Selenium oxysalts (selenites [4+] and selenates [6+]) occur relatively rare in natural environments even in comparison with, e.g., anoxic selenides [2–]. At the same time, Se-containing oxycompounds adopt a wide variety of atomic arrangements and crystal structures. For example, the interplay between stereochemical activity of lone electron pairs of Se4+ cations and the Jahn-Teller effect of spontaneous symmetry breaking in solids for a d9 electronic configuration of Cu2+ cations results in a number of crystal structures with unique structural topology. In particular, many natural and synthetic copper selenites have been shown to contain so-called ‘additional’ oxygen atoms, which are coordinated solely by Cu2+ cations resulting in the formation of oxocentered (OCu4)6+ tetrahedra combined into structural modules of different dimensionalities [1]. Herein, we present the results of our studies of a wide range of synthetic copper selenites and selenates, which have been prepared by different synthesis methods [2, 3]: chemical vapor transport reactions, evaporation from aqueous solutions, and mild hydrothermal techniques. These experiments can be considered as modelling of natural processes that occur in volcanic fumaroles or oxidation zones of copper mineral deposits. Topological relationships of the observed compounds with crystal structures of existing mineral species will be discussed.

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