

The idaite-nukundamite-bornite-chalcopyrite metastable solid solution : Crystal chemistry, superlattice architecture and bonding; thermochemistry and phase equilibria; natural occurrences, geochemistry and metallogenesis(MEMORIAL VOLUME TO THE LATE PROFESSOR TERUHIKO SAMESHIMA)

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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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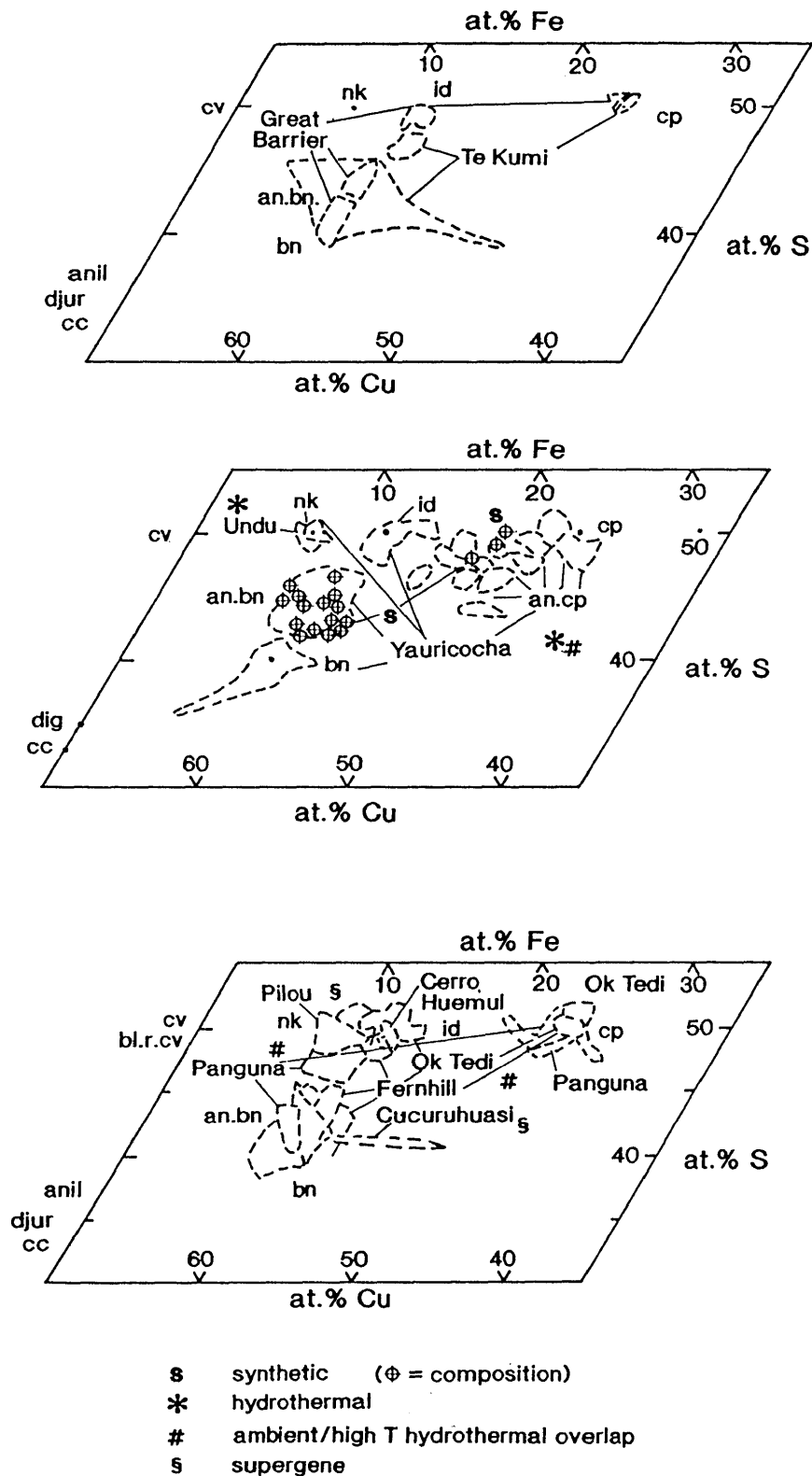


Fig. 1 Summary of electron microprobe analytical data for the metastable solid solution polytype series; natural and synthetic compositions are depicted; note especially the differences in compositional hiatuses for low and higher temperature polytype series.

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 >20000cm⁻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.

	hexagonal (111*) a ₀ -3.74Å c ₀ -9.16Å orthorhombic a ₀ -7.44Å b ₀ -7.50Å c ₀ - 10.52Å	8A integral 4.28	a ₀ -5.39Å c ₀ -10.92Å pseudocubic a ₀ -5.4-5.58Å	
Superstructures	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
Lustre	-metallic			
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		
Crystallisation T (Hydrothermal)	220-370°C	220°-320°C	220-250°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}

R₀ - 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}

R₀ - 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}

R₀ - 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: R₀ - 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 (= R₀ 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: R₀ - 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

