

Light-induced degradation dynamics in realgar: in situ structural investigation using single-crystal X-ray diffraction study and X-ray photoelectron spectroscopy

ATSUSHI KYONO,^{1,*} MITSUYOSHI KIMATA,¹ AND TAMAO HATTA²

¹Division of Earth Evolution Sciences, Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8572, Japan

²Japan International Research Center for Agricultural Sciences, Ohwashi 1-1, Tsukuba, Ibaraki 305-8686, Japan

ABSTRACT

Light-induced degradation in realgar (arsenic sulfide) has been studied by means of four-circle single-crystal X-ray diffraction and X-ray photoelectron spectroscopy. Because of the alteration of realgar exposed to light, the *a* lattice parameter and *c* sinβ value increase linearly from 9.327 to 9.385 Å and from 6.320 to 6.364 Å, respectively. In contrast, the *b* lattice parameter remains substantially constant. Anisotropic variations of the lattice parameters engender a continuous increase of the unit-cell volume from 799.5 to 810.4 Å³. Nevertheless, no correlation exists between the continuous increase of the unit-cell volume and the bond distance variations in As₄S₄ molecules because the As₄S₄ molecule in the unit cell expands very little during light exposure. The most pronounced change was in the distance between centroids in As₄S₄ cages. The spread of As₄S₄ intermolecular distances increases continuously from 5.642 to 5.665 Å, which directly affects the unit-cell volume expansion of realgar. In addition, the O1s peak increases rapidly after light exposure. The result substantiates the following reaction proposed by Bindi et al. (2003): 5As₄S₄ + 3O₂ → 4As₄S₅ + 2As₂O₃. That is, realgar is transformed into pararealgar if oxygen exists and produces the As₄S₅ molecule. The additional S atom contributes to anisotropic expansion for the *a* and *c* axes because the direction of the additional S atom points toward [4 $\bar{1}$ 4] in the unit cell. Furthermore, an S atom in the As₄S₅ molecule is released from one of the equivalent As-S-As linkages in As₄S₅ which becomes the As₄S₄ molecular of pararealgar. After the As₄S₅ molecule is divided into an S atom (radical) and the As₄S₄ (pararealgar type) molecule, the free S atom is re-attached to another As₄S₄ (realgar type) molecule, and reproduces an As₄S₅ molecule. The reproduced As₄S₅ molecule is again divided into an S atom (radical) and an As₄S₄ (pararealgar type) molecule. This cycle whereby realgar is indirectly transformed into pararealgar via the As₄S₅ molecule is promoted by light and repeated during light exposure.