Appendix B6

SEM observations, experiment 2

Coating stage pre $Ca(OH)_2$ addition

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Fe phosphate	amorphous coating with desiccation cracks, variable thickness	Fe-K±(Cu-Zn) phosphate	thin coating on ~75 % of chalcopyrite surfaces, one sphalerite grain coated
	Cu phosphate	spherical rosettes up to 20 μm diameter, often coalesced into a coating of radial splays; more rounded balls when substantial Si incorporated	Cu-K±(Si-Fe) phosphate	heterogeneous coating 100% of some grains, abundant on chalcopyrite, sparse on quartz and tetrahedrite
	Pb phosphate	coating of fine (<1 μm) acicular pincushions and dendrites; occasional large bladed (30 μm x 10 μm) crystals	Pb phosphate; large crystals ±K	acicular phases cover 100 % of galena surfaces; large crystals rarely on and adjacent to galena including on Cu-K phosphate rosettes
	Zn phosphate	scattered very large (200 μm x 100 μm) prismatic crystals; rare amorphous rounded precipitates	Zn-K phosphate; rounded precipitates Zn-K-(Si-S) phosphate	cover ~5 % of sphalerite surfaces
	Cu sulphate	fine grained euhedral crystals	Cu sulphate	rare isolated precipitates on phosphate phases

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column B	phosphate phases identical to those observed in column A with a slight increase in abundance except Zn-K phosphates, which were less common and of acicular morphology; Cu sulphates more common and rare Cu-Fe sulphates observed			
Column C	Fe phosphate	amorphous to flaky well-developed thick (~3 µm) coating with desiccation cracks	Fe-K$\underline{+}$(Cu-Zn-S) phosphate	coating on ~99 % of chalcopyrite, stannite (thick) and arsenopyrite (thin) surfaces, one tetrahedrite grain poorly coated
	Cu phosphate	spherical rosettes up to 30 µm diameter, often coalesced into a coating of radial splays; more rounded balls when substantial Si incorporated	Cu-K$\underline{+}$(Si-Fe-Al-S) phosphate	heterogeneous coating 100% of some grains, abundant on coated chalcopyrite, scattered on quartz, clays, tetrahedrite and oxides
	Pb phosphate	coating of fine acicular pincushions; larger bladed and leafy crystals	Pb phosphate	acicular phases cover 100 % of galena surfaces; large crystals rarely on and adjacent to galena including on Fe-K phosphate coating and Cu-K phosphate rosettes
	Zn phosphate	radial flow-like agglomerations of very fine-grained (100 nm x 10 nm) crystals; splays of acicular (50 µm x 1 µm) crystals; scattered large (200 µm x 30 µm) prismatic crystals;	Zn-K phosphate	cover ~50 % of sphalerite surfaces, always associated with sphalerite although often cover adjacent Fe and Cu phosphates

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C continued	sulphates	fibrous crystals (Cu) and euhedral rosettes	Cu and Fe sulphates	rare isolated precipitates
Column D	Fe phosphates identical to column C except generally richer in Zn and S, also poorly developed on ~10 % of sphalerite surfaces; tetrahedrite not observed			
	Cu phosphates identical to column C except in greater abundance and without incorporated Si, Al or S			
	Pb phosphate	coating of fine acicular pincushions; larger prismatic and leafy crystals; amorphous to scaly coating with desiccation cracks; amorphous spheroids.	Pb phosphate	acicular phases cover 99 % of galena surfaces; large crystals on ~10 % of galena and adjacent minerals; coatings and spheroids rare
	Zn phosphate	radial flow-like agglomerations and rosettes of very fine-grained (100 nm x 10 nm) crystals; scattered large (200 μm x 100 μm) prismatic crystals; amorphous spheroids	Zn-K phosphate; spheroids contain S	cover ~30 % of sphalerite surfaces; spheroids rare; all phases usually associated with sphalerite, some isolated prisms found on grains without sphalerite
	sulphates	euhedral rosettes (Cu, Fe); botryoidal, fibrous (Cu) and prismatic (Pb) crystals	Cu, Pb and Fe sulphates	associated with well-coated grains; Cu occasionally extensive; Pb and Fe rare isolated precipitates

Coating stage post $Ca(OH)_2$ addition

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Fe phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except no incorporated Zn was detected			
	Cu phosphate	spherical rosettes up to 20 μm diameter, often coalesced into a coating of radial splays; rare acicular crystals	Cu-K-Ca phosphate	heterogeneous coating 100% of some grains, abundant on chalcopyrite, sparse on quartz and tetrahedrite
	Pb phosphate	coating of fine (<1 μm) acicular pincushions; occasional large bladed crystals (30 μm x 10 μm)	pincushions Pb$\pm$Ca-K phosphate; large crystals Pb-Ca phosphate	acicular phases cover 100 % of galena surfaces; large crystals rarely on and adjacent to galena
	Ca phosphate	fine-grained granular agglomerations	Ca$\pm$K phosphate	rare precipitates
	sulphates	euhedral rosettes and botryoidal agglomerates (Cu); acicular (Cu-K) and prismatic (Ca) crystals	Cu, Cu-K, Ca (gypsum) sulphates	rare precipitates; Cu sulphates more common and associated with well-coated grains
Column B	Fe phosphate	amorphous coating with desiccation cracks, usually thin (<1 μm), occasionally granular and poorly-coalesced, especially when Ca, K or Al-rich	Fe-K$\pm$Ca-Cu-Al-(Si-S) phosphate	thin coating on ~75 % of chalcopyrite surfaces, one pyrite grain poorly-coated

