

The idaite-nukundamite-bornite-chalcopyrite metastable solid solution: Crystal chemistry, superlattice architecture and bonding; thermochemistry and phase equilibria; natural occurrences, geochemistry and metallogenesis

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Abstract At temperatures below 300°C restricted areas of metastable solid solution exist in the bornite(bn)-chalcopyrite(cp)-idaite(id)-nukundamite(nk) area of the Cu-Fe-S system; the solid solution is pronounced in the areas between id, bn and cp. The metastable phases of the solid solution are quenchable from above 500°C to 220°C; examples observed in natural assemblages form as a result of kinetic and energetic effects and as an accommodation of the Gibbs/Goldschmidt phase rule. The occurrence of phases is constrained by hydrothermal phase equilibria. The states of the systems involve small compositional adjustments which are dependent on solid state processes. Mineral phases exhibit slight variations in stoichiometry allowing ties to exist between them. An accommodation noted in nature allowing covellite(cv)-nk-cp colinearity is observed in experiments at 150-250°C where id compositions equilibrate so that the nk-cp tie connects. Transition metal (e.g., Zn) substitution occurs at low temperatures and chalcogenide (e.g., As) substitution occurs at high temperatures. Below 220°C (thermal maximum of non-stoichiometric chalcopyrite) and 260-270°C (where tie line switch reactions occur between id, cv and cp producing nk) the solid solution area becomes expansive widening toward cp; as a result of sympathetic energetic and kinetic effects a number of polytypes appear. The nk area remains restricted at high temperatures, variable stoichiometry and solid solution with id and an.bn polytypes is observed at temperatures below 171-220°C. At high temperatures non integral superstructures decompose to integral types which are involved in tie-line switch reactions. Permissive metastability below 300°C is associated with merged univariant equilibria and sustained by non relativistic atomic states in superlattices which influence spectacular solubility variations. Lattice distortion and electronic states indicated for these phases suggest the presence of strong bonding forces, imposed by vacancy superstructure nuclear interactions, not specified by current theory.

Idaite exhibits 2 or 3 polytype and several polymorphous conditions; - 12 polytype phases are recognised in the an.cp solid solution between id and cp. Crystal symmetry varies from hexagonal (360°C: cubic) in nk, pseudocubic/tetragonal (220°C: cubic) in id to orthorhombic/tetragonal in an.cp; these symmetry transformations correlate with stoichiometry, metal vacancies and oxidation states (dependent on environment of crystallization hence the variety of natural polytypes). Changing levels of site occupation and oxidation state result in distortion of the basic chalcogenide subcell with concomitant superstructure and optical effects. A new concept of bond development is introduced to explain observed physical and chemical variations-chalcogenide ligands are thought to be metallized; especially notable in nonstoichiometric phases. Analogous chalcogenide phases from other systems are discussed in terms of their multielement phase equilibria and periodic element topology. A restructured periodic table facilitates a better understanding of zonal/regional metallogenesis and multielement solid state phase equilibria applicable to broad fields of scientific research. The occurrence of Au and tectonically zoned chalcogenides-semimetals (e.g., Ge anomalies at tectonic inflections) with zones intermediate Cu-Fe-S solid solution-metastable solid solution (iss-mss) series will provide an interest for mineral exploration and natural hazard monitoring.

