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An insight into the inverse transformation of realgar altered by light

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Abstract

The light-induced alteration of realgar and β-As_4S_4 is a well-known phenomenon but still displays interesting aspects not completely explained. In the transformation from realgar to pararealgar the molecule As_4S_4 undergoes a structural modification, and ever since the initial studies two important issues have been highlighted: the influence of the oxygen and the reversibility of the process. The previous study on the reversibility of the altered β-As_4S_4 points out that this polymorph exhibits a dual behavior. When the light-induced alteration occurs with the presence of the air, pararealgar and arsenolite, along with amorphous material, are the products, while if the air is not present β-As_4S_4 turns completely into pararealgar. Moreover, when annealing the altered material in the realgar stability fields (220 °C), in the first case pararealgar and amorphous material turn into stoichiometric alacranite, while in the second case the alteration is completely reversible. Similarly, the present study focuses the attention on the question if realgar, when altered by means of the light and when annealed, might behave as β-As_4S_4 does. These results display that the phenomenon is more complex. The alteration of realgar with the presence of the air yields pararealgar along with arsenolite, a small quantity of uzonite and amorphous material, and when the air is not present pararealgar is the only product. In the first case, when annealing the products of alteration at 220 °C, alacranite, β-As_4S_4, realgar, and little amorphous material occur along with arsenolite. In the second case at first β-As_4S_4 crystallizes, then it turns into realgar, but this process yields orpiment and amorphous material as it moves forward, showing that from the products of alteration of realgar it is not possible to obtain the starting material. Examination of the stoichiometry of the products let to infer that the amorphous material occurring in the two cases has very different content of arsenic and sulfur.

Keywords: Realgar, light, heat, pararealgar, alacranite, uzonite, Rietveld