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column B continued	Cu phosphate	spherical rosettes up to 20 µm diameter, often coalesced into a coating of radial splays; more rounded balls when substantial Si or S incorporated	Cu-K-Ca$\pm$S-Si phosphate; rare Cu phosphate	heterogeneous coating 100% of some grains, abundant on chalcopyrite, sparse on quartz and tetrahedrite
	Pb phosphate	coating of fine (<1 µm) acicular pincushions (Pb$\pm$Ca), spheroids and botryoids (Pb-Ca); large bladed (Pb), prismatic (Pb$\pm$Ca) and acicular crystals (Pb) (up to 100 µm x 10 µm)	Pb$\pm$Ca phosphate	acicular and botryoidal phases cover 100 % of galena surfaces; large crystals cover up to 10 % of coated galena; spheroids and acicular crystals rare
	Zn phosphate	radial flow-like agglomerations of very fine-grained (100 nm x 10 nm) crystals (Zn-Ca); large (100 µm x 50 µm) prismatic crystals (Zn-K)	Zn-Ca phosphate; Zn-K phosphate	cover <5 % of sphalerite surfaces; prisms rare, associated with sphalerite
	Ca phosphate	fine-grained granular and flaky clay-like agglomerations	Ca$\pm$K phosphate	rare precipitates
	sulphates	euhedral rosettes and botryoidal agglomerates (Cu); prismatic (Ca-K), (Pb-K-Ca) crystals	Cu, Ca-K, Pb-K-Ca sulphates	rare precipitates; Cu sulphates more common and associated with well-coated grains
Column C	Fe phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except incorporated Pb was detected occasionally and rare acicular Fe-K phosphate crystals were observed; thin coatings also observed on pyrite and bournonite; no coating observed on tetrahedrite			

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C continued	Cu phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except that Ca was always incorporated and that Si, Fe and Al were not detected; when significant S was incorporated the phase formed a very fine precipitate			
	Pb phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except for the presence of common acicular pincushions and granular coats of Pb-Ca-K phosphate and rare granular Pb-Al phosphate precipitates			
	Zn phosphate	radial flow-like agglomerations of very fine-grained (100 nm x 10 nm) crystals (Zn-K-S); scattered large (200 μm x 30 μm) prismatic crystals (Zn-K); botryoidal agglomerates and euhedral rosettes (Zn-Ca)	Zn-K±S phosphate; Zn-Ca phosphate	cover ~50 % of sphalerite surfaces, always associated with sphalerite although often cover adjacent Fe and Cu phosphates
	Ca phosphate	fine-grained granular agglomerations	Ca±K phosphate	rare precipitates
	sulphates	euhedral rosettes and botryoidal agglomerates (Cu±K); prismatic crystals (Pb-K)	Cu±K, Pb-K sulphates	rare precipitates; Cu sulphates more common and associated with well-coated grains
Column D	Fe phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except generally richer in Cu, poorer in Zn and S and with occasional incorporated Ca; tetrahedrite uncoated			
	Cu phosphate phase abundance, morphology and chemistry identical to that observed before $Ca(OH)_2$ addition except that Ca was always incorporated			

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column D continued	Pb phosphate	coating of fine acicular pincushions (Pb); larger prismatic (30 µm x 10 µm) and acicular (90 µm x 5 µm) crystals(Pb); fine (<1 µm) granular agglomerations (Pb-Ca±Cu-K); rounded amorphous balls (Pb±Ca-Zn)	Pb phosphate; Pb-K phosphate; Pb-Ca±Cu-(K-Zn) phosphate	acicular phases cover 99 % of galena surfaces; large crystals on ~10 % of galena and adjacent minerals including anglesite
	Zn phosphate	acicular splays (200 µm x 3 µm) (Zn±K); large bladed crystals (300 µm x 50 µm) (Zn±Ca-K); amorphous agglomerates (Zn-Ca)	Zn± K phosphate; Zn-Ca±K phosphate	heterogeneous, usually rare precipitates, not closely associated with sphalerite
	sulphates	euhedral rosettes; botryoidal crystals	Cu sulphates	extensively developed on well-coated grains

Dissolution stage

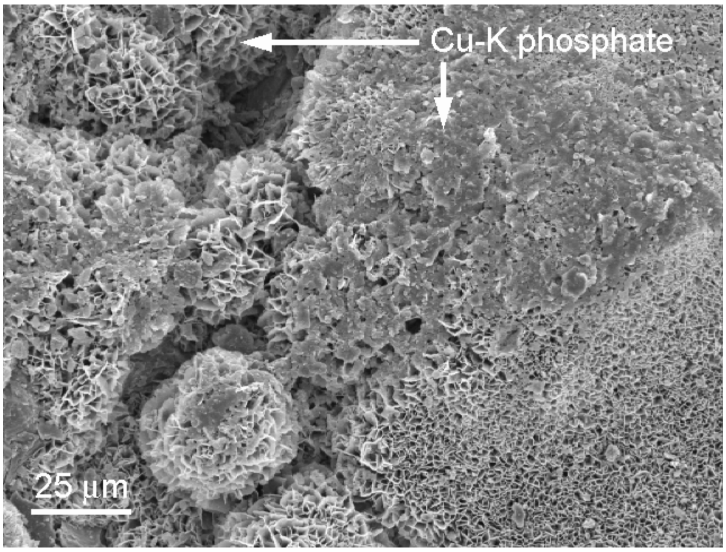
Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Fe phosphate	amorphous coating with desiccation cracks, variable thickness; occasional disaggregated rosettes are possibly slightly developed coating	Fe-K phosphate	thin coating on ~75 % of chalcopyrite surfaces, ~25 % arsenopyrite surfaces; rosettes on one tetrahedrite grain
	Cu phosphate	spherical rosettes up to 20 µm diameter coalesced into a coating of radial splays	Cu-Ca-K phosphate	heterogeneous, coat 95 % of grains where observed, absent otherwise
	Pb phosphate	coating of fine (<1 µm) acicular pincushions (Pb); botryoidal crust (Pb-Ca); fine wispy precipitates (Pb-K)	Pb phosphate; Pb-Ca phosphate; Pb-K phosphate	acicular phases and crusts cover 100 % of galena surfaces, wispy precipitates rare
	Ca phosphate	fine-grained granular agglomerations	Ca phosphate	rare precipitates
	Zn phosphate	bladed crystals	Zn phosphate	rare precipitates
	sulphate phases identical to those observed after $Ca(OH)_2$ addition except no Cu-K sulphates were observed.			
Column B	Fe phosphates identical in chemistry and morphology to that observed after $Ca(OH)_2$ addition except that no incorporated Al, Ca, Cu, Si or S was detected, pyrite was uncoated and stannite was ~50 % thinly coated			
	Cu phosphates identical in chemistry, morphology and abundance to those observed in column A after the dissolution stage			

