Fahlore Thermochemistry: Gaps Inside the $(Cu,Ag)_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$ Cube
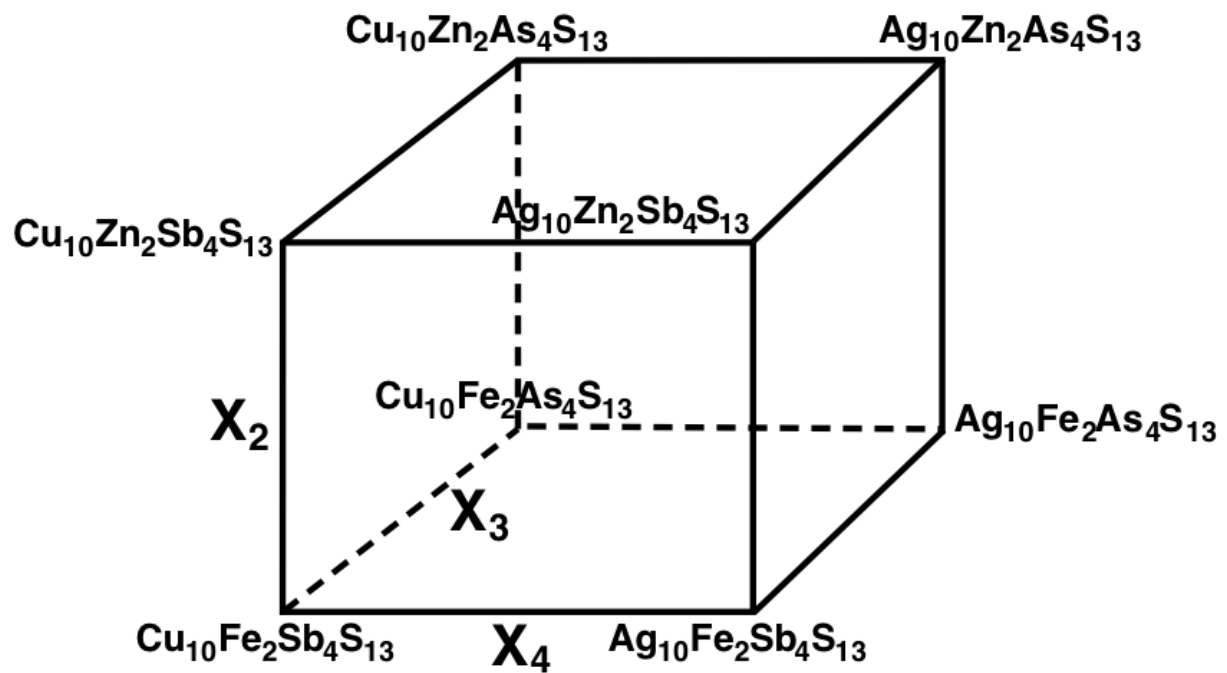
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30 years ago Mike O'Leary and I predicted that fahlores approximating the chemical formula $(Cu,Ag)_{10}(Fe,Zn)_2Sb_4S_{13}$,

fahlores on the front face of this fahlore cube would develop miscibility gaps at temperatures less than 190°C, based on Mike's study of Fe-Zn partitioning between Ag-bearing fahlores and Fe-Zn sphalerites and a simple thermodynamic model I cooked up to explain what he found.

Fahlore Structural Formula

$$(Cu,Ag)_6^{III}[(Cu,Ag)_{2/3}(Fe,Zn)_{1/3}]_6^{IV}(Sb,As)_4^{III}\,S_{12}^{IV}\,S^{VI}$$

Space Group

$$I\bar{4}3m$$
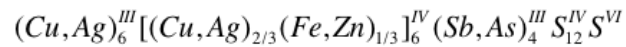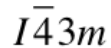
with two formula units per unit cell

Fahlores in the cube have this structural formula with 6 Cu and Ag in trigonal-planar or triangular coordination by S, 4 Cu and Ag and 2 Fe and Zn in tetrahedral coordination by S, 4 Sb and As bound to 3 basal S in a pyramidal arrangement, 12 sulfurs in tetrahedral coordination by metals and 1 sulfur at the corners and center of the unit cell that is in octahedral coordination by the Cu and Ag in the trigonal-planar sites.

Fe-Zn Exchange Reaction

$$ZnS + \tfrac{1}{2}\,Cu_{10}Fe_2Sb_4S_{13} = FeS + \tfrac{1}{2}\,Cu_{10}Zn_2Sb_4S_{13}$$