Key words: idaite, bonding-forces, thermochemistry, superlattice, metallogenesis

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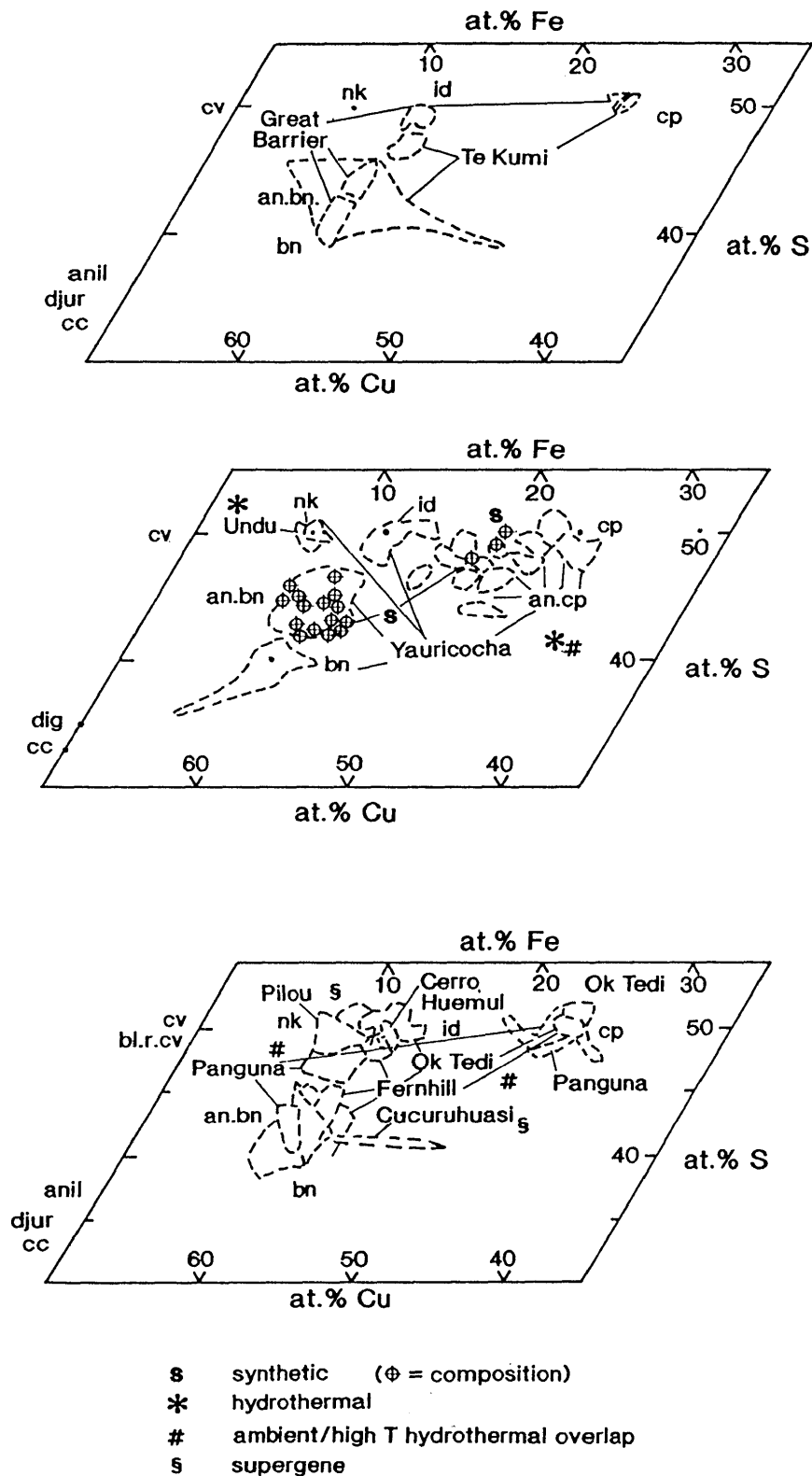


Fig. 1 Summary of electron microprobe analytical data for the metastable solid solution polytype series; natural and synthetic compositions are depicted; note especially the differences in compositional hiatuses for low and higher temperature polytype series.

INTRODUCTION

Idaite superstructures and polytypes belonging to the low temperature bn-nk-id-cp series (Fig. 1) are very complex (for key to abbreviations used

see Table 1); variations are observed between tropical and temperate climates. Variation in optical properties from bn to id (Ro direction often predominates) and superstructure development are consistent with the stepwise ordering of metal

Table 1 Abbreviations for mineral and other terms used in text.

anil	anilite
an.bn	anomalous bornite
an.cp	anomalous chalcopyrite
bl.r.cv	blue remaining covellite
bn	bornite
cc	chalcocite
col	colusite
cp	chalcopyrite
cv	covellite
dge	digenite
djur	djurleite
en	enargite
id	idaite
iss	intermediate Cu-Fe-S solid solution
luz	luzonite
maw	mawsonite
nk	nukundamite
pent	pentlandite
po	pyrrhotite
py	pyrite
tn	tennantite

vacancies modelled on the bn lattice (chalcogenide vacancies are also noted to vary sympathetically in individual analyses, e.g., S for Cu). Experimental quenched (Frenzel 1959; Czamanske 1974; Lee *et al.* 1975; Weigel 1978ms) and metastable intermediate phases are found in nature (Weigel 1978ms); these are analogous to metastable rhombohedral bn synthesised by Morimoto & Kullerud (1966).

Electronic configurations expected for these phases indicate that Fermi-level migration (metastability becomes limited at energetically lower Fermi-levels) must be critical in the shrinkage of the solid solution at temperatures above 140-220 °C. Vacancy superstructures reduce nuclear shielding, consequently nuclear processes are thought to be involved in perched Fermi-level metastability. Stoichiometric high temperature polymorphs exist up to 280 °C (id) and 500 °C (nk); remnant raised Fermi-level areas remain between bn and cp above these temperatures. Non-stoichiometric bn ($\text{Cu}_{5-x}\text{FeS}_{4+x}$) and non-stoichiometric cp ($\text{Cu}_{1.4+x}\text{FeS}_{2.5+x}$) occur as experimental quench products and as metastable relics in nature. The model proposed for the widespread metastability is a migrating temperature-dependent Fermi-level constrained by the margins of the metal-chalcogenide system. High spin metallised chalcogenide distortion in compound subcells is effected by vacancies, variable oxidation states and other constraints imposed by extreme environments of crystallisation. Perched Fermi-levels, produced by synergistic electronic-nuclear interactions within superlattice domains, are responsible for different levels of metastability and

complex polymorph-polytype occurrences between 220° and 25 °C. Probabilistic nuclear combinational effects are considered responsible for the abundance of compound polytypes in the Cu-Fe-S system (ca. 105 compound types are predicted; ca. 70-80 natural/synthetic mineral polytypes are known, however, geochemical equilibrium processes impose constraints on natural occurrences).