R₀ - 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**

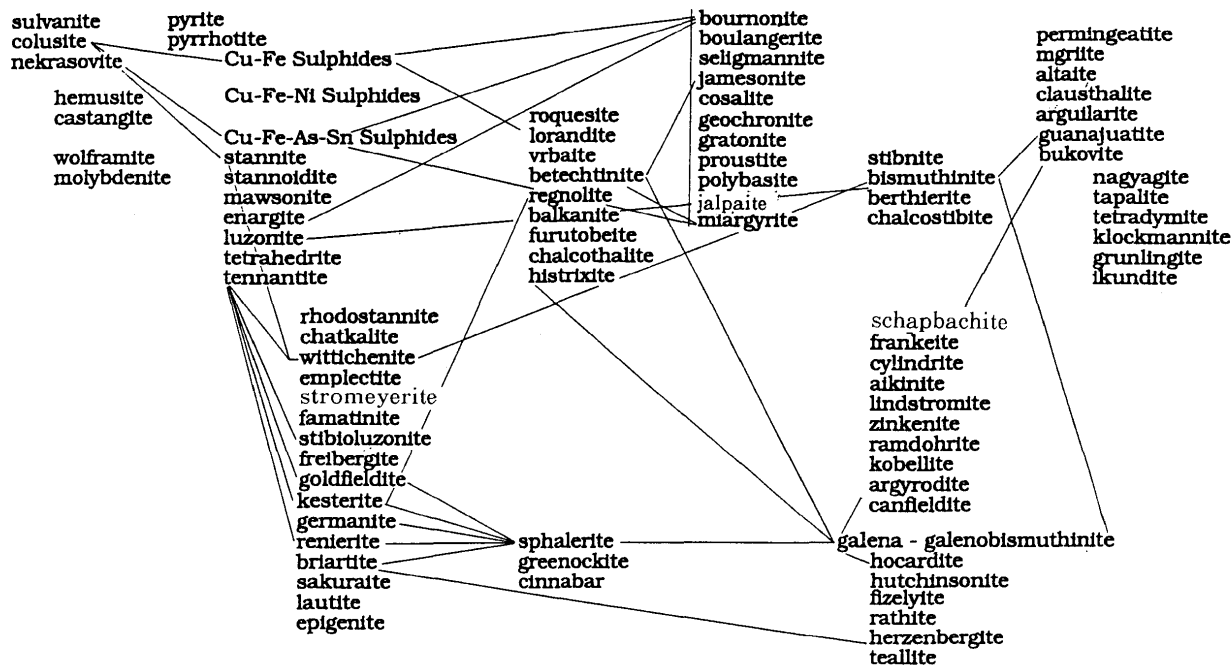


Fig. 2 Quasi periodic classification of ore minerals according to Mendeleev periodicity and their occurrence in hydrothermal mineral deposits. Tie lines are schematic; they would be expected to fan to limits according to invariant, univariant and divariant equilibria.

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

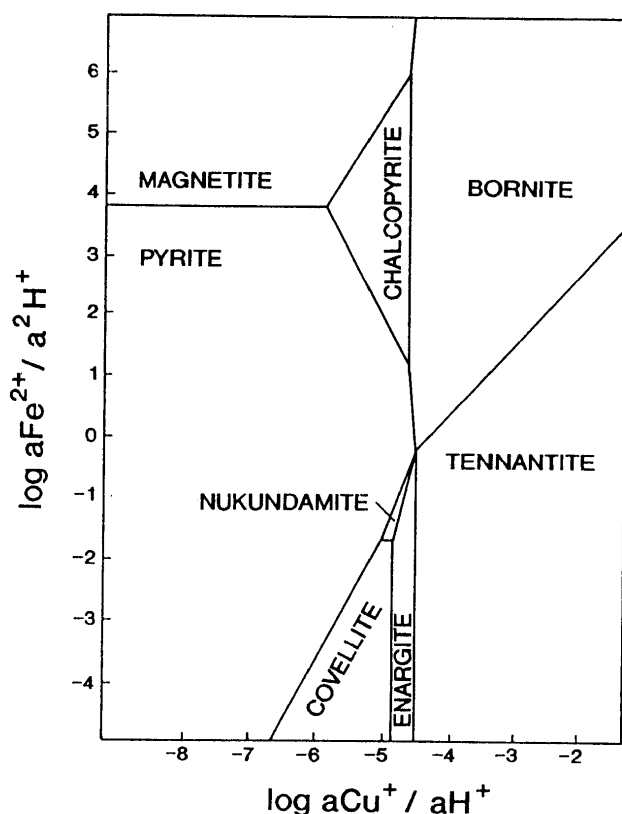


Fig. 3 Predicted hydrothermal phase equilibria for $\text{Cu}_2\text{O-FeO-As}_2\text{O}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{S-H}_2\text{O}$ system at 300°C , $\log a_{\text{AsOH}_4\text{-aH}^+} = -11$; $\log a_{\text{H}_2\text{O}} = 0$; $\log a_{\text{H}_2\text{S}} = 2$; based on thermodynamic data 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

permissive metastability below 300°C; colinear relations are favoured at low temperatures between cp-nk-cv.

CRYSTAL CHEMISTRY AND SOLID STATE PHASE EQUILIBRIA

The structural formula of id is thought to be $2\text{Cu}^{2+}\text{Cu}^+\text{Fe}^{3+}[\text{As}^{3-}\text{S}^{2-}]_4$ by analogy with data from Vaughan & Burns (1972) for germanite which has a density of 4.29gm.cm^{-3} , (after Dana) [cf. id = 4.28gm.cm^{-3}]. Substitution of As for S in the idaite lattice (hydrothermal) allows for equilibrium coexistence of cp and nk below 300°C. Id ($\text{Cu}_{3+x}\text{Fe}_{1-x}\text{S}_4$) – the low temperature polytype formula – exhibits extensive metastable solid solution at low temperatures (<220°C) with anomalous cp, bn (<75-140°C) and nk (<171°C) as a result of step-wise incongruent dissolution reactions; narrow miscibility gaps at limiting surface compositions are the result of arrested reaction. Non-stoichiometry and metastability in terms of the phase rule is observed below 171-140°C (an.bn-id-an.cp-bl.r.cv/nk-id-cv coexistence); metastable high temperature polytypes are preserved as a result of quenching.