Sph   Fah   Sph   Fah
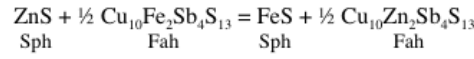
$$\overrightarrow{Q}_2^* \equiv RT \ln \frac{X_{Fe}^{FAH} a_{ZnS}^{SPH}}{X_{Zn}^{FAH} a_{FeS}^{SPH}} - \frac{1}{2}\Delta\overline{H}_{23}^{o} X_3^{FAH} = \Delta\overline{H}_{Zn(Fe)_{-1}}^{o} + \frac{1}{2}\Delta\overline{G}_{24}^{o} X_4^{FAH} + \frac{1}{2}\Delta\overrightarrow{G}_{2s}(s)$$

where $X_3 = As/(As+Sb)$, $X_4 = Ag/(Ag+Cu)$,

$$s = X_{Ag}^{III} - \frac{3}{2}X_{Ag}^{IV} ,$$

and
$$0 = \partial\overline{G}/\partial s$$

Reciprocal Reaction

$$Cu_{10}Zn_2Sb_4S_{13} + Ag_{10}Fe_2Sb_4S_{13} = Cu_{10}Fe_2Sb_4S_{13} + Ag_{10}Zn_2Sb_4S_{13}$$

Reciprocal-Ordering Reaction

$$\tfrac{1}{2}\,Cu_6^{III}(Ag_{2/3},Zn_{1/3})_6^{IV}Sb_4S_{13} + \tfrac{1}{10}\,Cu_{10}Fe_2Sb_4S_{13}$$
$$+ \tfrac{1}{2}\,Ag_6^{III}(Cu_{2/3},Fe_{1/3})_6^{IV}Sb_4S_{13} + \tfrac{1}{10}\,Ag_{10}Zn_2Sb_4S_{13} =$$
$$\tfrac{1}{2}\,Ag_6^{III}(Cu_{2/3},Zn_{1/3})_6^{IV}Sb_4S_{13} + \tfrac{1}{10}\,Ag_{10}Fe_2Sb_4S_{13}$$
$$+ \tfrac{1}{2}\,Cu_6^{III}(Ag_{2/3},Fe_{1/3})_6^{IV}Sb_4S_{13} + \tfrac{1}{10}\,Cu_{10}Zn_2Sb_4S_{13}$$
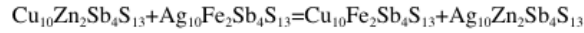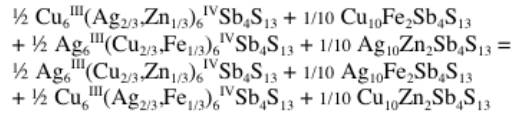
If we restrict our attention to near the Sb front face of the cube and use a simple thermodynamic formulation for Fe-Zn exchange between fahlores and (Zn,Fe)S sphalerites one would expect that RT times the logarithm of the distribution coefficient for Fe-Zn exchange, corrected for sphalerite nonideality and very minor As in natural Ag-bearing fahlores, this Q quantity would be linear in Ag/(Ag+Cu) ratio, with a slope of ½ of the Gibbs energy of the reciprocal reaction expressing the incompatibility between Zn and Ag in the fahlore structure, if Ag and Cu are randomly distributed between trigonal and tetrahedral metal sites or for this order variable s equal to zero. If this order variable s is not zero, then the departure from such a linear relationship will be determined by s and the energy of this reciprocal-ordering reaction.
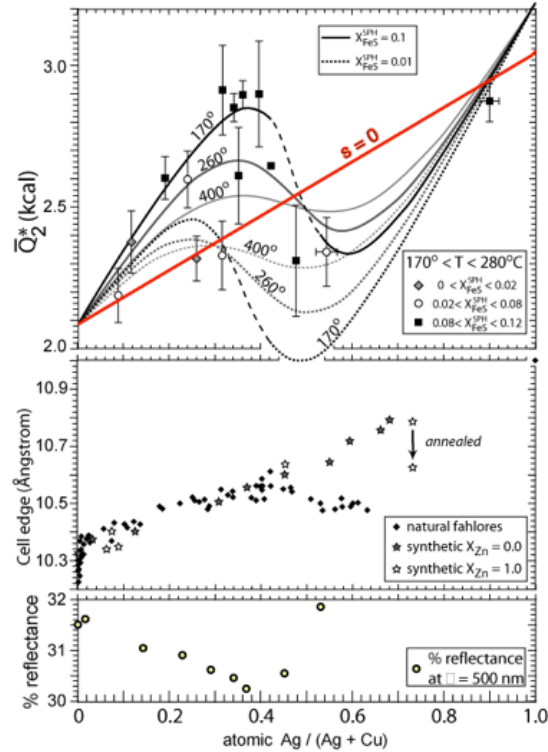
Mike O'Leary demonstrated that this Q quantity is sigmoid, initially rising above, and then falling below, the line for no Cu-Ag ordering between trigonal and tetrahedral metal sites at a given temperature and composition of sphalerite. This observation implies that Ag undergoes a change in site preference with Ag/Cu ratio. So if we assume that Ag prefers trigonal sites at low Ag/Cu ratios, it would prefer tetrahedral sites at higher Ag/Cu ratios. And it is noteworthy that local maxima in this Q quantity with Ag/(Ag+Cu) have parallels with local maxima and minima in cell edges and reflectivity of natural fahlores.
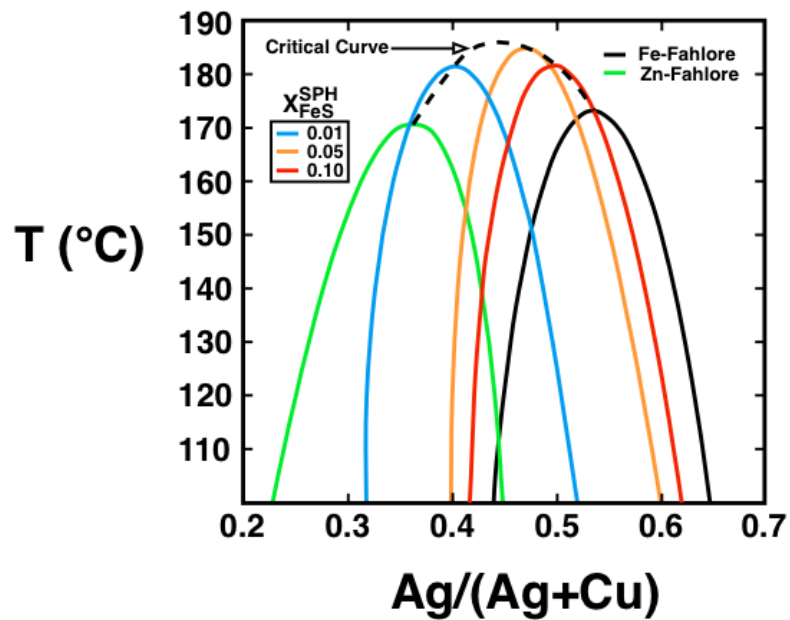
In calibrating the parameters of this thermodynamic model to get it to describe Mike's Fe-Zn exchange data, I discovered that there must be miscibility gaps such as those shown here for Zn fahlores, Fe fahlores, and fahlores in Fe-Zn exchange equilibrium with sphalerites with 1, 5, and 10 mole percent FeS, gaps which move to lower values of Ag/(Ag+Cu) ratio with increasing Zn in fahlore.