REFLECTED LIGHT OPTICS

The optical properties of the stoichiometric end members of the metastable solid solution are consistent with their crystal chemistry. Non-stoichiometric intermediate phases exhibit aspects of their nearest neighbours with gradations between polytypes, e.g., id and its polytypes, are similar except that phases nearer to bn are brown/bronze while those closer to cp are yellow/brown; polymorphs are isotropic (comparable to Ro-id) or hexagonal (nk-id solid solutions). Optical characteristics in plane polarised light and under crossed polars can be resolved in terms of wavelength spectra and the spectral-reflectivity curves of Lévy (1967). Unusual optical anisotropism, dispersion and unspecified scattering are considered to be related to out-of-phase electronic wave quanta (polytype loci at >46 atomic %S and >30 atomic %Cu exhibit increased cell distortion and covalency and superstructures; reduced nuclear shielding affects electron wave functions) interacting with light quanta.

Idaite: Many optical variations are noted according to stoichiometry (e.g., Ramdohr 1969); polytypes which overlap with the bn metastable solid solution, id, and the nk polytype are brown/bronze while the equivalent polymorph is orange-yellow/brown. Optically id polytypes exhibit longer wavelength (>5000 Å) and lower energy emission than nk (nk is expected to exhibit higher crystal field energy differences) consistent with its lower thermal stability and metastability. The 45° position id polarisation colours resemble the green hues associated with the Re plane polarised direction; they are similar to internal reflections and are considered to originate from unspecified scattering or fluorescence.

In plane polarised light id spectral inflection begins at ca. 4750 Å with maximum emission at ca. 5000 Å (based on data from Lévy 1967). The spectral reflectivity curves for id are sigmoidal, similar to the 'orange bornites' (Lévy, 1967) and the photoemission curves of some superconductors (Sleight 1988). Anomalous dispersion and change in optic sign varies from 4700 Å to 5700 Å in the series renierite, maw (5500 Å) and id (5700 Å). Optical emission at >20000 cm⁻¹ appears to coincide with the crystal field influence of Cu^{II} whereas the effects of Fe interactions influence nk emission

Table 2 Crystal and thermochemical data for metastable solid solution polytype phases.

	NUKUNDAMITE	IDAITE	ANOMALOUS CHALCOPYRITE	ANOMALOUS BORNITE
Formula :	Cu _{3.66} FeS _{6.66} * Cu _{3.38} Fe _{0.62} S _{4.0} Cu _{5.5} FeS _{6.5} */\$ Cu _{3.33} Fe _{0.66} S _{4.0} Cu ₅ FeS ₆ * Cu _{5.4} FeS _{6.6} √ Cu _{3.6} FeS _{4.7} √	Cu ₃ FeS ₄ *#√ Cu ₃ FeS _{3.7} * Cu _{2.3} FeS _{3.3} * Cu _{3.2} FeS _{3.7} # Cu _{3.3} Fe _{0.8} S _{3.9} # Cu _{3.1} FeS _{3.9} # Cu _{2.98} FeS ₄ # Cu _{3.07} Zn _{0.02} FeS _{3.91} √	Cu _{1.5} FeS _{2.5} \$ Cu _{1.75} FeS _{2.5} \$ Cu _{1.46} FeS _{2.46} \$ Cu _{1.7} FeS _{1.7} * CuFeS _{1.85} * Cu _{1.1} FeS _{2.15} * Cu _{1.3} FeS _{2.1} * Cu _{1.74} FeS _{2.38} * [Cu _{1.8} FeS _{2.46} - *** -Cu _{1.7} FeS _{2.31}]	Cu ₄ FeS _{4.09} * Cu _{5.5} FeS _{5.5} * Cu ₄ FeS ₄ \$ Cu _{3.5} FeS _{3.5} \$
Cell Content :	z = 0.6 - 0.66	z = 1,2 - 6+		
Univariant Free Energy Data				
	bn-cp-nk = -41592.67+49.5321T°K nk-py-bn = -41856.29+49.6858T°K nk-cv-py = -49065.17+61.7216T°K Fedig+cv+nk = -41751.09+5283T°K bn+cp+id = -42479.47+49.3529T°K ΔG°r ----- cal.mole ⁻¹ S ₂ (g)		Cu _{1.92} FeS _{2.63} * Cu _{1.83} FeS _{2.72} * Cu _{1.61} FeS _{2.37} * Cu _{1.45} FeS _{2.09} * Cu _{1.64} FeS _{1.72} * Cu _{1.07} FeS _{1.62} * Cu _{1.65} FeS _{2.09} *	Cu _{5.5} FeS _{5.34} \$ Cu _{3.6} FeS _{3.4} \$ ### Cu _{4.76} Fe _{0.88} S _{4.36} Cu _{4.84} Fe _{1.12} S _{4.05} Cu _{4.63} Fe _{1.06} S _{4.28} ### Cu _{4.5} FeS ₄ √ Cu _{4.2} FeS ₄ √ z = or <16
***: natural hydrothermal phase			z=3 - 4, 6 - 8	
###: ambient/hydrothermal overlap				
√√√: supergene				
\$\$\$: synthetic	hexagonal			
Crystallography	c ₀ -11.171Å a ₀ -3.768Å	pseudocubic a ₀ -5.26Å	orthorhombic a ₀ -7.7Å b ₀ -7.8Å c ₀ -10.92Å	tetragonal a ₀ -10.92Å c ₀ -21.65±0.05Å
Hexagonal	P/6mmm-P63/mmc P3m1 (1) pseudocubic a ₀ -5.30Å	Fm3m tetragonal a ₀ -5.30Å c ₀ -5.26Å	Pmmn tetragonal	pseudocubic cell edge: 10.87-10.91Å