At higher temperatures the solid solution is limited to id and its polytypes, cp and its polytypes, and bn and its polytypes (including quenchable phases); nk is not involved in the solid solution above 171°C. In calc-alkaline igneous rocks magmatic sequential crystallisation of metal sulphide phases is indicated across the Cu-Fe-S system from iss-po, iss-cp, iss-bn, iss-bn-cp to bn-cp (Weigel & Kobe 1993). An.bn and an.cp occur as quench products. Nk occurs as a fumerolic precipitate (Clark 1970) which is consistent with the experimental data of Roseboom & Kullerud (1958). The occurrence of the other polytypes are the result of post magmatic processes as evidenced by globular sulphides intergrown along phenocryst growth zones with glass ovoids and silicate microcrysts. A break down of textures to angular interstitial intergrowths occurs as a result of hydration and alteration below the po-py-S(liquid)-S(vapour) invariant at 790°C (Weigel 1978ms); the paragenesis indicates retention of Cu ions in residual silicate melt octahedral sites (after Burns 1970 and Feiss 1978). Similar but distinct high temperature globular sulphide/oxide textures and parageneses occur in West Coast N.Z. titanomagnetite sands and Central N.Z. Volcanic Plateau ignimbrites indicating higher temperatures of eruption and the provenance of the sands.

Nukundamite is stoichiometric (metal ratios are almost invariant) at high temperatures whereas the low temperature compositions trend toward sulphur deficient id polytypes; gradational associations are noted optically between nk and cp. The nk structure resembles the cv subcell (Cu_5S_6 , after Yund 1963), consequently Cu_5FeS_6 - $\text{Cu}_{5.5}\text{FeS}_{5.5}$

has been favoured as a structural formula. The long range basal repeats (3C) are equivalent to 2 cv cells; the formula $\text{Cu}_{5.5}\text{FeS}_{5.5}$ is consistent with experimental phase and theoretical thermodynamic data. Derivation of hydrothermal phase equilibria indicates that Cu_5FeS_6 is metastable; natural hydrothermal occurrences are almost always overgrown by $\text{Cu}_{5.5}\text{FeS}_{5.5}$. The anisotropy of the structure is related to planar layered repeating units (S-S linkages are weak forces) of $(\text{Cu}_2\text{Fe})\text{S}$ with intervening metal S' tetrahedra; Fe replaces ca. 2/3 of one Cu atom in 2/3 of the cv unit cell. The long range ordering of the subcell is related to Fe site occupancy; the superstructure approaches integral metal ratios. Id, however, exhibits a subcell structure similar to cp with 2Cu atoms filling 1/2 the Fe sites in the cp unit cell. Metal-metal interactions in nk (Sugaki *et al.* 1981) are similar to Fe^{II} - Fe^{III} interactions in cubanite (Vaughan & Burns 1972), charge transfer disproportionation processes relate to the model of metallised chalcogenide ligands discussed elsewhere in this paper; this concept would explain the non integral Fe/Cu cell ratios and the metallic character compared to id which exhibits covalency as indicated by optics, hardness and its reduced cell dimensions. Various metal interactions are important in determining properties of the polytypes; the nk 3C superstructure relates to Fe site occupancy between planar layers and tetrahedral interstices whereas id exhibits an 8A superstructure which relates to metal vacant layers in the bn parent lattice.

Idaite and its polytypes (e.g., marine volcanogenic occurrences and experimentally quenched phases) are less common as monomineralic precipitates and replacements. Common occurrences in epitaxial association with cp are related to structural similarities and compatibility with the an.cp series. Intermediate phase superstructures tend to be non-integral, exhibit a greater degree of metastability and lower thermal stability than integral end members; stable phases after occur at the margins of the s.s. phase space.

Some polytypes are polymorphous; optically distinct phases exhibit similar compositional variations, e.g., the Te Kumi submarine/volcanogenic id polytype (anisotropic) and the Panguna isotropic id are compositionally similar (Fig. 1). Other polymorphs are known: (i) pseudocubic $a_0 = 5.26\text{Å}$, 8A, polymorphic isotropic inversion at 20°C. (ii) tetragonal $a_0 = 5.26\text{Å}$ $c_0 = 10.46\text{Å}$, 40°C experimental dissolution product after bn (Utgarte & Burkin 1977).

Several metastable quenchable phases are known to occur in the phase space between bn and id polytypes at high temperatures; they are observed in advanced argillic assemblages in nature. These polytypes differ from the low temperature an.bn series (Fig. 1) in that they exhibit a restricted range of composition and they can be

synthesised as quench products of high temperature reactions, e.g., $\text{Cu}_4\text{FeS}_{4.2}$ - $\text{Cu}_{3.5}\text{FeS}_{3.6}$ quenched from 390° and 500°C respectively (Lee *et al.* 1975) and $\text{Cu}_{5.5}\text{FeS}_{5.3}$ (Czamanske 1974). A wider range of compositions from 500-550°C between those quoted in Lee *et al.* (1974) and Czamanske (1974) have been synthesised by the author. The metastable quenchable an.bn solid solution is restricted at high temperatures; above 250°C it shrinks to an area midway between bn-id-nk exhibiting a compositional range of ca. 5 atomic%. The metastable solid solution becomes more apparent below 220°C where the id solid solution expands toward cp. 12 polytypes of the non-stoichiometric chalcopyrite series are recognised in nature (Weigel 1978ms); 3 phases from the series have been quenched from 500-550°C; $\text{Cu}_{1.5}\text{FeS}_{2.4}$ - $\text{Cu}_{1.75}\text{FeS}_{2.5}$ - $\text{Cu}_{1.46}\text{FeS}_{2.46}$.

STRUCTURE AND CHEMISTRY OF THE POLYTYPES

Polytype symmetry translations are inherently complex relating to superstructure vacancies and consequent strong force effects (including Jahn Teller-variable oxidation states, d^4 , d^7 , d^8 levels of metal ions and non specified forces relating to the vacancy controlled superstructures) which impose space constraints on the alloyed chalcogenide framework. Migration of Fermi-levels effect different levels of metastability, i.e., the occurrence of polytypes, polymorphs, thermal stability and optical properties. Lowered Fermi-levels result in increased stabilisation; variation in optics are in sympathy with these levels. More stable phases exhibit higher energy emissions, e.g., the increasing wavelengths of cross-polar optical emission for the series stannite-maw-id (metastability increases in the direction of increasing wavelength). Direct alteration of high temperature stable compounds to metastable polytypes is effected by structural similarities whereas structural differences and kinetic obstacles at low temperatures often result in the occurrence of non-integral reaction intermediate superstructures. The direct alteration of high bn to id and/or an.cp polytypes occurs above 220°C (Weigel 1978ms); the volume reduction of ca. 11% is calculated and consistent with the extent of craquele shrinkage textures. The low temperature reaction intermediate trends are bimodal in response to a 2-step surface limiting kinetic model (Dutrizac & MacDonald 1974). Other polytypes exist in nature as a consequence of quenching and overgrowth preservation. The phase synthesised by Frenzel (1959) is probably akin to these and similar to the rhombohedral metastable bn polytype synthesised by Morimoto & Kullerud (1966).