- Makovicky (2006) RIMG v. 61, p. 54
- "Substitution by Ag is universally assumed to start in the triangular sites and spill over into the tetrahedral sites only when the former are (nearly) filled"

This prediction was, and continues to be, heresy, because, as we see from this quote from Makovicky, it is universally believed that Ag strongly prefers trigonal-planar sites independent of Ag/(Ag+Cu) ratio, that substitution by Ag starts in the triangular sites and spills over into the tetrahedral sites only when the former are (nearly) filled.
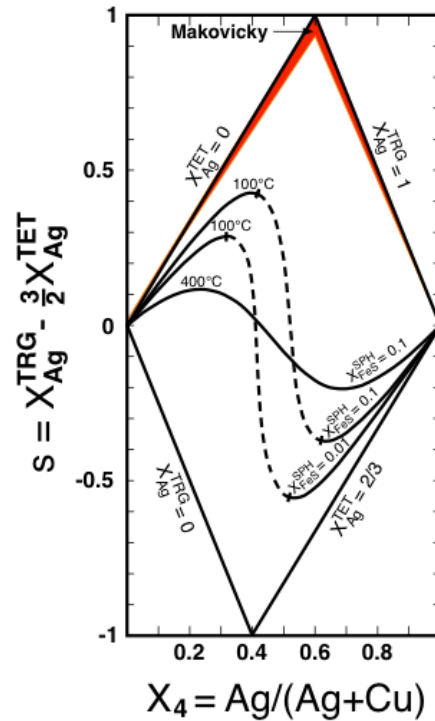
Accordingly, Sb-fahlores are supposed to be near the upper perimeter of this ordering variable—Ag/(Ag+Cu) ratio diagram. Instead the calibration of the thermodynamic model based on Fe-Zn exchange equilibria requires that fahlores exchange Ag and Cu substantially between trigonal to tetrahedral sites over a narrow range of Ag/(Ag+Cu) ratios well before you nearly fill up the trigonal sites, and this change