

The crystal chemistry of welshite, a non-centrosymmetric (*P1*) aenigmatite-sapphirine-surinamite group mineral

EDWARD S. GREW,^{1,*} JACQUES BARBIER,² JIM BRITTEN,² ULF HÅLENIUS,³
AND CHARLES K. SHEARER⁴

¹Department of Earth Sciences, University of Maine, 5790 Bryand Center, Orono, Maine 04469, U.S.A.

²Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

³Department of Mineralogy, Swedish Museum of Natural History, Box 50007, SE-104 05 Stockholm, Sweden

⁴Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A.

ABSTRACT

Previous attempts to refine the crystal structure of welshite, known only from Långban, Sweden, have been foiled by its extensive polysynthetic twinning, and without a structure determination, derivation of a reasonable formula has been difficult due its eclectic chemical composition. We report a successful refinement [$wR(F^2) = 0.0566$ for 8048 unique reflections] in the non-centrosymmetric space group *P1* of a relatively little twinned crystal (4% chiral) from sample NRM040068: $a = 10.394(3)$ Å, $b = 10.777(3)$ Å, $c = 8.896(2)$ Å, $\alpha = 105.953(4)^\circ$, $\beta = 96.294(4)^\circ$, $\gamma = 124.948(3)^\circ$, $V = 738.8(3)$ Å³, $Z = 1$. The refined formula, $\text{Ca}_{3.78}\text{Mg}_{7.87}\text{Sb}_{3.00}\text{Mn}_{1.35}\text{Si}_{5.73}\text{Be}_{3.33}\text{Al}_{1.71}\text{Fe}_{0.96}^{3+}\text{As}_{0.27}\text{O}_{40}$, is in reasonable agreement with a formula determined by electron microprobe and Mössbauer spectroscopy (Be from the refinement), $\text{Ca}_{3.81}\text{Mg}_{7.84}\text{Sb}_{3.03}\text{Mn}_{1.17}\text{Zn}_{0.04}\text{Fe}_{0.05}^{2+}\text{Si}_{5.57}\text{Be}_{3.24}\text{Al}_{1.54}\text{Fe}_{1.25}^{3+}\text{As}_{0.37}\text{O}_{40}$. The *P1* symmetry of welshite 040068 is mainly a result of its cation distribution, which is driven by charge ordering on both the octahedral and tetrahedral sites as supported by calculation of electrostatic site potentials. Welshite can accommodate up to 3.46 Be per 40 O atoms by including several T sites with 100% Be occupancies without the formation of unfavorable tetrahedral Be–O–Be linkages that would result in the related centrosymmetric structures of sapphirine, khmaralite, makarochkinitite, and høgtuvaite, none of which contain >2.1 Be per 40 O. A generalized formula for welshite is $(\text{Ca},\text{Mn})_4(\text{Mg},\text{Mn},\text{Fe}^{2+},\text{Fe}^{3+})_9(\text{Sb},\text{Fe}^{3+})_5\text{O}_4[(\text{Si},\text{As})_6(\text{Be},\text{Al})_4(\text{Al},\text{Fe}^{3+})_2\text{O}_{36}]$. Compositions of most of the samples, including NRM040068, can be expressed in terms of two idealized Al and Fe end-members $\text{Ca}_4\text{Mg}_9\text{Sb}_3\text{O}_4[\text{Si}_6\text{Be}_3\text{Al}_3\text{O}_{36}]$ and $\text{Ca}_4\text{Mg}_9\text{Sb}_3\text{O}_4[\text{Si}_6\text{Be}_3\text{AlFe}_2\text{O}_{36}]$, respectively; the latter is the most representative for welshite and could be used in databases. One sample is far more heterogeneous and is irregularly zoned on scales from <1 to 10 μm . Compositional variation in this sample and in a crystal from another lie between the end-members $\text{Ca}_4\text{Mg}_{8.55}\text{Fe}_{0.45}\text{Sb}_{3.0}\text{O}_4[\text{Si}_{5.15}\text{As}_{0.45}\text{Be}_{3.45}\text{Al}_{0.5}\text{Fe}_{2.45}\text{O}_{36}]$ and $\text{Ca}_4\text{Mg}_{7.05}\text{Fe}_{3.45}\text{Sb}_{1.5}\text{O}_4[\text{Si}_{6.65}\text{As}_{0.45}\text{Be}_{3.45}\text{Al}_{0.5}\text{Fe}_{0.95}\text{O}_{36}]$, which are related by the coupled substitution $^{\text{M}}\text{Sb}^{5+} + ^{\text{VI}}\text{Mg}^{2+} + ^{\text{IV}}\text{Fe}^{3+} = ^{\text{M}}\text{Fe}^{3+} + ^{\text{VI}}\text{Fe}^{3+} + ^{\text{IV}}\text{Si}^{4+}$, where M refers specifically to the M7, M3A, and M4A octahedral sites. The lowest measured Sb is 1.454/40 O, which may be close to the limit imposed by the need to maintain local charge balance.

Keywords: Welshite, beryllium, antimony, crystal structure, charge ordering, Mössbauer spectroscopy, electron microprobe, ion microprobe