Idaite Polytypes: Many polytypes and polymorphic forms of this phase exist, the formula

$\text{Cu}_{3+x}\text{Fe}_{1-x}\text{S}_4$ is only preferred at low temperatures because nk is stoichiometric and does not take part in the metastable solid solutions at high temperatures. Conclusions based on electron-probe, optical and X-ray data indicate that several polytypes exhibit derivative integral and non-integral superstructures with translations based on Cu^{2+} vacancies and statistical variation of lattice sites. Transition metal and linked chalcogenide vacancies are the result of incongruent dissolution of cp-bn, quenching, hydrothermal oxidation, supergene oxidation and dissolution. Idaite exhibits microdomains of optical variability including parquet, mimetic and lamellar twins which are also associated with polymorphic inversion at 220°C and epitaxial intergrowths of cp and an.cp.

X-ray data has been reported as follows:

1. Fm $\bar{3}$ m, pseudocubic/tetragonal - Cu_3FeS_4 ; $a_0 = 5.26 \text{ \AA}$ superstructure $8a = 42 \text{ \AA}$ (Weigel, 1978ms). Sample is natural hydrothermal incongruent dissolution product of bn from Yauricocha, Peru; contains ca.1% As; adjacent barite fluid inclusion filling temperatures: 220-320°C, decrepitation peaks for associated sulphides: 140-270°C, 260-300°C. Refined single crystal lattice dimensions measured across the reciprocal centre by way of 64 integral superstructure lattice rows: $a_0 = 5.30 \text{ \AA}$ $c_0 = 5.26 \text{ \AA}$ tetragonal cf. renierite: $a_0 = 10.60 \text{ \AA}$ $c_0 = 10.54 \text{ \AA}$ (after T. Le Bihan in Lévy, 1967).
2. tetragonal $a_0 = 10.52 \text{ \AA}$ $c_0 = 10.72 \text{ \AA}$ (Wang 1976).
3. tetragonal $a_0 = 5.26 \text{ \AA}$ $c_0 = 10.46 \text{ \AA}$; 40°C synthetic alteration product of bn (Utgarte & Burkin, 1977).
4. hexagonal $a_0 = 3.90 \text{ \AA}$ $c_0 = 16.95 \text{ \AA}$ (Frenzel 1959) high temperature synthetic quench phase.

Idaite is considered to be metastable (it exhibits greater thermal stability than non-integral polytypes but hydrothermal phase equilibria indicate mutual exclusion by phases with stable larger subcells) on the basis of thermochemical data, residuality (occurrence as an alteration product is almost ubiquitous) and its positioning in the Cu-Fe-S system (the nk-cp tie line requires stoichiometric variations in id for stable coexistence).

Idaite from Fern Hill, is restricted in composition (Fig. 1) and similar to the sulphur deficient polytypes from Cerro Huemul and Te Kumi (Weigel 1978ms); the Fern Hill occurrence is considered to relate to an overlap between retrograde regional metamorphism and supergene effects in an area subject to rapid uplift.

Supergene alteration of hydrothermal bn from Great Barrier Is. is typical of the low temperature polytype series with narrow miscibility gaps and a reaction series to stoichiometric id. The Te Kumi

an.bn polytypes exhibit variable compositions (cf. synthetic quenched types) in association with a sulphur deficient id polytype (a submarine hydrothermal alteration/quench product-quasi supergene effects result from seawater encroachment).

The Panguna and Ok Tedi polytype series exhibit wide compositional gaps; the Ok Tedi id is stoichiometric while the Panguna polytypes extend toward nk and id polytypes and polymorphs suggesting an overlap between waning hydrothermal and emerging supergene processes. This phenomenon is also observed in geothermal wells (unpublished report by Weigel) and in Cenozoic epithermal gold deposits.

Degrees of metastability are exemplified by non-integral superstructure polytypes which are less stable than integral types, and varying degrees of thermal stability exhibited by the metastable polytype series: an.bn — 75-140 °C (Brett & Yund, 1964); nk-id polytypes — 171 °C (Weigel 1978ms); id-an.cp polytypes — 220 °C (Weigel 1978ms). The quenchable an.bn solid solution is restricted compositionally between S-deficient id polytypes and ca. 42 atomic% S in bn (quenchable from above 220-550 °C). Id exhibits a polymorphic transition at 220 °C and a maximum thermal stability of ca. 280 °C (products: bn-cp±nk). Id and cv react at ca. 260 °C to produce nk; id and cp react at 270 °C producing nk.

Nukundamite: The occurrence of nk under hydrothermal conditions is limited by geochemical environments and hydrothermal phase equilibria. Its occurrence is constrained by its activity space locus (Fig. 3) in the $\text{Cu}_2\text{O}-\text{FeO}-\text{As}_2\text{O}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{S}-\text{H}_2\text{O}$ system. Arsenite activity constraints severely limit the occurrence of nk in hydrothermal ore deposits; e.g., at 300 °C a quintuple point (nk-py-bn-en-tn) is predicted for the condition $a_{\text{AsOH}_4^-} \cdot a_{\text{H}^+} = 10^{-11}$, $a_{\text{H}_2\text{S}} = 10^{-2}$ while at higher arsenite activities the nk space is replaced by en-tn. At lower arsenite activities the nk space is bounded by 3 triple points involving py, cv and bn. Oxidative and H^+ metasomatic processes limit the preservation of nk ($\text{Cu}_{5.5}\text{FeS}_{6.5}$) and preferential cv-en-tn replacement is predicted; id and Cu_5FeS_6 activity spaces do not exist under predicted hydrothermal conditions. At low temperatures cv-nk-cp colinearity is predicted.