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column B continued	Pb phosphate	coalescences of fine (<1 µm) acicular pincushions (Pb±Ca, Cu); flow-like agglomerations, spheroids and rosettes (Pb); large bladed (Pb), prismatic (Pb +/- Ca) and acicular crystals (Pb-Ca) (up to 100 µm x 8 µm)	Pb±Ca phosphate; Pb-Cu phosphate	acicular phases cover 100 % of galena surfaces; large crystals cover up to 10 % of coated galena; spheroids and acicular crystals rare
	Zn phosphate	bladed (Zn) and tabular (Zn-Ca) crystals; flow-like agglomerations of acicular crystals (Zn-Cu); some tabular crystals show evidence of corrosion	Zn±Ca, Cu phosphate	isolated precipitates, usually associated with sphalerite
	Ca phosphate	fine-grained granular agglomerations	Ca phosphate	rare precipitates on clays and Fe oxides only
	sulphates, arsenates	euhedral rosettes (Cu, Ca, Fe); botryoidal agglomerates (Cu), prisms, platelets, amorphous coverings (Pb); dustings of fine (<1 µm) crystals (Fe-As)	Cu, Ca (gypsum), Pb, Fe, Zn sulphates; Fe-arsenate (scorodite ?)	Cu and Pb sulphates common and associated with well-coated grains; other phases rare precipitates
Column C	Fe phosphate	amorphous to flaky well-developed thick (~3 µm) coating with desiccation cracks	Fe-K±Cu-Zn-(As) phosphate	coating on ~99 % of chalcopyrite and stannite (thick), 90 % arsenopyrite (thin) surfaces

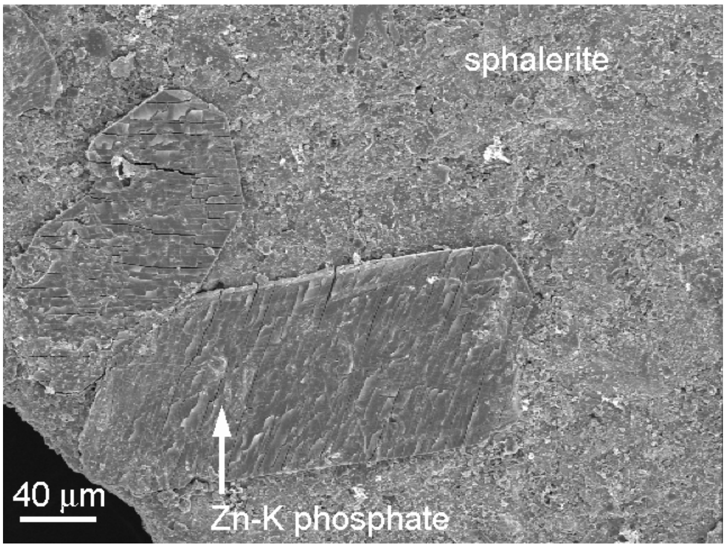
Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C continued	Cu phosphate	spherical rosettes up to 30 μm diameter, often coalesced into a coating of radial splays (Cu-Ca-K); amorphous flow-like coatings and tabular crystals (Cu-Zn)	Cu-Ca-K±(Fe-S) phosphate; Cu-Zn phosphate	heterogeneous coating 100% of some grains, abundant on coated chalcopyrite, scattered on other phases; Cu-Zn phases on well-coated grains only
	Pb phosphate	coating of fine acicular pincushions	Pb±Ca phosphate	acicular phases cover 100 % of galena surfaces
	Zn phosphate	radial flow-like agglomerations of very fine-grained (100 nm x 10 nm) crystals (Zn-K); scattered large (150 μm x 30 μm) tabular crystals, rosettes (Zn±K); blocky prisms (40 μm x 20 μm) and acicular pincushions (Zn-Ca); some tabular and blocky crystals show evidence of corrosion	Zn phosphate; Zn-K phosphate; Zn-Ca phosphate	cover ~50 % of sphalerite surfaces, always associated with sphalerite
	K phosphate	platy irregular coating	K-(Cu) phosphate	rare coating on tetrahedrite
	sulphates	euhedral rosettes, dendrites and botryoidal agglomerates (Cu); prismatic crystals (Zn)	Cu, Zn sulphates	Cu sulphates common and associated with well-coated grains, Zn sulphates rare precipitates
Column D	Fe phosphate	amorphous to flaky well-developed thick (~3 μm) coating with desiccation cracks	Fe-K±Ca phosphate	coating on ~99 % of chalcopyrite and stannite (thin), 50 % arsenopyrite (thin) surfaces

