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THE GIBBS FREE ENERGY OF NUKUNDAMITE ($Cu_{3.38}Fe_{0.62}S_4$): A CORRECTION AND IMPLICATIONS FOR PHASE EQUILIBRIA

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ABSTRACT

The Gibbs free energy of formation of nukundamite ($Cu_{3.38}Fe_{0.62}S_4$) was calculated from published experimental studies of the reaction 3.25 $Cu_{3.38}Fe_{0.62}S_4 + S_2 = 11\ CuS + 2\ FeS_2$ in order to correct an erroneous expression in the published record. The correct expression describing the Gibbs free energy of formation (kJ•mol^{-1}) of nukundamite relative to the elements and ideal S_2 gas is $\Delta_fG°_{nukundamite,\ T(K)} = –549.75 + 0.23242\ T + 3.1284\ T^{0.5}$, with an uncertainty of 0.6%. An evaluation of the phase equilibria of nukundamite with associated phases in the system Cu–Fe–S as a function of temperature and sulfur fugacity indicates that nukundamite is stable from 224 to 501°C at high sulfidation states. At its greatest extent, at 434°C, the stability field of nukundamite is only 0.4 log $f(S_2)$ units wide, which explains its rarity. Equilibria between nukundamite and bornite, which limit the stability of both phases, involve bornite compositions that deviate significantly from stoichiometric Cu_5FeS_4. Under equilibrium conditions in the system Cu–Fe–S, nukundamite + chalcopyrite is not a stable assemblage at any temperature.

Keywords: nukundamite, bornite, thermodynamic properties, Gibbs free energy, phase equilibria.

SOMMAIRE

L'énergie libre de formation de Gibbs de la nukundamite ($Cu_{3.38}Fe_{0.62}S_4$) a été calculée à partir des études expérimentales déjà publiées portant sur la réaction 3.25 $Cu_{3.38}Fe_{0.62}S_4 + S_2 = 11\ CuS + 2\ FeS_2$ afin de corriger une expression en erreur dans la littérature. L'expression correcte pour décrire l'énergie libre de formation (en kJ•mol^{-1}) de la nukundamite par rapport aux éléments et une phase gazeuse idéale de composition S_2 est $\Delta_fG°_{nukundamite,\ T(K)} = –549.75 + 0.23242\ T + 3.1284\ T^{0.5}$, avec une incertitude de 0.6%. D'après une évaluation des équilibres de phases affectant la nukundamite et les phases associées dans le système Cu–Fe–S en fonction de la température et de la fugacité du soufre, la nukundamite serait stable entre 224 et 501°C dans un milieu à taux de sulfuration élevé. A sa plus grande étendue à 434°C, le champ de stabilité de la nukundamite n'est que 0.4 unités de log $f(S_2)$ en largeur, ce qui explique sa rareté. Dans les équilibres impliquant nukundamite et bornite, qui limitent le champ de stabilité des deux phases, les compositions de bornite dévient de façon importante de la composition stoechiométrique, Cu_5FeS_4. Aux conditions d'équilibre dans le système Cu–Fe–S, l'assemblage nukundamite + chalcopyrite est instable, quelle que soit la température.

(Traduit par la Rédaction)

Mots-clés: nukundamite, bornite, propriétés thermodynamiques, énergie libre de Gibbs, équilibres des phases.

INTRODUCTION

Certain copper-iron sulfide minerals, such as chalcopyrite and bornite, are very common in hydrothermal mineral deposits, whereas others, such as nukundamite, $Cu_{3.38}Fe_{0.62}S_4$, are rare (Inan & Einaudi 2000). An accurate understanding of the phase equilibria and thermodynamic properties of less common phases in the system Cu–Fe–S is essential to the study of ore deposits, because these aspects shed light on the unusual circumstances surrounding their formation.