The limited occurrence of nk can be attributed to progressive oxidative trends in surficial environments. In terms of predicted aqueous phase equilibria (Weigel 1978ms) in the $\text{Cu}_2\text{O}-\text{FeO}-\text{H}_2\text{SO}_4-\text{H}_2\text{S}-\text{H}_2\text{O}$ system at 25 °C, cv precipitation progressively overtakes nk precipitation for progressive decreases in $a_{\text{H}_2\text{S}}$ (by 1-3 orders of magnitude). Reaction trends for the bn-id incongruent dissolution series in tropical climates approach nk; supergene nk from Pilou, New Caledonia replaces stoichiometric cp. Adjacent to cp, nk is intergrown with id and varies in composition from

$\text{Cu}_{5.5}\text{FeS}_{6.5}$ toward tropical supergene id polytypes (cf. Panguna) and sulphur deficient polytypes.

Hydrothermal nk appears as $\text{Cu}_{5.5}\text{FeS}_{6.5}$ whereas overgrown types from deposits prone to quenching approach Cu_5FeS_6 (e.g., Undu mine, Fiji where Cu_5FeS_6 crystals are overgrown by nk and further overgrown by cv-luz). Thus, limited solid solution occurs at high temperatures whereas at low temperatures complete solid solution occurs between id, an.bn and nk (Weigel 1978ms; Ottemann & Frenzel 1979). Hydrothermal nk exhibits spiral growth twinning, rotation about the c-axis on 0001 and a 30° increment of rotation. Coarse arborescent intergrowths and hexagonal plates with pinacoid, prism and pyramid forms occur and crystals quenched from above the inversion temperature (ca. 360 °C) exhibit lamellar twinning. Cell dimensions derived from refined calibrated powder-camera X-ray data are $a_0 = 3.768 \text{ \AA}$, $c_0 = 11.171 \text{ \AA}$; the a_0 parameter translates to a_0 cubic of 5.30 Å, Diffractometer traces indicate depressed and split basal peaks and long range ordering of the subcell reflections is indicated by a series of reflections from 6.03 to 20.79 Å.

Zero level precession X-ray exposures of hydrothermal nk in a univariant assemblage (nk-py-cv-luz) from Undu mine, Fiji, indicate the following lattice dimensions:

$$a_0 = 3.81 \pm 0.01 \text{ \AA} \quad c_0 = 11.26 \pm 0.06 \text{ \AA}$$

supercell - 3C
Cell- $\text{Cu}_{3.38}\text{Fe}_{0.62}\text{S}_4$

Nukundamite and cv are uniaxial positive, morphologically similar and possess the same primitive lattice types, but they appear to differ in space group configuration as a result of superlattice influences.

Nonstoichiometric-Anomalous Chalcopyrite Solid Solution Series: The an.cp solid solution extends from id to cp and toward bn in the Cu-Fe-S system; commonly adjacent to cp it varies by about 5 atomic% constituent elements in the vicinity of the bn-cp and cp-id ties. The stoichiometric variability is ascribed to extreme environments of crystallisation and solid state phase rule adjustment (vein assemblages containing this phase exhibit equilibration features). Maximum thermal stability commonly occurs at ca. 220 °C where this phase decomposes to bn + cp (a DTA endotherm was noted between 200° and 220 °C) whereas in some experiments chalcopyrite segregations appeared above 230 °C; decomposition to bn-cp occurred at 320 °C. An.cp has been synthesised at 500-550 °C in evacuated sealed tubes, and has quench compositions varying from $\text{Cu}_{1.5}\text{FeS}_{2.4}$ to $\text{Cu}_{1.75}\text{FeS}_{2.5}$. The schapbachite-matildite polytype series exhibits similar subcell dimensions (Ramdohr 1969) and symmetry transformations to those exhibited

by an-cp and the metastable solid solution series (orthorhombic/tetragonal inverts to isometric at about 225°C).

In the specimens studied from supra-porphyry pipes from Yauricocha, an.cp occurs in association with acid hydrothermal alteration products of an early bn-dge-cp stage and a high djur, bn and barite vein assemblage equilibrated with a wall assemblage containing an.cp, id, bl.r.cv, nk, cp, dge, djur and barite. An.cp varies optically from an id-like phase ($\text{Cu}_{1.9}\text{FeS}_{2.7}$) to a cp-like ($\text{Cu}_{1.1}\text{FeS}_{2.15}$) phase which varies in subcell dimensions from ca. 5.4 to 5.58 Å with a large non-integral orthorhombic/tetragonal superstructure. Median compositional data approach $\text{Cu}_{1.5+x}\text{FeS}_{2.5-x}$ (e.g., $\text{Cu}_{1.6}\text{FeS}_{2.4}$). An.cp exhibits a brownish-yellow metallic lustre with a distinct cleavage; twinning of rhombic crystal mosaics about the c-axis is observed in precession X-ray exposures. Twelve distinct polytypes have been identified (Weigel 1978ms), varying from $\text{Cu}_{2-x}\text{FeS}_{3-y}$ (id-like polytypes with smaller cell dimensions than the cp side of the series e.g., $\text{Cu}_{1.8}\text{FeS}_{2.7}$ - $\text{Cu}_{1.6}\text{FeS}_{1.7}$) to $\text{Cu}_{1.1}\text{FeS}_{2.15}$. At first sight, single crystal X-ray data indicate a tetragonal cell with the following lattice dimensions: $a_0 = 5.39 \text{ \AA}$ $c_0 = 10.92 \text{ \AA}$; precession exposures of twinned mosaics indicate an orthorhombic/pseudotetragonal subcell: $a_0 = 7.74 \text{ \AA}$ $b_0 = 7.52 \text{ \AA}$ $c_0 = 10.92 \text{ \AA}$ (equivalent to a 5.45 Å pseudocubic cell). Refined X-ray powder camera data indicate an orthorhombic cell, space group Pmmn with the following dimensions: $a_0 = 7.67 \text{ \AA}$ $b_0 = 7.82 \text{ \AA}$ $c_0 = 10.92 \text{ \AA}$. Long range ordering observed in powder patterns confirms the superlattice architecture indicated by precession exposures. Single crystal supercell reflections occurring in twinned relation to the subcell indicate the following superlattice dimensions: $a_0 = 10.32 \text{ \AA}$ $b_0 = 24.67 \text{ \AA}$ $c_0 = 21.84 \text{ \AA}$ which is a nonintegral superstructure consonant to metastability and the decomposition at 220°C to phases with integral structures.