at longer wavelengths (lower wave numbers).

Nukundamite: The anisotropic emission is considered to be <5000 Å energetically higher than the crossed polar emission exhibited by id (>57kcal); inflection of the spectral reflectivity curves (Lévy, 1967) is in the range 5000-6250 Å; maximum reflectivities occur at longer wavelengths (5500-6000 Å) than the id profile. The nk profile is similar to that of cv, a known superconductor (Sleight, 1988), and not related to curves attributed to the id series. The fact that nk absorbs light at higher energy levels (shorter wavelengths) indicates the occurrence of a larger band gap, indicating a greater thermal stability compared to id which exhibits a lower absorption energy level and longer wavelength polarisation.

The enormous optical effects exhibited by id polytypes may involve a superstructure grating, although the intense green polarisation colours are considered due to crystal field effects in the Cu^{II} region of the visible spectrum. The vacancy superstructure is considered to contribute to the level of optical activity.

Variation in optical properties is related to lattice distortion of polytypes from bn to id and nk-integral superstructures; distortion from cp to

an.cp and id involves non-integral superstructures. The level of optical activity exhibited by the polytypes is greater in large isotropic superstructures and less prominent in anisotropic superstructures; optical activity is less prominent in the transition from orthorhombic to tetragonal symmetry. Similarly increased metallic properties result in reduced optical activity. Biaxial optics are indicated by some id crystals, which is consistent with the orthorhombic aspect observed in precession exposures and microscopic sections.

Optical characteristics of some of the polytypes are as follows:

Te Kumi, New Zealand; 46-48 atomic% S Cu_{3.2}FeS_{3.7}
R_o - light brown R_e - light yellow brown (air)
Anisotropism - intense green/yellow-greyish green (45°)

Origin: submarine volcanogenic hydrothermal alteration/quench product of the bn-id series.

Fern Hill, New Caledonia; 47-49 atomic% S

Cu_{3.12}FeS_{3.88}

R_o - yellow/orange-brown R_e - light green yellow
Origin: retrograde metamorphic and/or low temperature alteration product of stratiform/

continued to Table 2.

	3C integral	8A integral	2C-1.3A-3.1B nonintegral	nonintegral
Density g.cm ⁻³	4.53-4.6	4.28	4.24-4.68 4.36-4.83	4.64
Habit	hexagonal plates pyramids/spiral growth twins	sphenoidal/parquet twins-cp epitaxy octahedral mimetic surfaces c-axis rotation twins	prism (100) pyramid (101) pinacoid (4/m)	
Cleavage	0001 perfect	111/124/001 indistinct-perfect	110/100/111 distinctive prismatic -poor	
Hardness	<id >cv submetallic	<cp >nk >bn non-submetallic	<cp >id >djur submetallic -metallic	nonmetallic
Enthalpy ΔH°cal.mole ⁻¹ 298.15°K	-102598 -96122	-70335 -69867	-56756 -50200	-82112 -79992
Thermal Stability	525±25°C cp/nk tie 171±20°C or 450°C	300±20°C 260-270°C id-cv-cp/nk tie reaction 380(DTA) - 400°C(invpt)	220°C-290±30°C 500-550°C synthetic quenched	75°-140°C (4) 370-550°C (2) (3) (5)
Inversion T	360°C	220°C	220-250°C	220-320°C
Crystallisation T (Hydrothermal)	220-370°C	220°-320°C		

(1) Sugaki *et al.* (1981); (2) Lee *et al.* (1975); (3) Czamanske (1974); (4) Brett *et al.* (1964); (5) Weigel (1978ms)

volcanogenic bn.