in Ag site preference creates the miscibility gaps indicated by the dashed curves for antimony fahlores coexisting with sphalerites with 1 and 10 mole percent FeS at 100°C.
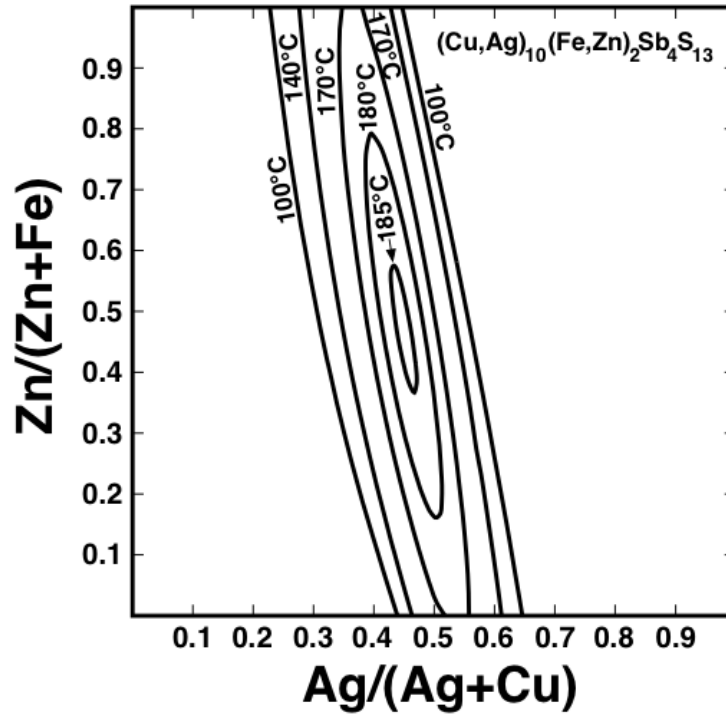
These predicted gaps were also problematic, because they hadn't been reported in the economic petrology literature, but I rationalized this based on the fact that they would only occur in epithermal, or slowly cooled mesothermal ore deposits, and could easily be overlooked, because they are quite narrow.
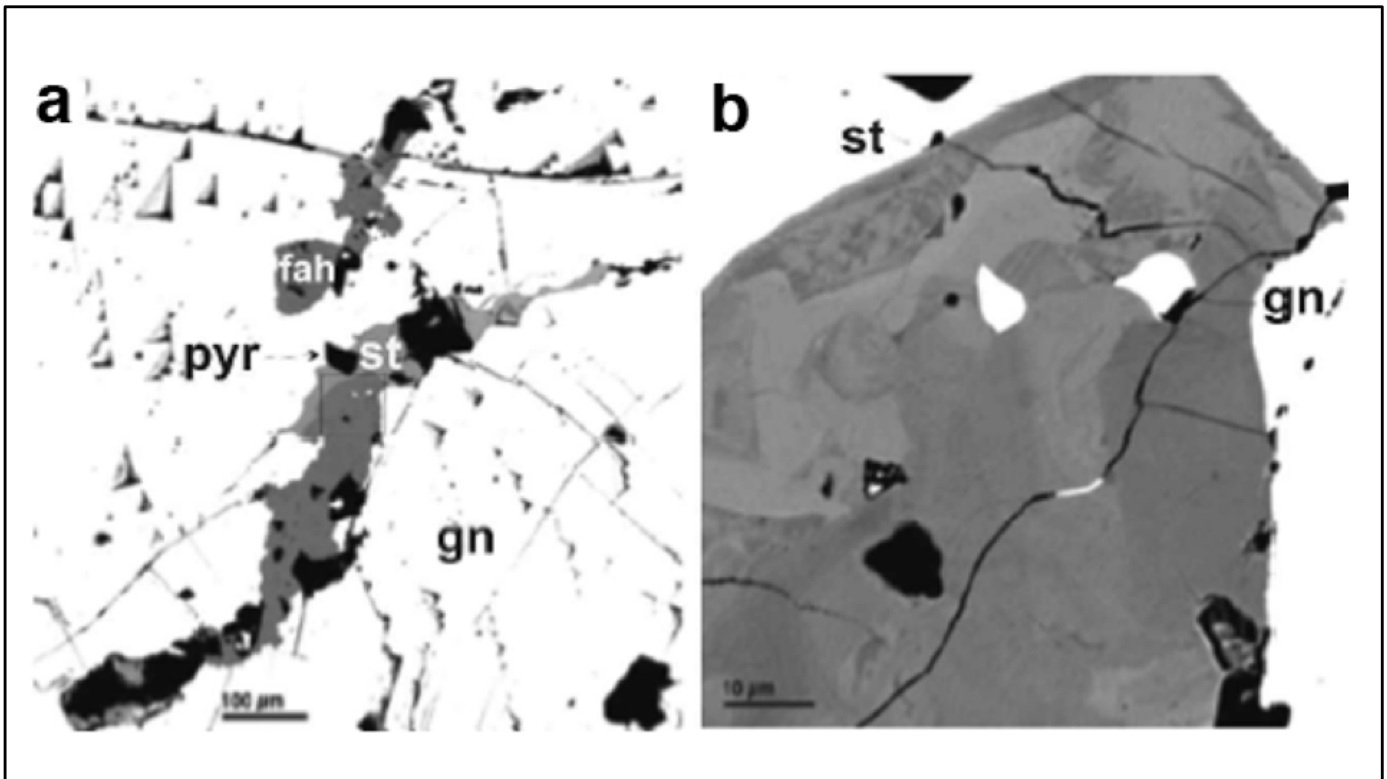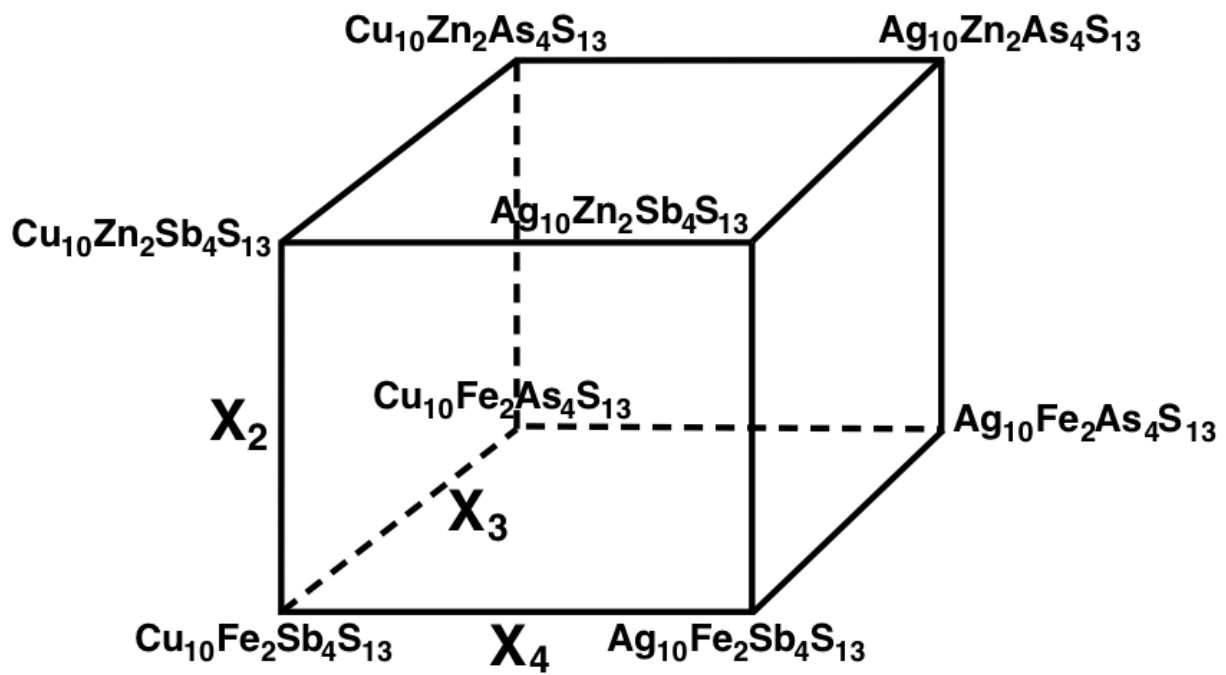
In 2003 I found evidence for such gaps in Ag-Pb-Zn ores from the Husky mine from the Keno Hill district in the Yukon. And in this BSE image we see this evidence for unmixing of a homogeneous fahlore into Ag-rich (brighter) and Ag-poor (darker) fahlores on the outer margins of a fahlore grain in an assemblage that including the mineral stephanite, a mineral that is stable only below 197°C.