The Nonstoichiometric Anomalous Bornite Metastable Solid Solution Series: Homogeneous anomalous bornite metastable polytypes have non-integral superlattices resulting from random extraction of ordered metal (and linked metal-chalcogenide species as indicated by covariant analytical data and climate/latitudinal/altitudinal-dependent incongruent reaction schemes) layers from the parent polytype, controlled by low T solution kinetics. These superstructures change with time or varying physicochemical conditions to integral polytypes with limited stoichiometries. Some of the natural low T intergrowths (bn-cp±id±djur±anil±cc±cv±an.cp±etc) appear to result from solid state decomposition of an.bn polytypes while other intergrowths relate to incongruent reaction/alteration; low T unmixing intergrowths often occur in porous oxidised ores while

homogeneous S rich polytypes occur in impermeable ores. Exothermic reactions involved in advanced oxidation are expected to promote decomposition of the an.bn metastable solid solutions.

The optical properties of the polytype members of the an.bn metastable series vary considerably owing to lattice translation and distortion which are influenced by symmetry environment (cubic-tetragonal-orthorhombic). X-ray data indicate that cell volumes are reduced compared to bn. An isotropic dark brown an.bn polytype adjacent to id-cp intergrowths from a oxidised submarine volcanogenic deposit in Northland, N.Z. had a cell edge 10.87 Å and an indexed tetragonal fit: $a_0 = 10.93 \text{ \AA}$ $c_0 = 21.63 \text{ \AA}$. A yellow/brown isotropic an.bn polytype from a supergene assemblage occurring in a sub/volcanic pipe deposit, Great Barrier Island. (Cu_4FeS_3 - $\text{Cu}_{4.5}\text{FeS}_4$) had a cell edge 10.91 Å and indexed tetragonal fit: $a_0 = 10.92 \text{ \AA}$ $c_0 = 21.70 \text{ \AA}$. The indexed lines indicate that the 2 phases are structurally different and they individually possess different space group configurations.

The thermal stability limits of an.bn appear to range from 75°C (Brett & Yund 1964) and 140°C (Yund & Kullerud 1966) for a solid solution area extending from bn-nk-id to cp with extensions toward fukuchilite (Ottemann & Frenzel 1979). Low T reaction controlled surface limiting compositions are responsible for narrow miscibility gaps (Fig. 1), different from the range of compositions exhibited by the high T quenchable an.bn solid solution. At higher temperatures, changes in the bn structure prevent the development/preservation of reaction intermediates. In hydrothermal examples above the bn-inversion (220°C) reaction intermediates are not observed between bn and its alteration products; quench products are preserved by stable phase overgrowths.

Many of the so called 'anomalous bornites' are in fact sub-microscopic domain and epitaxial intergrowths (related to the low temperature structure of bn which exhibits alternating sphalerite and antiferite domains, Koto & Morimoto, 1975) of bn-cp-an.cp-id-nk-cv-anil-djur-etc.; when heated above 230°C these decompose into bn-cp-nk. The low T bn mixed-domain structure appears to be susceptible to differential replacement and incongruent dissolution (cf. cp which does not behave in the same manner). At high temperatures preservation of reaction intermediates is not common. Quench compositions observed in advanced argillic and submarine volcanogenic assemblages exhibit limited compositional variability from the S-deficient id polytype to Cu_4FeS_3 - $\text{Cu}_{3.6}\text{FeS}_4$ to $\text{Cu}_5\text{FeS}_{4.5}$; the miscibility gaps are more distinct in high T assemblages. Reaction trends are between id-bn and an.cp. Approximate limits of the quenchable solid solution based on experimental data (Lee *et al.* 1973; Czamanske 1974; Weigel 1978ms) from 370-550°C (and from natural assemblages 220-350°C)

are as follows: $\text{Cu}_{5.5}\text{FeS}_{5.5}$ - Cu_4FeS_4 - $\text{Cu}_{3.5}\text{FeS}_{3.5}$ - $\text{Cu}_{3.6}\text{FeS}_{3.4}$. The miscibility gap in the high T. an.bn series is close to stoichiometric bn, but below 220°C it migrates to higher S stacking levels according to environment.

EPILOGUE, CONCLUSIONS AND FUTURE PERSPECTIVES

It has been shown that variation in chemical and physical properties of the metastable solid solution polytype phases in the bn-cp-id-nk part of the Cu-Fe-S system are related to crystal chemistry and bonding effects. In some cases wavelengths of emission correlate with bonding effects; some wavelengths of emission correspond to constituent element crystal field energies – often expressed by the ion which controls the symmetry of the subcell. Compounds which exhibit higher thermal stabilities have higher energy optical emissions than similar metastable polytypes (especially those with non-integral superstructures), e.g., in the series: stannite (isostannite, hexastannite), maw, id. Crossed polar optical emissions exhibit increasing wavelength and decreased energy in the direction of decreasing thermal stability. Polytypes with comparatively larger subcells exhibit metallic properties whereas corresponding polytypes with smaller subcells exhibit nonmetallic characteristics (covalency in stoichiometric types; atomic metal-chalcogenide alloys in non-stoichiometric types). Quantification of optical anisotropy will lead to a better understanding of the chemistry of these and other anisotropic compounds, e.g., the green optical anisotropic effects observed in most of the lower symmetry high S polytypes from nk to id (emission wavelength increases across the series which includes their S deficient polytypes) to the an.cp polytypes with high Cu/Fe ratios. Analogous to internal reflections, and still visible under plane polarised light in id, these hues are considered to be effected by a fundamental scattering phenomenon and/or fluorescence. The concept of covalence would seem to preclude the latter in id because the reduced cell dimensions suggest that electronic quanta are severely constrained by nuclear effects; the superstructure is thought to be involved in the unusual optical emission.