Column	Major phases	Habit and morphology	Chemistry	Abundance
	Cu phosphates identical in chemistry and morphology to that observed after $Ca(OH)_2$ addition except significant Fe was often incorporated; coalesced Cu phosphate rosette coats occasionally graded into Cu sulphate coats			
	Pb phosphate	coating of fine acicular pincushions; larger prismatic (40 μm x 5 μm) crystals; botryoids; amygdales	Pb phosphate	acicular phases cover 99 % of galena surfaces; large crystals on ~10 % of galena and adjacent minerals including anglesite
	Zn phosphate	acicular splays (200 μm x 3 μm) and large bladed crystals (300 μm x 50 μm) (Zn); bean-shaped platelets (Zn-Ca)	Zn phosphate; Zn-Ca phosphate	heterogeneous development, precipitates common on well-coated grains
	sulphates	euhedral rosettes; fine-grained coatings; botryoids and fibrous (Cu), acicular (Pb-Fe) and prismatic (Ca) crystals	Cu, Pb-Fe and Ca sulphates	Cu sulphates extensively developed on well-coated grains, other phases rare precipitates

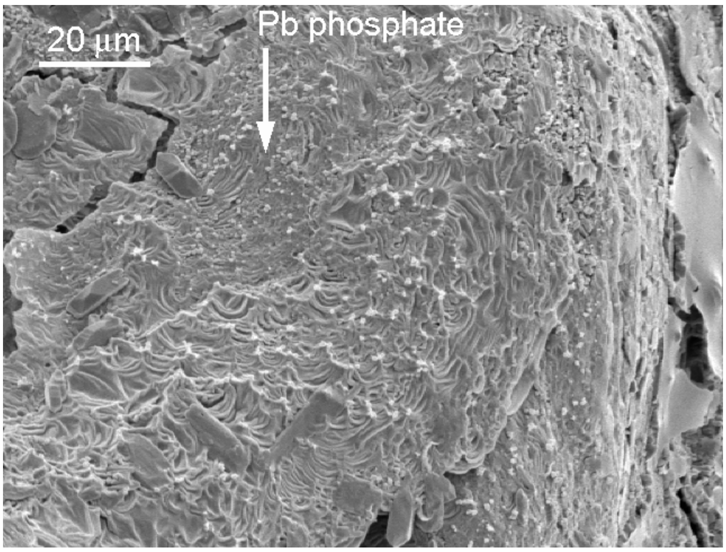
Additional SEM micrographs, experiment 2



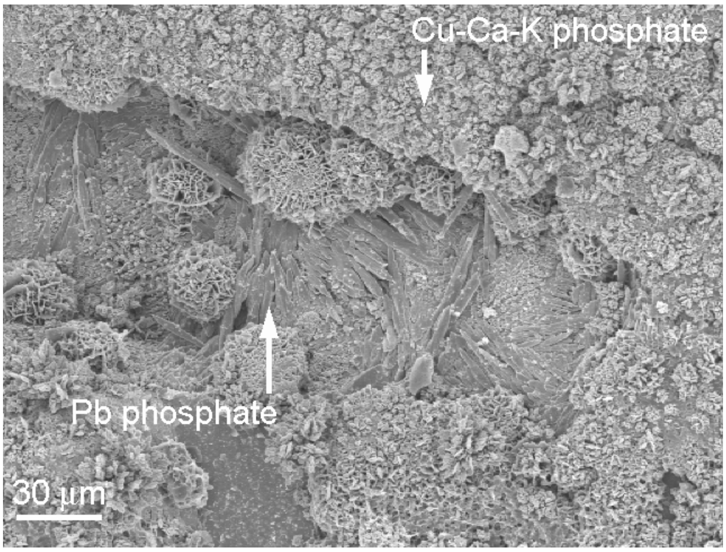
Detail of coalescence of Cu-K phosphate rosettes, column A, post-coating stage, pre-$Ca(OH)_2$ addition.



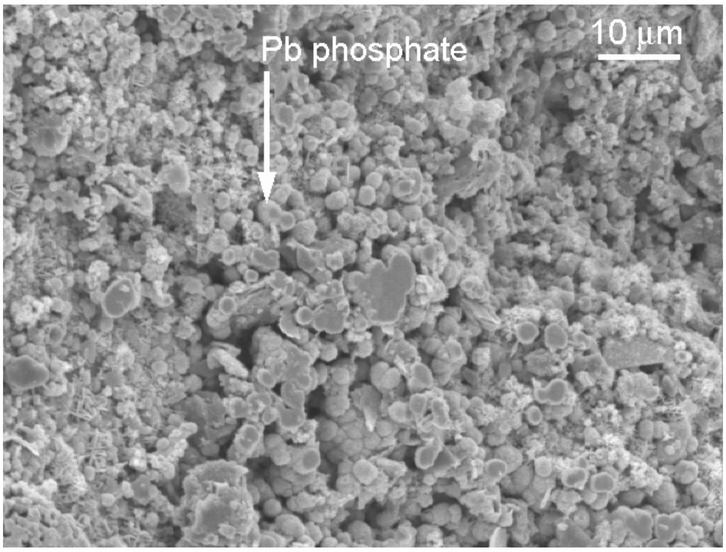
Large prismatic Zn-K phosphate crystals precipitated on otherwise uncoated sphalerite, column A, post-coating stage, pre-$Ca(OH)_2$ addition.