Chinchilla and others (2016)
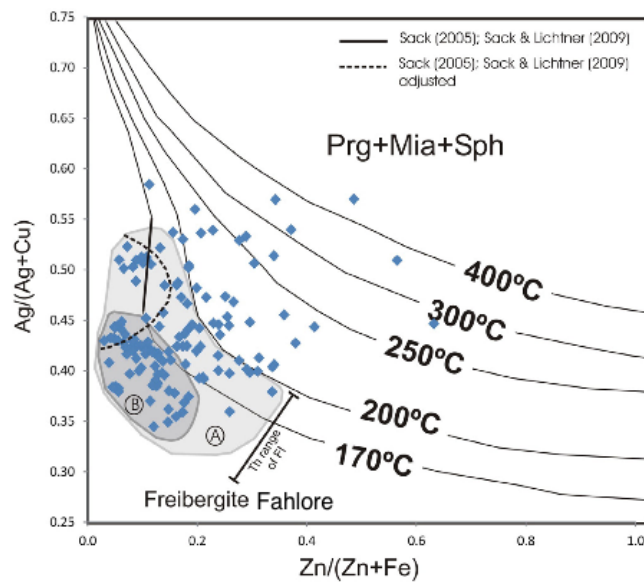
And the compositions of these unmixed phases are where we predicted them to be for a temperature of about 170°C. More recently Dario Chinchilla and others discovered this gap in fahlores from the Patrica epithermal Ag-Pb-Zn deposit. They demonstrated that the gap in fahlore compositions occurs at temperatures below 200°C based on fluid inclusions temperatures for the fahlore stage of mineralization of between 140 and 200°C, and the stability limits of fahlores at these temperatures defined by my thermodynamic database for fahlores in equilibrium with sphalerite, pyrargyrite and miargyrite. Fahlores with compositions indicating temperatures in excess of 200°C are probably due to compositional resetting during a post ore thermal event which fluid inclusions and textures indicate had temperatures in the mid 200s and above. But the gap in fahlore compositions is right where it should be when one adjusts for differences in microprobe standards and assemblages.