The correlation observed (Sleight 1988) between metastability (various levels of metastability correlate with different perched Fermi-levels) and superstructures in superconductors is relevant when considering these polytype series. Phases exhibiting metal-metal interaction and vacancy controlled superstructures could be prepared by quenching and incongruent dissolution. The metastable products are expected to exhibit higher energy Fermi-levels than stable polytypes; long range ordering of vacancy defects will increase

molecular distortion and obviate covalent effects which are responsible for localising electronic regimes. It is interesting that phases within complex assemblages exhibit variations in composition in what can be described as a molecular accommodation of the phase rule. Variations in phase rule obligations are more noticeable at high T, while violations are more common at low T; accommodations affect assemblages less than the effects of T dependent metastability. Metastable assemblages that persist in terms of geological time exhibit compositional adjustments (associated with crystallisation and hydrothermal reactions; postcrystallisation solid state substitution and surface absorption) so that constraints imposed by concepts of the phase rule are obeyed, e.g., hydrothermal id from Yauricocha is S-deficient with ca. 1%As as a chalcogenide substitute (cf. low T id which contains transition metal substitutes) allowing divariant ties between the observed phases cv-nk-id-cp (up to 5 phases coexist in close proximity). Equilibrium attainment in the Yauricocha example is indicated by simultaneous duplicated paragenetic sequences, bn-djur-an.cp and cv-nk-cp-id in each of adjacent wall and vein systems.

At lower temperatures metastability becomes permissive because of the energetic similarities of univariant assemblages (invariant points become difficult to define) thus crystallisation conditions and hydrothermal phase equilibria are important in determining final assemblages. The complex paragenesis associated with polytype series in advanced argillic subvolcanic hydrothermal/supraporphry/epithermal Au and submarine volcanogenic environments commonly contains a persistent Au component and a suite of rare element (Mo/U/V/W/Bi/Ge/Re) phases; these elements act as sympathetic oxidants in combination with the incongruent dissolution equilibria. The overlap between late stage advanced argillic volcanogenic hydrothermal processes and supergene alteration in tectonically active regions produces mixed enigmatic mineral assemblages (< 75-220°C) similar to those found in submarine volcanogenic sediment/seawater interface assemblages containing low temperature hydrothermal phases. The imbalance between predicted and proven or estimated Au reserves in the regional metallotects investigated for variations in polytype chemistry in terms of the Au cycle is probably accounted for by low temperature sinks (e.g., the earth's oceans and sedimentary and low temperature epithermal deposits). Mention has also been made of the possible application of rare element associations of the polytype series to earthquake prediction, however, it should be stressed that further detailed study of the metamorphic geochemistry of veins attendant to major faults would shed light on the chemistry of sequestered ions and species

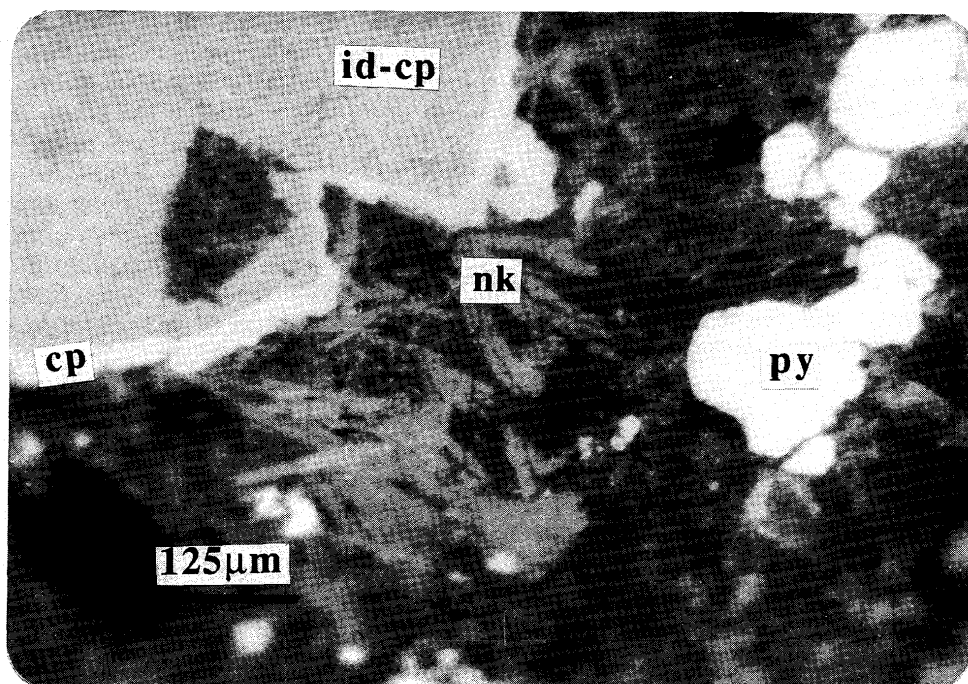


Fig. 4 Photomicrograph illustrating the contrast in optical properties of idaite (upper left, R_0 - yellow/brown, R_90 - light green yellow) and nukundamite (centre R_0 - pink/brown, R_90 - brown/grey); plane polarised light/ oil immersion; magnification $\times 1260$. Sample from Youricocha, Peru. Contact between the altered bn wall assemblage and the advanced argillic vein assemblage; nk is intergrown in optical continuity with stoichiometric cv and seeded off cp/an.cp segregation - shrinkage - reaction surface overgrowths to id-cp epitaxial/ lamellar twin intergrowths pseudomorphic after bn; cv-nk partially pseudomorphs id-cp intergrowths. Within veins the cv-nk-py univariant assemblage occurs with former bn crystals exhibiting various states of dissolution and replacement, cp-id relics occur intergrown with cv/nk.

released by crustal failure.