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Considerable confusion has surrounded the identity and characteristics of nukundamite relative to idaite. For example, early experimental work in the system Cu–Fe–S (Merwin & Lombard 1937, Roseboom & Kullerud 1958, Yund & Kullerud 1966, Sugaki *et al.* 1975) investigated the stability of $Cu_{5.5}FeS_{6.5}$ (= $Cu_{3.38}Fe_{0.62}S_4$), but referred to it as idaite. Wang (1984) and Kojima & Sugaki (1985), in their experimental studies, referred to $Cu_{5.5}FeS_{6.5}$ as nukundamite. We accept the distinction made by Sillitoe & Clark (1969), Clark (1970), Cabri (1973), and Rice *et al.* (1979), who defined nukundamite as approximated by the formula $Cu_{3.37}Fe_{0.66}S_{3.97}$ (~$Cu_{5.5}FeS_{6.5}$) and idaite by the formula Cu_3FeS_4. For the purposes of our paper, we will use the formula $Cu_{3.38}Fe_{0.62}S_4$, which corresponds to the stoichiometry $Cu_{5.5}FeS_{6.5}$ commonly reported in the experimental literature. Published results of analyses of both natural and synthetic material suggest that this phase shows limited incorporation of other elements and that the deviation of its composition from the ideal $Cu_{3.38}Fe_{0.62}S_4$ stoichiometry is extremely limited (Merwin & Lombard 1937, Roseboom & Kullerud 1958, Yund 1963, Clark 1970, Sugaki *et al.* 1975, 1981a, Rice *et al.* 1979, Lupulescu 1993, Inan & Einaudi 2000). Rice *et al.* (1979) reported a unit-cell volume for a specimen of natural nukundamite of 138.6 ± 0.4 Å^3 ($Z = 1$), which corresponds to a molar volume of 83.47 ± 0.2 cm^3. Sugaki *et al.* (1981a) reported a unit-cell volume for a specimen of synthetic nukundamite of 138.75 Å^3 ($Z = 1$), which corresponds to a molar volume of 83.56 cm^3. Robie *et al.* (1994) erroneously reported a molar volume of 278.00 cm^3.

Robie *et al.* (1994) presented new heat-capacity data for bornite, which they used as a basis for re-evaluating the thermodynamic properties of bornite and other phases in the system Cu–Fe–S. Nukundamite was one of the phases included in their investigation. In the course of their re-evaluation, an error was made in the computations for the Gibbs free energy of nukundamite. The purpose of our paper is to correct the computational error of Robie *et al.* (1994) and to re-evaluate phase equilibria that limit the stability of nukundamite.

PREVIOUS STUDIES

Prior studies of the stability of $Cu_{5.5}FeS_{6.5}$ (= $Cu_{3.38}Fe_{0.62}S_4$) include the work of Merwin & Lombard (1937), Roseboom & Kullerud (1958), Yund & Kullerud (1966), Sugaki *et al.* (1975), and Wang (1984), who investigated phase relations in the system Cu–Fe–S, and Sugaki *et al.* (1981b) and Kojima & Sugaki (1985), who examined phase relations in the system Cu–Fe–Zn–S, respectively. Wang (1984) concluded that idaite is a metastable phase that breaks down upon heating to nukundamite + chalcopyrite above 543 K. Kojima & Ueno (1994) investigated thermodynamic constraints on nukundamite-bearing assemblages.

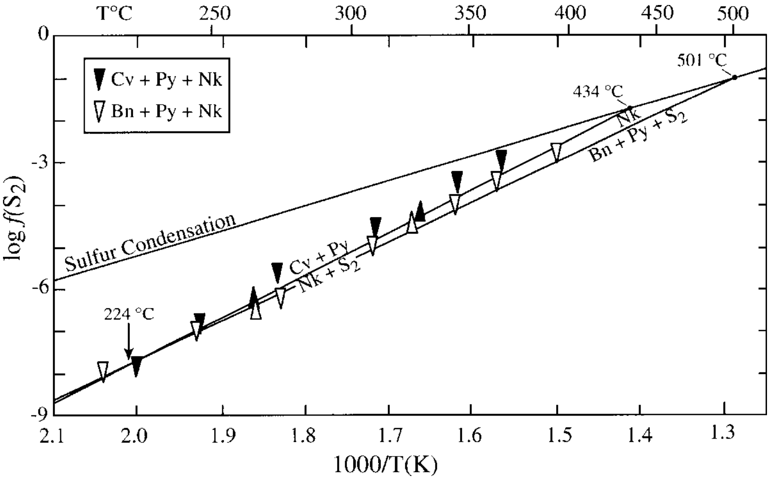

FIG. 1. log $f(S_2)$ – T diagram for nukundamite-bearing univariant reactions investigated by Schneeberg (1973) and Roseboom & Kullerud (1958). The position of the sulfur condensation curve is plotted for reference and was calculated on the basis of the data summarized by Robie *et al.* (1994). Abbreviations: Cv, covellite; Py, pyrite; Bn, bornite; Cp, chalcopyrite; Nk, nukundamite. The symbols for the Cv + Py + Nk and Bn + Py + Nk assemblages represent reversal brackets from the data of Schneeberg (1973). Symbol size is proportional to analytical uncertainty of the log $f(S_2)$ value. The solid circles along the sulfur condensation curve indicate the Cv + Py and Nk breakdown temperatures determined by Roseboom & Kullerud (1958).