The cube diagram shows the following vertices:

- Top back left: $Cu_{10}Zn_2As_4S_{13}$
- Top back right: $Ag_{10}Zn_2As_4S_{13}$
- Top front left: $Cu_{10}Zn_2Sb_4S_{13}$
- Top front right: $Ag_{10}Zn_2Sb_4S_{13}$
- Bottom back left: $Cu_{10}Fe_2As_4S_{13}$
- Bottom back right: $Ag_{10}Fe_2As_4S_{13}$
- Bottom front left: $Cu_{10}Fe_2Sb_4S_{13}$
- Bottom front right: $Ag_{10}Fe_2Sb_4S_{13}$

Axis labels: X_2, X_3, X_4

Now that we have established the structural role of Ag and miscibility gap relations for fahlores on the Sb front face, it is appropriate to ask what miscibility gaps look like on the As back face and in interior of the cube.
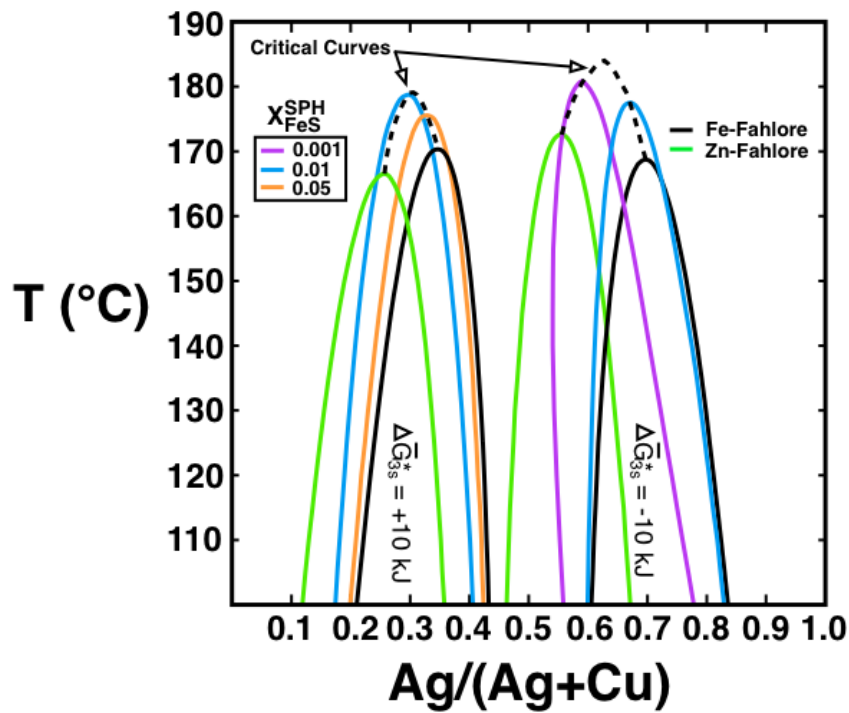
In our simple model there is only one new energetic parameter introduced for fahlores on the As back face, and the critical temperatures of these gaps are very much like those in Sb fahlores, but they are displaced to higher or lower Ag/(Ag+Cu) ratios depending on whether this parameter, ΔG_{3s} is negative or positive, here -10 and +10 kJ, respectively
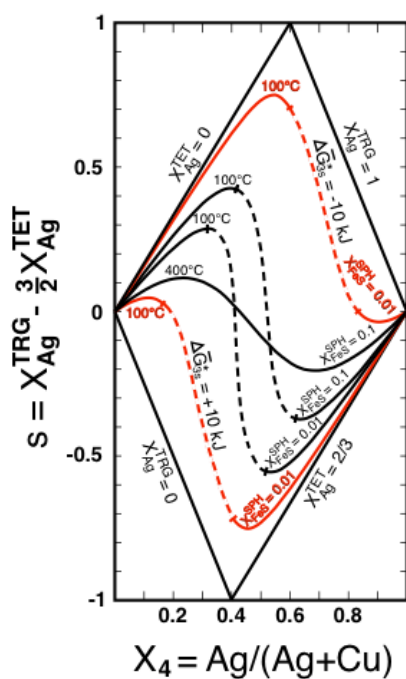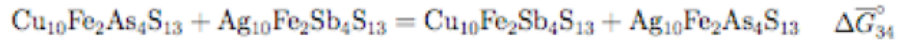
Again, if we give this parameter a positive value like the +10kJ illustrated here, we stabilize Ag in tetrahedral sites in As fahlores and move our miscibility gaps to lower Ag/Cu ratios. Alternatively, if we assign a value of − 10kJ to this parameter, we stabilize Ag in trigonal sites, move our miscibility gaps to higher Ag/Cu ratios, and achieve a distribution of Ag and Cu between trigonal and tetrahedral sites in As fahlores more like that suggested by the spectroscopic community for their Sb cousins.
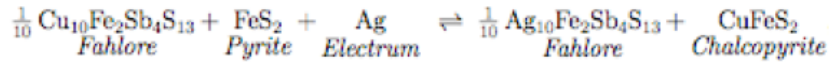
Condition of Homogeneous Equilibrium

$$0 = RT \ln \frac{(X_4 + \frac{2}{5}s)(\frac{2}{3}[1 - X_4] + \frac{2}{5}s)}{(1 - X_4 - \frac{2}{5}s)(\frac{2}{3}X_4 - \frac{2}{5}s)} + \frac{5}{12}(\Delta \overline{G}_s^\bullet + \Delta \overline{G}_{2s}^\bullet(X_2) + \Delta \overline{G}_{3s}^\bullet(X_3))$$

$$+ \frac{1}{24}(\Delta \overline{G}_{4s}^\bullet + 6\, W_{AgCu}^{TET} - 4\, W_{AgCu}^{TRG})(2X_4 - 1) + \frac{1}{30}(6\, \Delta \overline{G}_{4s}^\bullet - 9\, W_{AgCu}^{TET} - 4\, W_{AgCu}^{TRG})(s)$$

