of cage anions SO_4^{2-} and S_3^-, close to unity, found at the Malo-Bystrinskoye deposit, was used as a standard sample. Experiments in air at 800 °C for 8 h with particles of <0.04 and 0.1–0.2 mm size showed that the former partially or completely decolorize, and the latter darken in the bulk and acquire a violet hue. The effect is practically independent of the structure features of the starting material (incommensurately modulated cubic, orthorhombic, monoclinic), although the non-cubic varieties easily lose S_3^- chromophore in small particles. In the sample initially containing the molecular center S_4, neither S_4 nor S_3^- retains in small grains. Raman spectra do not reveal any bands that allow for identifying the nature of the species responsible for the preservation and deepening of the color tone of the "large" grains. FTIR data do not exclude the presence of thiosulfate, but mainly record the tetrahedral framework vibrations, S-O stretching and bending modes, and the presence of H_2O, CO_2, and CO_3^{2-} in the structures of the initial samples. TA and SEM data reveal significant development of calcite microinclusions in LTM samples. We propose a model according to which in relatively large grains calcite microinclusions and subgrain boundary segregations play the role of an internal buffer that maintains the equilibrium coexistence of oxidized (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$) and reduced (S_3^-) sulfur. As a result, the blue coloration due to the S_3^- chromophore is retained and even becomes more saturated, acquiring a violet hue due to the admixture of the $S_2O_3^-$ radical ion or a change in the configuration of the trisulfide radical. In small grains, microinclusions and grain-boundary calcite precipitates are mostly exposed to the surface or isolated, resulting in loss of buffering properties, S_3^- instability with respect to air oxygen, and discoloration of the grains. In lazurite pigment with properly selected grain size, the stability of the chromophore is provided by the internal buffer, which can eliminate the discoloration of paints used for architectural and graphic art projects. With the optimal particle size, lapis lazuli pigment in paints is a stable phase and will not discolor over time in air.

Keywords: Lazurite-type minerals, coloration and discoloration, grain-size effect, chromophores, sulfur speciation