Schneeberg (1973) studied equilibria involving a phase that he called "idaite" by electrochemical methods, but failed to report the chemical composition of this phase in his experiments. In light of the results of Wang (1984) regarding the metastability of idaite, we tentatively assume here that the equilibria measured by Schneeberg (1973) actually involved the phase nukundamite rather than idaite.

Schneeberg (1973) determined the equilibrium sulfur fugacity associated with nukundamite (Nk), covellite (Cv), and pyrite (Py) for the reaction:

$$3.25\,\underset{\text{Nk}}{\mathrm{Cu_{3.38}Fe_{0.62}S_4}} + \mathrm{S_2} = 11\,\underset{\text{Cv}}{\mathrm{CuS}} + 2\,\underset{\text{Py}}{\mathrm{FeS_2}} \qquad (1)$$

from 491 to 667 K. Roseboom & Kullerud (1958) determined an equilibrium temperature of 707 K (434°C) for this reaction on the sulfur-condensation curve (Fig. 1).

Schneeberg (1973) also determined the equilibrium sulfur fugacity associated with the assemblage nukundamite + pyrite + bornite from 491 to 667 K. Roseboom & Kullerud (1958) determined an equilibrium temperature of 774 K (501°C) for this reaction along the sulfur-condensation curve (Fig. 1). Kojima & Sugaki (1985) demonstrated experimentally that bornite in equilibrium with nukundamite + pyrite + vapor has a Cu:Fe ratio that is significantly higher than stoichiometric $\mathrm{Cu_5FeS_4}$ (Fig. 2). The reaction describing the equilibrium nukundamite, pyrite, bornite solid-solution ($\mathrm{Bn_{ss}}$) with the composition reported by Kojima & Sugaki (1985) between 400 and 500°C, and vapor can be written as:

$$0.58\,\underset{\mathrm{Bn_{ss}}}{\mathrm{Cu_{5.85}Fe_{0.65}S_4}} + 0.24\,\underset{\text{Py}}{\mathrm{FeS_2}} + 0.60\,\mathrm{S_2} = \underset{\text{Nk}}{\mathrm{Cu_{3.38}Fe_{0.62}S_4}} \qquad (2),$$

which provides a high-temperature limit to the stability of nukundamite for a given fugacity of sulfur (Fig. 3).

Experimental studies of Roseboom & Kullerud (1958), Yund & Kullerud (1966), and Kojima & Sugaki (1985) also produced an assemblage of covellite + nukundamite + bornite solid-solution + vapor. Roseboom & Kullerud (1958) determined an equilibrium temperature of 755 K (482°C) for this assemblage on the sulfur condensation curve. Authors of all three studies and Sugaki *et al.* (1975) reported bornite with Cu:Fe ratios higher than that involved in Reaction 2, as would be expected from topological considerations (Fig. 2). Using compositional data from Kojima & Sugaki (1985), the equilibrium among nukundamite, bornite solid-solution, covellite, and vapor at 400°C can be described as the sulfidation reaction:

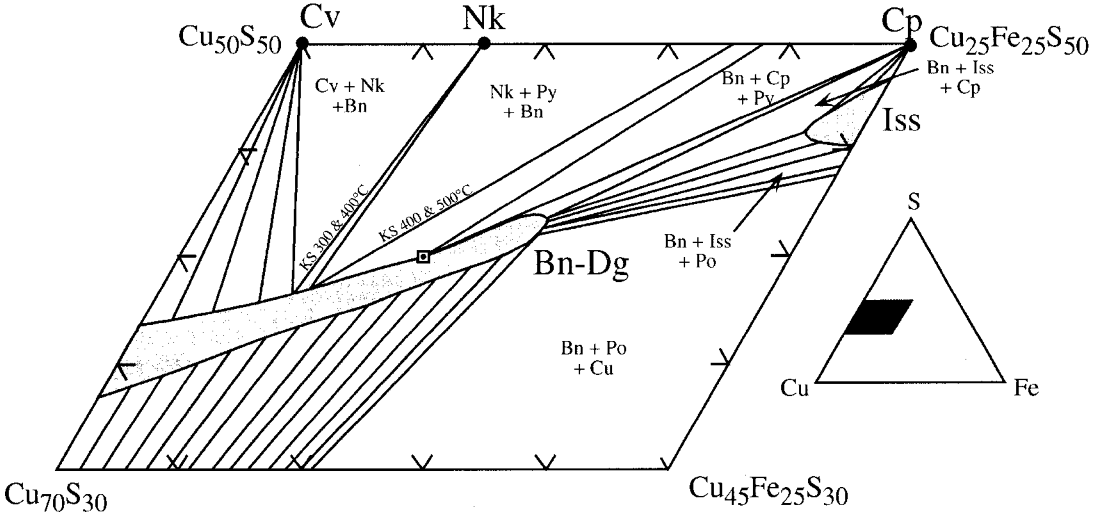

FIG. 2. Phase relations in a portion of the system Cu–Fe–S at 500°C. Compositions of bornite solid-solution are plotted from Kojima & Sugaki (1985), "KS", for reference at the indicated temperatures. Abbreviations: Cv, covellite; Dg, digenite; Py, pyrite; Po, pyrrhotite; Bn, bornite; Cp, chalcopyrite; Nk, nukundamite; Iss, intermediate solid-solution; Cu, native copper. Compositions are depicted as molar percentages. Shaded fields represent intermediate solid-solution (Iss) and bornite solid-solution ($\mathrm{Bn_{ss}}$). The square symbol is stoichiometric bornite ($\mathrm{Cu_5FeS_4}$). The preferred tie-lines for nukundamite-bearing assemblages are shown as solid lines (see text). Temperatures associated with the bornite compositions in three-phase (+vapor) assemblages are indicated along the relevant tie-lines.