Reciprocal Reaction

$$Cu_{10}Fe_2As_4S_{13} + Ag_{10}Fe_2Sb_4S_{13} = Cu_{10}Fe_2Sb_4S_{13} + Ag_{10}Fe_2As_4S_{13} \quad \Delta \overline{G}_{34}^\circ$$

Ag-Cu Exchange Reaction

$$\underset{Fahlore}{\tfrac{1}{10} Cu_{10}Fe_2Sb_4S_{13}} + \underset{Pyrite}{FeS_2} + \underset{Electrum}{Ag} \rightleftharpoons \underset{Fahlore}{\tfrac{1}{10} Ag_{10}Fe_2Sb_4S_{13}} + \underset{Chalcopyrite}{CuFeS_2}$$

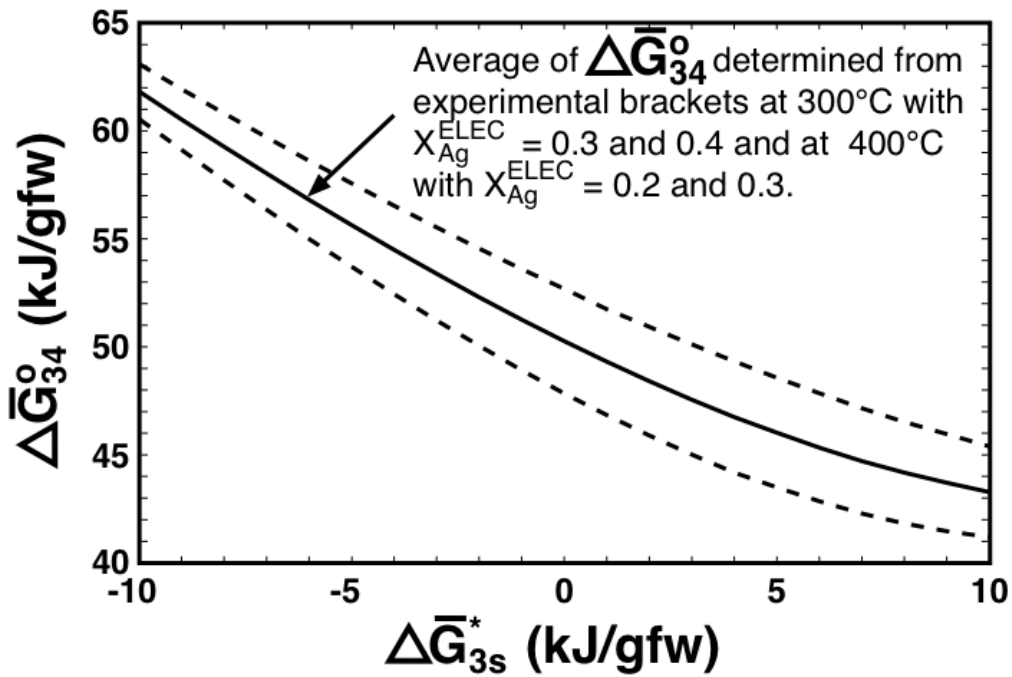**Condition of Ag-Cu Exchange Equilibrium**

$$\overline{Q}_{X_4}^\bullet \equiv RT \ln[(a_{FeS_2}^{PYR})(a_{Ag}^{ELEC})] - \frac{1}{10}[RT \ln \frac{(X_4 + \frac{2}{5}s)^6(\frac{2}{3}X_4 - \frac{2}{5}s)^4}{(1 - X_4 - \frac{2}{5}s)^6(\frac{2}{3}[1 - X_4] + \frac{2}{5}s)^4} + \Delta \overline{G}_{24}^\circ(X_2)]$$

$$- \frac{1}{50}(\Delta \overline{G}_{4s}^\bullet + 6\, W_{AgCu}^{TET} - 4\, W_{AgCu}^{TRG})(s) - \frac{1}{10}(\Delta \overline{G}_{4s}^\bullet + W_{AgCu}^{TET} + W_{AgCu}^{TRG})(1 - 2X_4)$$

$$= \Delta \overline{G}_{Ag(Cu)_{-1}}^\circ + RT \ln(a_{CuFeS_2}^{CPY}) + \frac{1}{10}\Delta \overline{G}_{34}^\circ(X_3),$$

To establish the value of this unknown parameter DG_{3s} in the condition of homogeneous equilibrium, we first have to determine the relationship between it and the Gibbs energy of the reciprocal reaction expressing the incompatibility of As and Ag, this DG_{34}, the parameter that controls the size of the miscibility gap in the interior of the cube. We may establish this relationship from the tightest experimental brackets of Ebel and Sack (1989, 1991) on the Ag/(Ag+Cu) ratios of fahlores in Ag-Cu exchange equilibrium with an assemblage that swamped it by mass in the experiments: chalcopyrite, pyrite and electrum with various fixed Ag/Au ratios. Evaluating this condition of Ag-Cu exchange equilibrium we obtain tight brackets on DG_{34} from brackets on this Qx quantity as a function of As/(As+Sb) ratio of fahlore (or X_3) from four sets of experiments at fixed temperatures and Ag/Au ratios of electrums.

