Exploratory studies of substitutions in the tetrahedrite/tennantite-goldfieldite solid solution

Phases on the Fe-tetrahedrite-goldfieldite and Fe-tennantite-goldfieldite joins were synthesized from high purity elements in evacuated silica glass tubes at 450 °C and analyzed using electron microprobe analysis and X-ray powder diffraction. The synthetic studies confirm that the compositions on these joins are determined by a (formal) interplay of the Fe$^{3+}$ + Cu$^{+}$ → 2Fe$^{2+}$, Cu$^{+}$ + Te$^{4+}$ → Fe$^{2+}$+(Sb,As)$^{3+}$, Cu$^{+}$ + 2Te$^{4+}$ → Fe$^{3+}$ + 2(Sb,As)$^{3+}$, and Cu$^{+}$ + Te$^{4+}$ → Cu$^{2+}$+(Sb,As)$^{3+}$ substitutions, and also for the region close to Te = 2 apfu by A + Te$^{4+}$ → Cu$^{2+}$ + Sb$^{3+}$. The latter exchange determines the Te-tennantite/ tetrahedrite-goldfieldite join. For the region of goldfieldite just above and below 2 Te atoms pfu, the latter exchange is modified by the Fe$^{n+}$→nCu$^{+}$ exchange. Incomplete elimination of Fe, compensated by early onset of Cu vacancies, results in a gradual transition between the region of tellurian td/tn and goldfieldite sensu stricto. This variety of substituting and omission mechanisms determines the proportions of alternative endmembers and intermediate members: Cu$_{10}$Fe$_{2+2}$(Sb,As)$_4$S$_{13}$, Cu$_{11}$Fe$_{3+}$(Sb,As)$_4$S$_{13}$, Cu$_{12}$(Sb,As)$_4$S$_{13}$, Cu$_{12}$Te$_2$(Sb,As)$_2$S$_{13}$, and Cu$_{10}$Te$_4$S$_{13}$, plus a measure of the Fe$^{n+}$→nCu$^{+}$ exchange. Natural goldfieldite conforms with the synthesis results in its compositional extent. The natural data are mostly not good or complete enough to examine the compositional details suggested here because the calculations described above are very sensitive to the quality of the analyses.