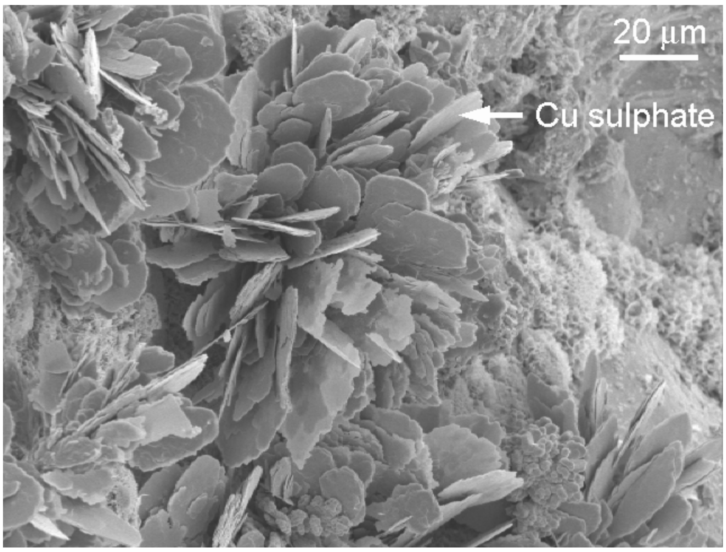
Scaly coating of Pb phosphate on galena, column D, post-coating stage, pre-$Ca(OH)_2$ addition.



Tabular Pb phosphate crystals covered by calescence of Cu-Ca-K phosphate rosettes, column B post-dissolution stage.



Granular to botyroidal Pb phosphates precipitated on galena, column D post-dissolution stage.



Cu sulphate rosettes, column D post-dissolution stage.

Appendix B7

SEM observations, experiment 3

Coating stage

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Mn phosphate	generally thick (>3 µm) amorphous coatings (Fe or Pb); precipitates of flaky, globular, granular and fine-grained rosette (Cu) aggregates, all usually with desiccation cracks.	Mn-K±Ca, Cu, Fe, Pb, S, Zn phosphate, related to substrate, eg Mn-K-Pb phosphate on galena, Mn-K-Fe phosphate on chalcopyrite	coating on >99% chalcopyrite, galena, stannite, >75 % sphalerite, >50 % tetrahedrite; amorphous coatings only observed on chalcopyrite and galena; arsenopyrite and pyrite uncoated
	Cu phosphate	spherical rosettes up to 100 µm diameter, occasionally coalesced into a covering of radial splays; amorphous coating with desiccation cracks; granular precipitates (Cu)	Cu-K±Ca phosphate; Cu phosphate	rosettes heterogeneous, cover 90 % of some coated grains, absent on other minerals; amorphous Cu phosphate rare coating
	Fe phosphate	thick (~10 µm) amorphous coating with desiccation cracks, usually covered in turn by granular Mn phosphate	Fe-K phosphate	rare coating on chalcopyrite
	Pb phosphate	large (100 µm x 30 µm) tabular and acicular radial splays and isolated crystals	Pb±Ca-K phosphate	rare scattered precipitates on coated galena

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A continued	Cu sulphate	hexagonal rosettes (10 µm diameter) and prismatic crystals	Cu sulphate	sulphate rosettes associated with coalescences of Cu phosphate rosettes cover <5% of grains; prisms rare precipitates
Column B	Mn phosphate	chemistry, morphology and abundance of coatings generally identical to those in column A except amorphous Mn-K-Fe phosphate coats more abundant and globular/granular/rosette phases less abundant; tetrahedrite less well-coated; globular Mn-K phosphate often on quartz and clays demonstrating its precipitate nature		
	Cu phosphate	chemistry, morphology and abundance of coatings generally identical to those in column A except rosettes often contain significant Mn, rare amorphous coatings also contain K and occasional rosettes are pure Cu phosphate		
	Pb phosphate	fine-grained (0.5 µm x 5 µm) acicular pincushions (Pb-Ca); granular precipitates (Pb-Ca); bi-pyramidal crystal (Pb); euhedral booklets (Pb)	Pb$\pm$Ca phosphate	pincushions cover ~5 % of coated galena surfaces; other phases scattered precipitates
	K-Ca phosphate	granular precipitates; amorphous coating	K-Ca$\pm$S phosphate	rare coats and precipitates on tetrahedrite, chalcopyrite, clays and quartz
	sulphates	Cu sulphates identical to those observed in column A; very rare Pb-Al-Cu and Fe-Zn-Cu sulphates also observed		
Column C	Cu phosphate	spherical rosettes up to 10 µm diameter often coalesced into a coating of radial splays	Cu-Ca-K$\pm$(S, Fe) phosphate	heterogeneous development, cover 100 % of some grains, associated with chalcopyrite or Cu sulphate substrates

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C continued	Pb phosphate	amorphous coating (Pb-Ca-K); acicular pincushions (Pb$\pm$Ca); large (100 µm x 5 µm) acicular crystals (Pb-Ca); radial splays (Pb-K); rosettes(Pb-Ca-K)	Pb phosphate; Pb$\pm$Ca-K (Zn) phosphate;	pincushions cover ~75 % of galena surfaces; other phases common precipitates on coated galena, rare precipitates on other minerals
	Fe phosphate	amorphous coating with desiccation cracks	Fe-K-Cu phosphate	thin coating on <50 % of chalcopyrite
	Ca phosphate	granular and globular precipitates; amorphous coats with desiccation cracks	Ca+K phosphate	scattered precipitates and coats covering <10 % of chalcopyrite, tetrahedrite, other phosphate phases, clays and quartz
	sulphates	rosettes, fibres, dendrites (Cu); prisms (K-Ca)	Cu, K-Ca sulphates	scattered precipitates, extensive on well-coated grains covering ~5 % of surfaces
Column E	Mn phosphate	generally thick (>5 µm) coatings of granular (Mn-rich), amorphous (Fe-rich), rosette (Cu-rich) aggregates often with desiccation cracks; amorphous coat often covered by granular or rosette phase; granular precipitates at top of column cement grains together forming induration 3 cm thick	Mn-K-Ca$\pm$Fe, Cu, Pb, (Zn, As) phosphate, metal related to substrate	coating on ~99 % chalcopyrite, galena, >50 % sphalerite; pyrite uncoated, tetrahedrite and arsenopyrite not observed – possibly obscured by phosphates; precipitates on all phases including quartz