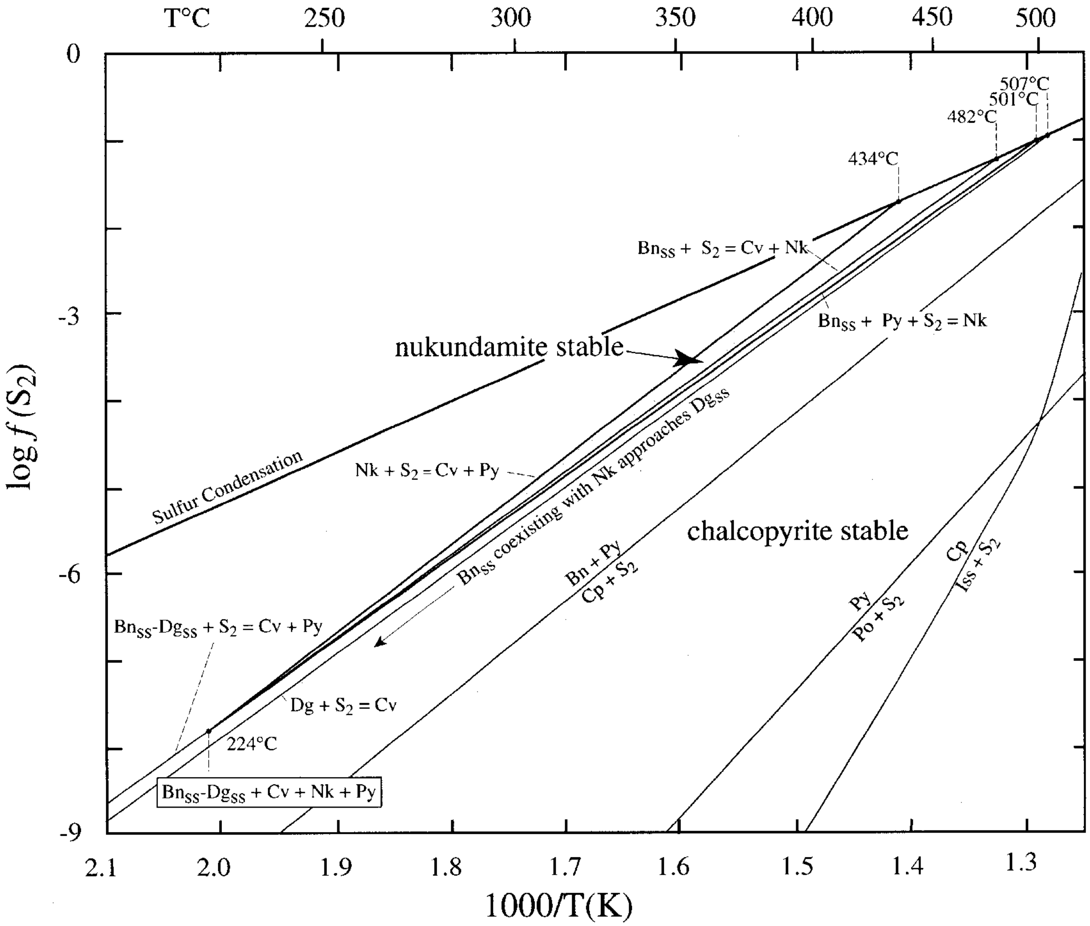

FIG. 3. log $f(S_2)$ – T diagram for selected equilibria in the system Cu–Fe–S with an emphasis on the stability of nukundamite. The positions of the pyrite – pyrrhotite, covellite – digenite, and chalcopyrite – Iss reactions are plotted for reference (Barton & Skinner 1979, Robie *et al.* 1994). Abbreviations: Cv, covellite; Dg, digenite; Dg_{ss}, digenite solid-solution; Py, pyrite; Po, pyrrhotite; Bn, bornite; Bn_{ss}, bornite solid-solution; Iss, intermediate solid-solution; Cu, native copper; Cp, chalcopyrite; Nk, nukundamite. Shaded areas represent the stability field of nukundamite.

$$\underset{Bn_{ss}}{1.16\ Cu_{6.07}Fe_{0.53}S_4} + 1.51\ S_2 = \underset{Cv}{3.66\ CuS} + \underset{Nk}{Cu_{3.38}Fe_{0.62}S_4} \quad (3).$$

Although there is some spread in compositional data of bornite, experimental results indicate that the bornite solid-solution in equilibrium with nukundamite (Reactions 2 and 3) becomes more copper-rich and evolves toward a digenite ($Cu_{2-x}S$) solid-solution end member with decreasing temperature.

Kojima & Ueno (1994) studied thermodynamic constraints on nukundamite-bearing assemblages, but did not consider the effect of nonstoichiometry of bornite on Reactions 2 and 3. All reported compositions of bornite in Reactions 2 and 4 have a higher Cu:Fe ratio than nukundamite, whereas stoichiometric bornite has a lower Cu:Fe ratio than nukundamite. The sulfidation reaction of Kojima & Ueno (1994) for the assemblage bornite + nukundamite + pyrite + vapor is:

$$\underset{Bn}{22/23\ Cu_5FeS_4} + S_2 = \underset{Nk}{20/23\ Cu_{5.5}FeS_{6.5}} + \underset{Py}{2/23\ FeS_2} \quad (4),$$

and for the assemblage bornite + covellite + nukundamite + vapor, it is:

$$\underset{\text{Bn}}{Cu_5FeS_4} + 0.5\ \underset{\text{Cv}}{CuS} + S_2 = \underset{\text{Nk}}{Cu_{5.5}FeS_{6.5}} \quad (5).$$

These reactions are inconsistent with the compositions of bornite solid-solution determined in the experimental studies cited above.

REVISED GIBBS FREE ENERGY

Robie *et al.* (1994) attempted to calculate an expression for the Gibbs free energy of formation for nukundamite on the basis of a best-fit curve to the experimental reversals of Schneeberg (1973) and the isobaric invariant point of Roseboom & Kullerud (1958) for the assemblage nukundamite + covellite + pyrite + S_2 vapor as represented in reaction 1 (Fig. 1). This curve is described in terms of temperature and sulfur fugacity by the equation:

$$1\text{n}f\left(S_2\right) = \frac{-23.686 \times 10^3}{T(K)} + 29.492 \quad (6)$$