Pilou, New Caledonia; Cu_{5.37}FeS_{6.6} - Cu_{3.6}FeS_{4.7}

R_o - pink brown R_e - grey brown

Anisotropism-greenish/grey

Origin: low temperature nk polytype, compositions approach S-deficient id polytypes; occurs after cp intergrown with cv; relic id occurs as a precursor between cp and nk-cv.

Great Barrier Island, New Zealand; Cu_{3.07}Zn_{0.02}FeS_{3.91}

R_o - brownish yellow R_e - light greenish yellow

Origin: supergene alteration product after hydrothermal subvolcanic pipe bn.

Ok Tedi, Papua-New Guinea; Cu_{2.98}FeS_{4.02}

R_o - red/brown R_e - light green/yellow

Anisotropism-greenish yellow

Origin: low temperature/late hydrothermal alteration of porphyry bn. Nk occurs as overgrowths on symmetric id (2 polytypes) - cp epitaxial/lamellar intergrowths; nk is enveloped by stoichiometric cv shrinkage rims (260°C); lower temperature bl.r.cv replaces id-cp.

Panguna, Bougainville Island.

I Id: R_o - brown/yellow R_e - grey/brown

Anisotropism-greenish/grey

Fine oriented intergrowths with polytype II

II Cu_{3.3}Fe_{0.89}S_{3.87}; 48 atomic% S

Isotropic polymorph of the sulphur-deficient id polytypes;

Yellow/brown (= R_o id); another isotropic polytype is light brown

Origin: incongruent dissolution products after porphyry bn; supergene overlap with late waning hydrothermal conditions.

Undu, Fiji; Cu₅FeS₆ - Cu_{5.6}FeS_{6.5}

Nk: R_o - pink/red-brown R_e - light brown/grey

Anisotropism: green-grey/yellow-grey

Origin: marine subvolcanic hydrothermal (220-320°C) intergrown with py, cv and luz.

Yauricocha, Peru; coexisting hydrothermal id and nk

I Id, associated polytypes are listed in Table 2.

Cu₅FeS₄ - ca. 1% As substitution

R_o - yellow/brown R_e - light greenish yellow

Anisotropism - intense yellow green

Origin: symmetrical epitaxial/mimetic/lamellar intergrowths with cp, an.cp, cv and nk (an.bn reaction series not observed - restricted quench products occur); hydrothermal (220 - 320°C) incongruent dissolution reaction product after high temperature bn (300-700°C in supraporphry pipes)

II Nk, $\text{Cu}_{5.66}\text{FeS}_{8.66}$

R_o - pink red-brown/dark brown R_c - brown-grey

Anisotropism grey - yellow/green

Origin - as euhedral crystals intergrown with an open space advanced argillic assemblage cv, py, enargite-luzonite, barite (220-350°C); nk also occurs as a reaction product (after cv, cp, id, an.cp, an.bn - 260-270°C; the quench phases often exhibit rims) within the vein and in the bn wall assemblage. Cv intergrown with id and nk decrepitate at ca. 270°C, consistent with tie line switch reactions.

CRYSTAL CHEMISTRY: IMPLICATIONS FOR ARCHITECTURE, PHASE EQUILIBRIA AND METALLOGENESIS

Metastable solid solution superstructures are compositionally dependent; they disappear at high temperatures as a result of disordering (polymorphic transitions) or decomposition into compounds with integral stoichiometric structures. Variation of superstructure architecture appears to affect the level of optical activity rather than colour properties.

Variable statistical occupation of superstructured vacancies and associated oxidation state disproportionation of higher oxidation state cations are involved in symmetry distortion (chalcogenide ligands are stabilised by metalisation). The concept of bonding is reduced to a level of atomic welding, with true bonding only occurring between cleavage and lattice planar rows. Non integral atomic relationships suggest that departures from relativistic states may sustain metastability and influence mass enhancement in metallized chalcogenide ligands.

The symmetry translations of subcell units of polytypes, twinning and preferred orientation are responsible for much of the ambiguity relating to the structure of id and nk, e.g., the 111* aspect of id is hexagonal a_c : 3.74 Å c_c : 9.16 Å (cf. quenched rhombic metastable bn; Morimoto & Kullerud 1966). Comparable multielement polytype series suitable for topological research include: germanite-idaite-sulvanite-hemusite-nekrasovite-colusite; mawsonite-chatkalite-rhodostannite-hexastannite-nk-epigenite; kesterite-stannoidite-regnolite-briartite-sakuraite-renierite-en/luz-id.