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column E continued	Cu phosphate	spherical rosettes up to 100 µm diameter, often coalesced into a coating of radial splays	Cu-Ca –K$\underline{+}$ S phosphate	rosettes coat 50 % of some grains, preferentially associated with grains with well-developed granular and amorphous coatings
	Pb phosphate	acicular pincushions (Pb); granular precipitates (Pb-Ca)	Pb phosphate; Pb-Ca phosphate	scattered precipitates on coated galena
	Ca phosphate	granular precipitates; large (100 µm x 50 µm) euhedral prisms and radial splays	Ca$\underline{+}$K phosphate	scattered precipitates on all phases, prisms and splays often associated with relict Trifos granules
	sulphates	rosettes, dendrites(Cu); prisms (Ca)	Ca, Cu sulphates	scattered precipitates preferentially on well-coated grains
Column F	Mn phosphate identical in morphology and chemistry to the phases observed in column E except richer in Ca and significant Al, S and Si often incorporated into coatings; amorphous and rosette forms less common and granular coatings more abundant though often only thin dustings on grains; induration at top of column thinner (~1 cm) and less well-developed			
	Cu phosphate	identical to the phases observed in column E		
	Ca phosphate	identical to the phases observed in column E though more common, cover <1 % of grains; large euhedral prisms cement some grains together in the induration at the top of the column		
	sulphates	rosettes	Cu sulphate	heterogeneously scattered precipitates covering up to 10 % of well-coated grains

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column G	Ca phosphate	thin (<1 µm) granular to amorphous aggregates often with desiccation cracks; granular precipitates at top of column cemented together grains forming thin (1 cm) fragile induration	Ca±Cu, Fe, Al, S, Pb, Cl (As, Zn) phosphate, related to substrate; Ca phosphate	heterogeneous covering >80 % chalcopyrite (Ca-Fe-Al), ~50 % galena (Ca-Pb) and arsenopyrite (Ca-Fe-As), ~40 % tetrahedrite (Ca-Cu-Fe); sphalerite and bournonite uncoated
	Cu phosphate	spherical rosettes and botryoids (Fe, Cl) up to 70 µm in diameter, usually coalesced into coverings of radial splays	Cu-Ca±Fe, Cl phosphate	heterogeneous development, cover 80 % of some grains
	sulphates	rosettes	Cu sulphate	scattered precipitates usually associated with Cu phosphate rosette coalescences

Dissolution stage

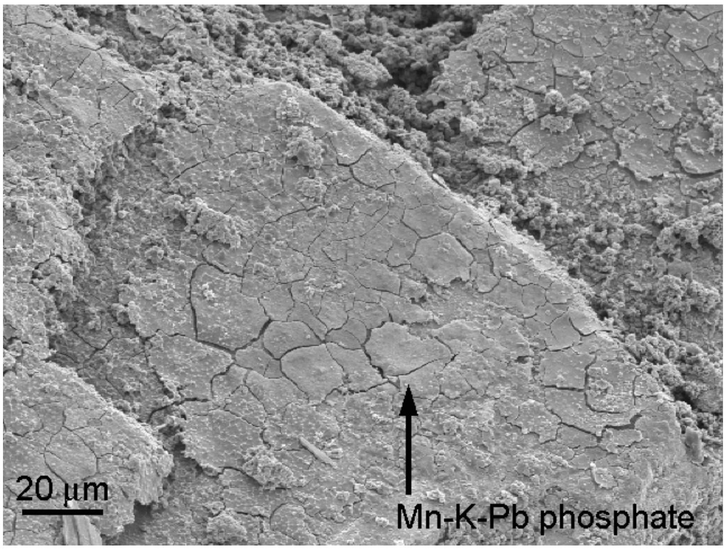
Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Mn phosphate	identical in morphology and chemistry to those observed in column A post-coating stage material except for presence of scattered prismatic Mn$\pm$Zn phosphate crystals and radial splays; flaky, granular and globular phases less abundant; amorphous coatings appear more abundant and observed heterogeneously on all sulphides (including tetrahedrite, pyrite, sphalerite and arsenopyrite); precipitates often observed on quartz and clays		
	Cu phosphate	spherical rosettes always coalesced into coatings of radial splays, more Mn – more granular; rare evidence of corrosion	Cu-Mn$\pm$Ca-K, Fe, (S, Cl) phosphate	heterogeneous, extensive where present (covers ~90 % of grain); no scattered precipitates
	Pb phosphate	coalesced fine-grained (<1 µm) acicular pincushions; euhedral (25 µm x 5 µm) prisms	Pb phosphate	rare precipitates on or adjacent to coated galena
	Cu sulphates	identical to sulphates observed in column A post-coating stage material except no prismatic crystals were observed		
Column B	Mn phosphate	identical in morphology and chemistry to those observed in column B post-coating stage material except for presence of scattered euhedral radial splays of Mn$\pm$Ca phosphate and rare Mn-Zn phosphate prisms; globular/granular phases less abundant; amorphous coats observed on sphalerite, arsenopyrite and pyrite; Fe-rich amorphous coats rare		
	Cu phosphate	identical in morphology, chemistry and abundance to those observed in column B post-coating stage material		
	Pb phosphate	fine-grained (0.5 µm x 5 µm) acicular pincushions	Pb-Ca phosphate	cover ~1 % of coated galena surfaces