The experimental studies of Sugaki *et al.* (1975) and Kojima & Sugaki (1985) indicate that all of the solid phases in equilibrium in this assemblage are stoichiometric within analytical uncertainty, and thus can be considered to have unit activities. In their analysis, Robie *et al.* (1994) chose an incorrect coefficient for the Gibbs free energy of pyrite, which resulted in an incorrect expression for nukundamite. Recalculation of the Gibbs free energy of formation for nukundamite, relative to the elements and ideal S_2 gas, using equation 6 in conjunction with the thermodynamic data in Robie *et al.* (1994) for pyrite and covellite, yields the corrected expression (kJ•mol^{-1}):

$$\Delta_f G^o_{\text{nukundamite, T(K)}} = -549.75 + 0.23242\ T + 3.1284\ T^{0.5} \quad (7),$$

which is valid from 298 to 774 K (25 to 501°C) with an estimated uncertainty of 0.6%. This expression yields molar Gibbs free energy of formation values for nukundamite that are 10 to 15 kJ less negative than the values estimated by Kojima & Ueno (1994) from 523 to 673 K. Part of this difference can be attributed to the use of different thermodynamic data for associated phases in our study and that of Kojima & Ueno (1994). In addition, Kojima & Ueno (1994) used stoichiometric bornite in their calculations and reactions rather than the solid-solution compositions discussed above.

Phase equilibria

The revised Gibbs free energy of formation for nukundamite and the insights gained from the nonstoichiometry of bornite in reactions 2 and 4 permit a better evaluation of the stability of nukundamite relative to other phases in the system Cu–Fe–S. Reactions 1 and 2 provide an upper and lower limit, respectively, to the sulfidation state of nukundamite-bearing assemblages. Reaction 4 places an upper sulfidation limit on the stability of bornite–digenite solid-solution relative to nukundamite + covellite. The locations of these reactions along the sulfur condensation curve have been determined by Roseboom & Kullerud (1958) to be 434°C for reaction 1, 482°C for reaction 3, and 501°C for reaction 2 (Fig. 3). These reactions meet at an isobaric invariant point, the temperature of which can be calculated by equating the log $f(S_2)$ expressions of Schneeberg (1973) for reactions 1 and 2. The resulting temperature is 224 ± 20°C with consideration of the uncertainties reported for the measurements of Schneeberg (1973). Below this temperature, nukundamite is not stable. Instead, covellite and pyrite react to form a bornite–digenite solid-solution and S_2 gas (Fig. 3). Thus, the results of the experiments of Schneeberg (1973), as interpreted in the context of Reactions 1, 2, and 3, indicate that the field of stability of nukundamite is extremely narrow (Fig. 3). At its greatest range of log $f(S_2)$ values at 434°C, the field of stability is only 0.4 units wide. This narrow field of stability explains the rarity of nukundamite in mineral deposits.

The reactions depicted in Figure 3 indicate that nukundamite + chalcopyrite is not a stable equilibrium assemblage at any temperature in the system Cu–Fe–S, in agreement with some experimental data (Merwin & Lombard 1937, Roseboom & Kullerud 1958, Kojima & Sugaki 1985), but in disagreement with others (Sugaki *et al.* 1975, 1981b, Wang 1984). Kojima & Ueno (1994) also concluded that nukundamite + chalcopyrite is a metastable assemblage that might occur at high sulfidation states and low pH on the basis of their analysis of phase equilibria assuming stoichiometric phases. Barton & Skinner (1979) suggested that nukundamite + chalcopyrite may precipitate under conditions of pyrite supersaturation. The curves that limit the stabilities of nukundamite and chalcopyrite are one to two log $f(S_2)$ units apart at all temperatures. Displacements of the limiting reactions by one to two log $f(S_2)$ units would require activities less than unity for nukundamite on the order of a_{Nk} = 0.15 to 0.40 or for chalcopyrite on the order of a_{Cp} = 0.65 to 0.80 to produce a stable assemblage of nukundamite + chalcopyrite. Analyses of natural and synthetic nukundamite and chalcopyrite show negligible solid-solution (Clark 1970, Sugaki *et al.* 1975, 1981a, Rice *et al.* 1979, Kojima & Sugaki 1985, Kojima & Ueno 1994), suggesting that the extent of solid solution required to achieve the necessary reduction in activity is unlikely in nature. Thus, natural associations of nukundamite and chalcopyrite either reflect metastable or disequilibrium assemblages.

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