MULTIELEMENT POLYTYPE TRANSITION METAL CHALCOGENIDE SERIES : PHASE EQUILIBRIA-GEOCHEMISTRY-METALLOGENIC IMPLICATIONS FOR NUKUNDAMITE AND IDAITE SERIES

In considering the multi-element analogues of these phases (transition metal substitutes: V, Zn, Ga, Ge, Ag, In, Sn, Sb, Bi; chalcogenide substitutes: As, Se, Te) one soon realises that the complexity requires modification of the methods of depiction. In this respect it is suggested that the symmetry-arrangement of the periodic table of elements be modified to accommodate ties and solid solution areas between transition metals and chalcogenides etc. The solid state phase equilibria exhibited by complex multi-element systems can be visualized as strings with attached interphase ties and solid solution series. Interphase ties are arranged along the strings which spiral across the transition groups of a curved periodic table; a periodic compound phase diagram (a tabular section of chalcogenide mineral phases) is depicted schematically in Fig. 2.

Hydrothermal phase equilibria (Fig. 3) require complex construction but they are useful in that they relate directly to natural processes, sequence and zonation. Between these two depictions an atomic accommodation of the phase rule takes place in the coexistence of disparate multiphase assemblages. Substitutional polytype (1-2 atomic %) shifts allow ties to connect phases which would otherwise be considered metastable, e.g., bn is often intergrown with/or contains cotectic/exsolved inclusions of rare element containing phases (e.g., renierite, argyrodite, sakuraite, briartite, colusite, wittichenite, goldfieldite, Au, gallite, etc. often favour bn over cp and other phases which precipitate at lower metal aqueous ion/ aH^+ quotients, Fig. 3). As a result of progressive H^+ metasomatic reactions with silicate wall rocks, increasing Metal/ aH^+ aq. ratios in solution concentrate the rare phases with bn which normally precipitates in response to high $a\text{Metal}/aH^+$ ratios.

Numerous successive phases precipitate in response to H^+ metasomatic (e.g., py-cp-bn-col) or acid dissociation reaction paths (complex cyclic sequences and phase zonation arise from simultaneous peritectic/cotectic reactions) across phase boundaries; intersections of the latter-triple, quaternary-quintuple (etc.) points occur where up to five or more phases co-precipitate, e.g., bn-nk-en-tn-py (Fig. 3).

The periodic paradigm is particularly striking when one considers zonation and paragenesis in magmatic-constrained hydrothermal metalliferous ore deposits. Periodic groupings of mineral phases, grouped according to their constituent elements and the string concept, exhibit occurrence groupings (parallels occur at a regional scale,