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column B continued	sulphates	rosettes up to 50 µm diameter(Cu); fine-grained (2 µm x 0.2 µm) acicular pincushions (K-Mn)	Cu and K-Mn sulphates	rosettes associated with coalescences of Cu phosphate rosettes cover <5% of grains; pincushions rare precipitates
Column C	Cu phosphate	spherical rosettes up to 70 µm diameter often coalesced into a coating of radial splays	Cu-Ca-(K)±Zn, S phosphate	heterogeneous, extensive where observed, associated with Cu sulphate and occasionally chalcopyrite substrates
	Pb phosphate	acicular pincushions; tabular crystals; radial splays; globular agglomerates; botryoids; bean-shaped crystals	Pb±Ca, K, Zn, Cu phosphate	pincushions cover >90 % of galena surfaces, other phases common precipitates on galena, scattered on sphalerite (Zn-rich phases only)
	Zn phosphate	rosettes up to 50 µm diameter; large (50 µm x 10 µm) prisms	Zn-Ca phosphate; Zn phosphate	rare precipitates associated with sphalerite
	Fe phosphate	amorphous coating with desiccation cracks; granular and globular precipitates	Fe-K-Cu phosphate; Fe-K-Ca phosphate	thin coating on ~25 % of chalcopyrite surfaces; precipitates scattered on chalcopyrite and tetrahedrite
	Ca phosphate	granular precipitates	Ca±K phosphate	rare precipitates on all minerals
	sulphates	rosettes, radial splays (Cu±Ca, Zn); globular agglomerates (Fe); subhedral prisms and amorphous precipitates (Pb±Cu)	Cu±Ca,Zn; Fe; Pb±Cu, sulphates	Cu and Pb sulphates common precipitates on well-coated grains; Fe sulphates rare precipitates

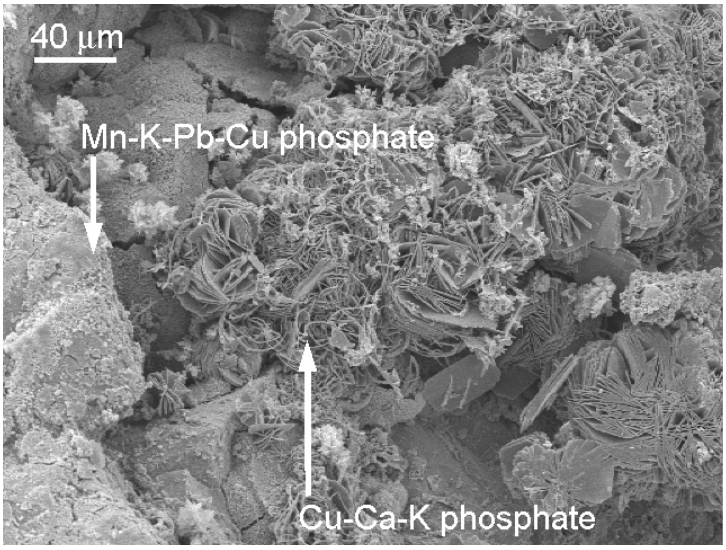
Column	Major phases	Habit and morphology	Chemistry	Abundance
Column E	Mn phosphate	identical to phases observed in column E post-coating stage except richer in Ca and more heterogeneous; chalcopyrite usually well-coated, ~10 % of grains completely uncoated; galena 99 % coated; tetrahedrite ~30 % coated; arsenopyrite not observed; induration persisted through dissolution stage		
	Cu phosphate	spherical rosettes of ~10 μm diameter, often coalesced into a coating of radial splays; Mn-rich rosettes more granular	Cu-Ca$\pm$Mn phosphate	extensive where observed, cover 50 % of some grains; Cu sulphates form preferential substrate, occasionally on quartz
	Pb phosphate	acicular pincushions	Pb-(Ca-Mn) phosphate	scattered precipitates on coated galena
	Ca phosphate	granular precipitates	Ca$\pm$Mn phosphate	scattered precipitates on all phases, appears more abundant than in columns post-coating stage
	sulphates	rosettes and dendrites (Cu); prisms and fibres (Ca);	Cu, Ca sulphates	scattered precipitates preferentially on well-coated grains; Ca sulphates more abundant than in coated columns and often associated with relict Trifos granules
Column F	Mn phosphate	identical to phases observed in column F post-coating stage; tetrahedrite also ~20 % coated; amorphous coatings appear abundant and granular precipitates less abundant		
	Cu phosphate	identical to phases observed in column E post-dissolution stage except often significant S incorporated		
	Ca phosphate	identical to phases observed in column F post-coating stage except granular precipitates more abundant		

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column F continued	sulphates	identical to phases observed in column E post-dissolution stage except or the presence of botryoidal Cu sulphates and scattered radial splays of prismatic (7 μm x 2 μm) Ca sulphates		
Column G	Ca phosphate	identical in morphology and chemistry to phases observed in column G post-coating stage except for presence of radial splays of large (200 μm x 50 μm) prisms; amorphous phase less abundant; granular precipitates not observed on tetrahedrite; induration appeared degraded		
	Cu phosphate	granular agglomerates (Ca-S rich) grading to euhedral rosettes (Cu-rich), usually forming coalesced coating	Cu-Ca$\pm$S, Fe, (Cl, Al) phosphate	usually extensive where observed and associated with substrate of Cu sulphate, rarely precipitated on quartz
	sulphates	rosettes, botryoids (Cu); prismatic (7 μm x 2 μm) radial splays (Ca)	Cu, Ca sulphates	scattered precipitates; Cu sulphates associated with abundant Cu-Ca phosphates; Ca sulphates commonly precipitated on quartz