This paper explains some of the diversity of polytype crystal chemistry of the id-cp-bn area of the Cu-Fe-S system. Variations observed in nature are the result of thermally dependent kinetics; serendipitous energetic constraints and crystallisation environment. Stepwise stoichiometric variable series at low temperatures have surface limiting miscibility gaps which are wider and restricted at temperatures above 140-220 °C, e.g., Panguna low T an.bn varies in composition from bn to an id polytype with a limiting miscibility gap at 43-45 atomic % S. The low T reaction paths are sensitive to climatic changes; in tropical climes, supergene alteration products exhibit higher Cu/Fe ratios and reaction paths trend to higher S contents while temperate supergene assemblages are shifted toward lower Cu/Fe ratios and lower S contents. Similarly low temperature hydrothermal reaction paths are distinct, trending toward cp and id; and hence the occurrence of both low T and hydrothermal polytypes/polymorphs of these phases. However, nk is the exception being stoichiometric at high temperatures and compositionally variable below 171-220 °C; polytypes trend toward id and bn.

Conceptual depiction of phase equilibria for

multielement analogues of the metastable Cu/Fe chalcogenide polytype series as a string of ties spiralling across the transition rows of a curved periodic table and involving connections with the chalcogenides, appears as a powerful model of multielement solid state phase equilibria. Transition groupings of analogous phases, as depicted by the model, exhibit trends parallel to those observed in natural ore deposit zonation and also those observed in regional metallogenic provinces. It can be shown, a priori, that environment of crystallisation relates directly to the symmetry of polytype lattices; distortion of subcell units must involve significant interaction/displacement of the outer limits of chalcogenide units. Highly distorted subcells exhibit metallic tendencies, whereas isotropic covalent influences are less metallic. Transition metal periodicity and associated crystal chemical trends in the polytype series appear to provide a window of understanding to the subtle nature of atomic interaction at the molecular level. Vacancy controlled superstructures in polytypes will provide an important research focus for atomic structure resolution in the future.

Polytype phases on the Cu>Fe side of the bn-id tie exhibit nonorthogonal/rhombic/hexagonal distortion. Structural anisotropy is related to

superstructures which persist parallel to the c-axis. Cu electronic contribution to the distortion is obviously important (Jahn-Teller effects) but other effects declared by vacancy superstructures such as nuclear orbital and quench imposed strains are probably equally as important. Phases on the Fe>Cu side of the id-bn tie exhibit orthogonal/rhombic/tetragonal distortion with isotropic superstructures. Degeneracy of orbitals developed by specified electronic states relates to lattice distortion. However, the theory is lacking in that description of the molecular states needed to specify nuclear/electronic wave-spatial particle interaction (non specified strong forces not accounted for by Jahn-Teller effects). The metallised chalcogenide ligand is a satisfactory model for ligand-metal distribution in superstructured metal sulphide polytypes in that it would account for non-integral supercell metal ratios, possible nuclear orbital/charge influence on electronic/light quanta and localised (1μ) analytical covariation between transition metal and chalcogenide elements. The concept of an alloyed atomic ligand may require some theoretical modification but it allows for a realistic perception of molecular crystal structure. Further progress in crystal structure modelling will be made when analytical microbeam diameters are reduced to the sub-micron/angstrom range. Analytical subtleties for polytype superstructure series at the 10-110 Å range will provide very important data leading to realistic molecular crystal models when considered in terms of changing perceptions of atomic theory probably in conjunction with a unified theory. Atomic scale crystallography should become an important area of research although another aspect of the symmetry of baryon force fields in metastable superstructures is the effect of non-integral charge distribution and parity violations which promote non relativistic phenomenon sustaining metastability and influencing mass enhancement of chalcogenide ligands.

Important conclusions arising from research presented in this paper are:

1. Natural polytype variation relates to environment of crystallisation. In all cases complex phase coexistence is by an accommodation of the phase rule after chemical equilibration. The nk-cp tie is constrained by substitutional accommodation effects ($400^\circ\text{C} + \text{Cu}/\text{As}/\text{Zn}/\text{Mo}/\text{Re} \equiv 171\text{-}320^\circ\text{C}$ $\text{Cu}/\text{Sn}/\text{Ag}/\text{Sb}/\text{As}/\text{Bi}/\text{Te}$) and the occurrence of 2 invariant points ($171\text{-}450^\circ\text{C}$).
2. Translation of polytype symmetry relates to subcell reduction and distortion under the influence of strong forces and superstructures which affect levels of optical activity. Chalcogenide deficiencies are statistically linked to metal nonstoichiometry and the metallised ligands which are mobilised in alteration reactions. Integral superstructures exhibit polymorphic transitions at high T; non-

integral superstructures are quenchable from high T and decompose on heating to integral types. Polytype superlattices exhibit isotropic, anisotropic and spiral symmetry – the latter being non-integral influenced by rotational twinning. Non-integral structures are metastable relative to integral types. Variable atomic states and distortion are indicated by levels of metastability and polytype abundance; several types of strong forces are involved in lattice distortion. Atomic processes are thought to be more heuristic than previously realised.

3. Prograde (H^+ metasomatic) and reversed (acid dissociation equilibria) parageneses containing metastable solid solution polytypes are controlled by heat source equilibria and consequently distal parageneses are a useful guide to cryptic ore zonation; these can be modelled on the basis of hydrothermal phase equilibria. Discrepancies in solubility data for multielement chalcogenide phases appear to require a revision of the hydrothermal mass action relation to take account of cluster concepts and nonspecified strong forces.

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