**Continental / Cordilleran
and Platform Deposits.**

**Epithermal and Continental
Margin Deposits**

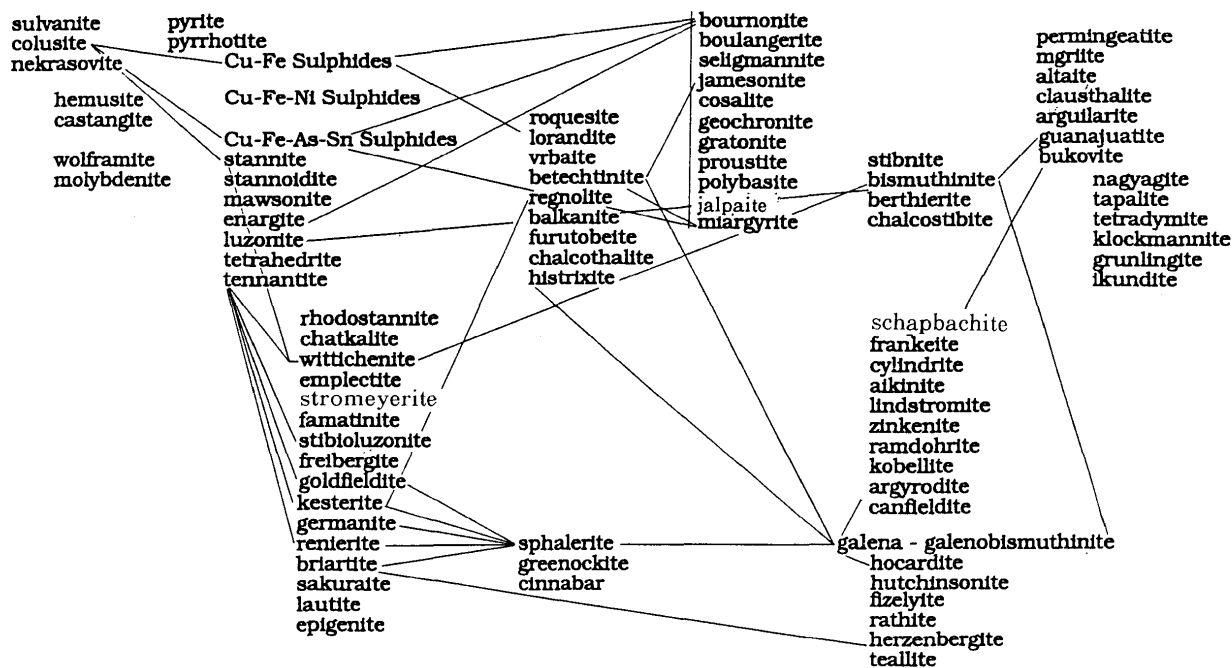


Fig. 2 Quasi periodic classification of ore minerals according to Mendeleev periodicity and their occurrence in hydrothermal mineral deposits. Tie lines are schematic; they would be expected to fan to limits according to invariant, univariant and divariant equilibria.

Weigel & Kobe, 1993) with zonation and paragenetic trends observed as time-space events in ore deposits from left to right across the scheme (Fig. 2). Telescoping trends appear to follow diagonal tie lines from left to right; depth-surface egress zonation exhibits similar trends. Complex Cordilleran type intrusive deposits (e.g., Butte [Weeds 1912] and Yauricocha [Weigel and Kobe 1993]) exhibit a wide succession of zones and parageneses (left side phases predominate in Fig. 2) right across the curved periodic table strings from V (colusite) to Te (goldfieldite) with influences related to rare ensialic element concentrations (e.g., germanite, gallite, renierite) to mantle derived transuranic decay products (Te-Bi-Pb) occurring. Similarly continental margin/island arc porphyry to epithermal gold deposits exhibit a wide range of paragenesis and zonation across the curved periodic scheme, i.e., right side phases predominate at higher levels in epithermal Au zones; e.g., Wafi River, Papua-New Guinea (unpublished reports by Weigel) a zoned auriferous calc-alkaline caldera complex containing a molybdenite, Sn-tetrahedrite, V-tennantite, enargite, colusite, stannoidite core zone enveloped by successive Cu-Pb-Ag-As zones which include bournonite-seligmannite and boulangerite-cosalite series.

Island arc epithermal Au deposits are less complex; id is rarely observed as disseminations after bn, with its origin thought to result from waning acid hydrothermal alteration overlapping with supergene processes produced by rapid uplift in relatively young active tectonic regions, e.g., Lihir Island (unpublished reports by Weigel).

Complex mineralogical sequences are also seen in continental and oceanic margins which surcome to crustal-plate rotation with consequent mantle transuranic influences, e.g., at the margins of the Tasman protocontinent of the SW Pacific Archipelago – the Fiji Metallotect and the Coromandel Metallotect (Weigel & Kobe, 1993) of the North Island of New Zealand – where chalcogenide distribution is tectonically zoned and successive plate rotation and opening of spheno-grabens is evidenced by separate fault-bounded Te, Ge and Se zones. Regional structural zonation of chalcogenides, semi-metals and mantle influenced radiogenic pairs (e.g., P/S, Bi/Te, As/Se, Ga/Ge, etc.) suggest that monitoring of these elements in natural waters could be useful for earthquake prediction. Adjacent passively subducted metallotects often contain an order of magnitude less gold (in Northern New Zealand the variation is 3,000-30,000 tonnes total Au mobilised by