The plot shows $\Delta\bar{G}^{o}_{34}$ (kJ/gfw) on the vertical axis versus $\Delta\bar{G}^{*}_{3s}$ (kJ/gfw) on the horizontal axis. Annotation: Average of $\Delta\bar{G}^{o}_{34}$ determined from experimental brackets at 300°C with X^{ELEC}_{Ag} = 0.3 and 0.4 and at 400°C with X^{ELEC}_{Ag} = 0.2 and 0.3.

If we average these four estimates, we obtain these average values of DG_{34} at each assumed DG_{3s}, and you'll note that the standard errors of the estimates of DG_{34} decrease from slightly greater than 5% of its value to less than 2% of its value for a variation of DG_{3s} from plus 10 to -10 kJ, strongly suggesting that DG_{3s} is negative.
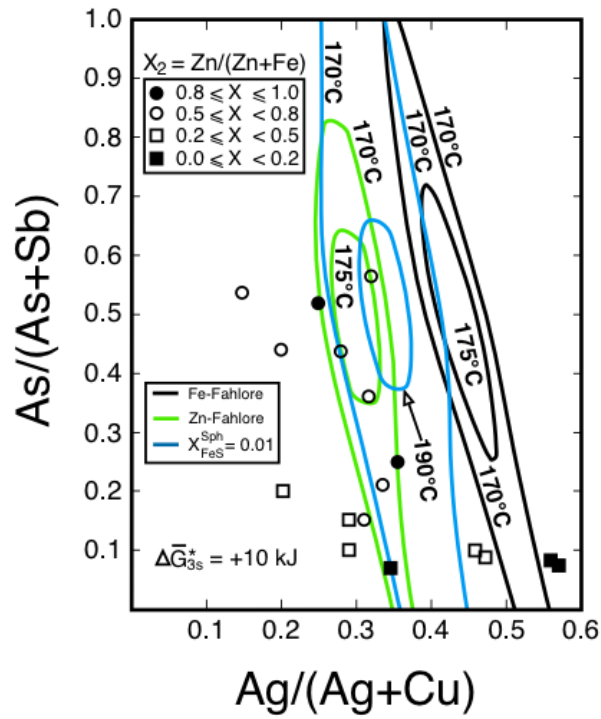
Starting with this DG$_{3s}$ of +10 kJ, we see that the gaps in the center of the cube have critical temperatures only slightly above those on the Sb front and As back faces. But these critical temperatures rise as we decrease DG$_{3s}$ (and increase DG$_{34}$) and the Ag-rich binodes of these gaps increase in Ag/(Ag+Cu) ratio so that the gaps fill up the space not occupied by natural fahlores.
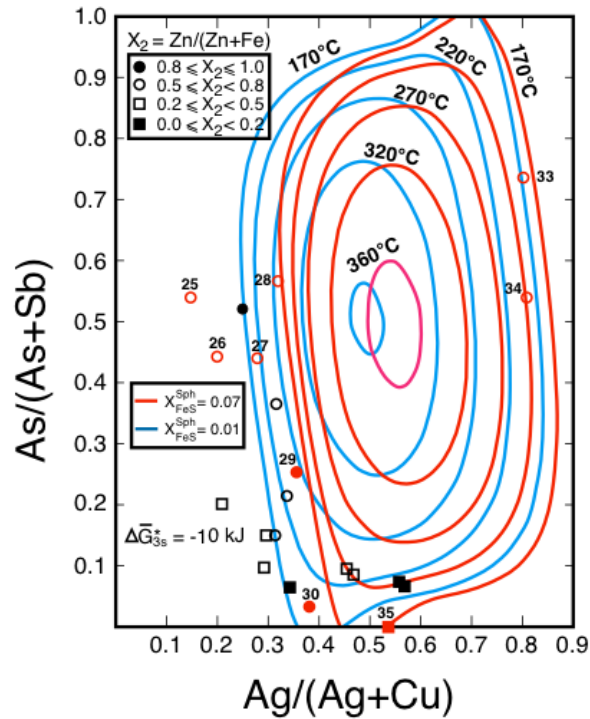
This is shown here by red numbered symbols for fahlores that occur as the inclusions in chalcopyrite and galena in Ag-Pb-Zn ores from the Hope mine on little Sark in the Channel Islands, as reported by Ixer and Stanley (1985). You will note that, with DG_{3s} equal -10 kJ, the fahlores closest to these gaps are roughly symmetrically disposed outside of them for a temperature of about 250°C, and this is the minimum bound on the mineralization temperature of fahlore number 30 based on very tight experimental constraints. Accordingly, this may be considered additional evidence that DG_{3s} is negative with a value of about -10 kJ. But this speculation is no substitute for actually finding these miscibility gaps in As-bearing fahlores, a discovery which will help refine our knowledge of the Gibbs energy surface of this remarkable petrogenetic indicator.