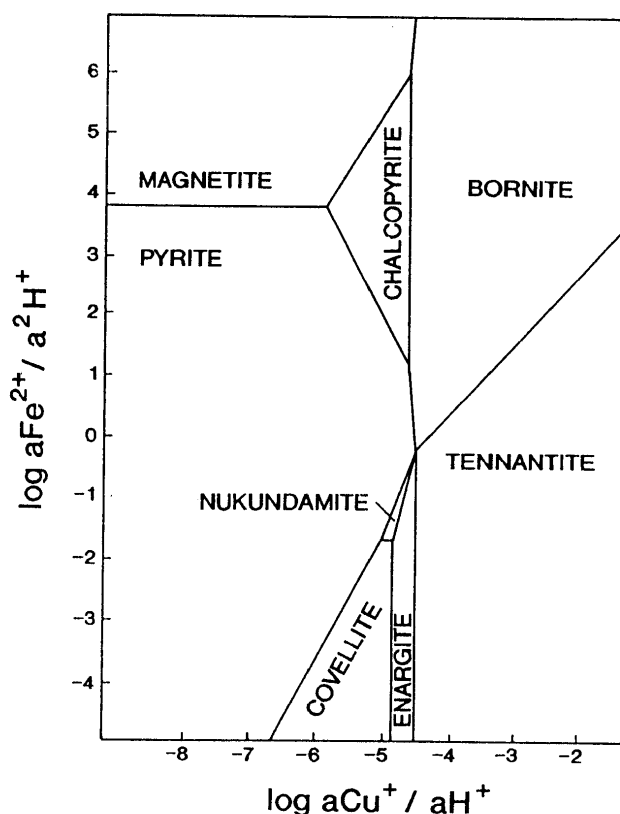


Fig. 3 Predicted hydrothermal phase equilibria for $\text{Cu}_2\text{O-FeO-As}_2\text{O}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{S-H}_2\text{O}$ system at 300°C , $\log a_{\text{AsOH}_4\text{-aH}^+} = -11$; $\log a_{\text{H}_2\text{O}} = 0$; $\log a_{\text{H}_2\text{S}} = 2$; based on thermodynamic data from Helgeson (1969), Knight (1977) and Weigel (1978ms). The nk activity space is bounded by two triple points (en-cv-nk and cv-nk-py) and one quintuple point (en-nk-py-bn-tn).

hydrothermal reactions) which is often associated with polytypes discussed in this paper (sulphides associated with Au exhibit severe etching effects).

MULTIPHASE CHALCOGENIDE HYDROTHERMAL SOLUBILITY DATA

Multi-element polytype phases exhibit structural similarities (Lévy 1967; Wang 1976; Weigel 1978ms), e.g., maw, $a_0=5.38\text{ \AA}$ pseudocubic, germanite $=5.29\text{ \AA}$ stibioluzonite $=5.28\text{ \AA}$ id $=5.26\text{ \AA}$. They vary from polytype to polytype according to structural translations of common chalcogenide subcells and more importantly hydrothermal chemical phase equilibria. It is in this respect that discussion of equilibria and incongruent dissolution processes that are responsible for polytype series leads us to another important problem - irreconcilable differences shown by multiphase chalcogenide hydrothermal solubility data.

Calculated metal and simple metal sulphide

hydrothermal solubilities appear to obey mass action laws, and natural solubility and mass balance constraints can be reconciled. In contrast there is a 1-2 order of magnitude difference in molal metal solubilities observed between predicted and experimental solubility data for multielement metal sulphide phases. Prior to the work of Crerar & Barnes (1976) difficulties occurred when attempts were made to reconcile this solubility data with metal zonation in ore deposits, mass balance data and the occurrence of daughter phases in fluid inclusions. According to H. Barnes (pers. comm.) net errors in heat capacity/entropy model derived equilibrium constants are up to ± 7 log units. Consequently the author revised (Weigel 1978ms) hydrothermal mutual solubilities for phases appearing in the $\text{Cu}_2\text{O-FeO-H}_2\text{SO}_4\text{-H}_2\text{S-HCl-NaCl-H}_2\text{O}$ system (hydrothermal phase equilibria after Helgeson 1969) calculated by taking into account differences between experimental (Crerar & Barnes 1976) and entropy/heat capacity modelled triple point solubilities at 300°C (1-3 molal NaCl); solubility errors are ca. 1.0 order of magnitude lower than experimental data for Fe and ca. 1.5 orders of magnitude lower than experimental data for Cu. The improvements in the accuracy allow us to reconcile observations made on natural assemblages; the differences in solubility data appear to be based on fundamental processes relating to the law of mass action. The fact that Cu solubilities are more prone to error probably relates to lattice effects where Cu ions are more commonly subject to strong forces.

The revised solubility data for the nk-cv-py triple point indicates that the $m\Sigma\text{metal} = m\Sigma\text{S}$ locus is consistent with advanced argillic alteration equilibria whereas the $m\Sigma\text{metals} - m\Sigma\text{S}$ locus for the bn-cp-py assemblage is consistent with phyllic and/or potassic wall rock equilibria; advanced argillic fluids are considerably undersaturated in respect to bn hence the development of id polytype series in these zones. In terms of $f\text{O}_2/\text{pH}$ variables where sulphide univariant boundaries are close $m\Sigma\text{metal}$ and $m\Sigma\text{S}$ are important in determining mineralogy, but when univariant boundaries are not coeval $f\text{S}_2$ exerts a strong control over mineralogy. $M\Sigma\text{Fe} = m\Sigma\text{S}$ loci always occur at higher pH levels than $m\Sigma\text{Cu} = m\Sigma\text{S}$ loci. Incongruent Cu dissolution is related to advanced argillic equilibria and incongruent Fe dissolution occurs in peripheral and distal propylitic zones (po, pent, cp alteration; temperature dependent zonation effects are observed from the an.cp.ss to the iss).

The important univariant/invariant equilibria to consider in relation to the incongruent dissolution phenomenon is the cp-bn-nk-py invariant point estimated to be at 171°C . The location of the tie line switch reaction is ambiguous because the univariants merge at low angles in the area of