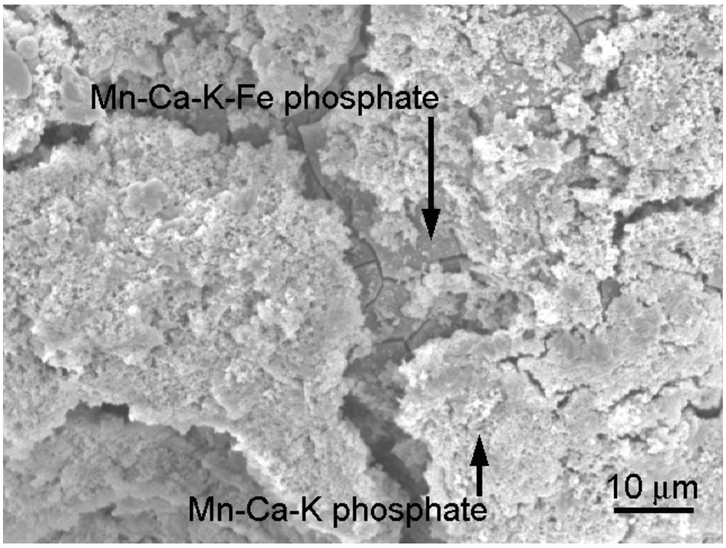
Additional SEM micrographs, experiment 3



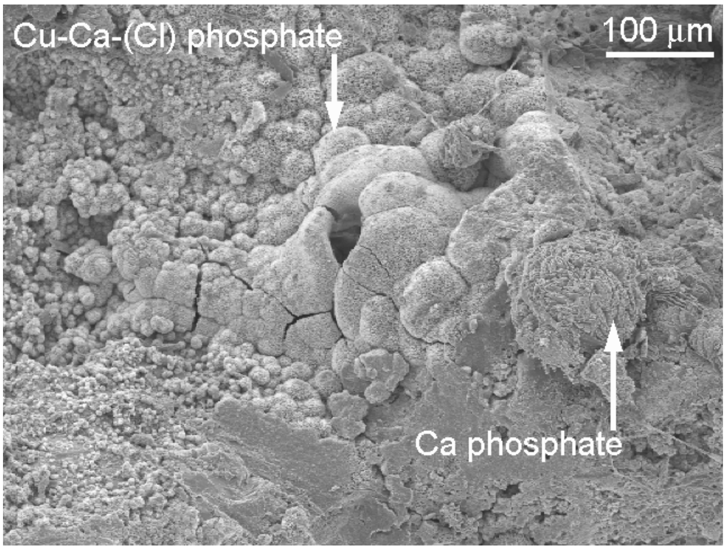
Coating of Mn-K-Pb phosphate on galena showing extensive desiccation cracks, column A post-coating stage.



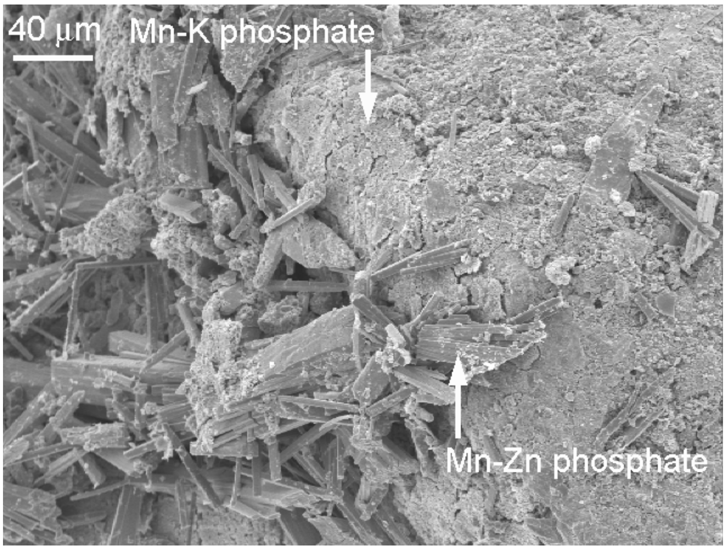
Spherical rosettes of Cu-Ca-K phosphate precipitated on Mn-K-Pb-Cu phosphate coating, column A post-coating stage.



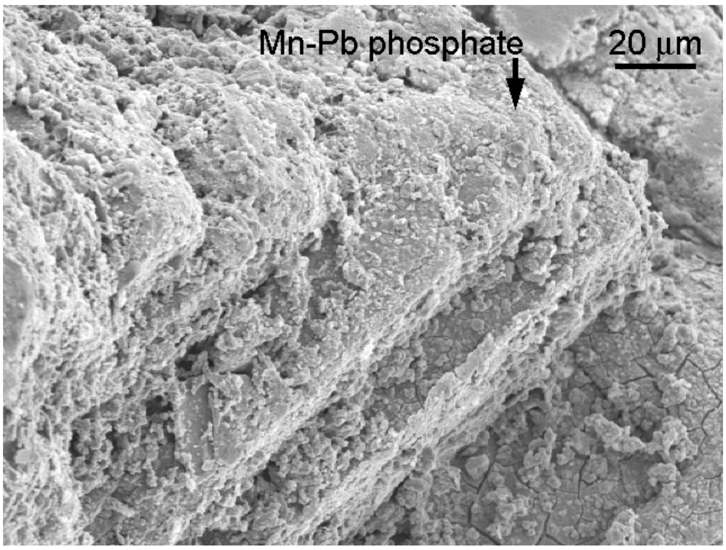
Coating of amorphous Mn-Ca-K-Fe phosphate with extensive desiccation cracks covered by precipitates of Mn-Ca-K phosphate, column F post-coating stage.



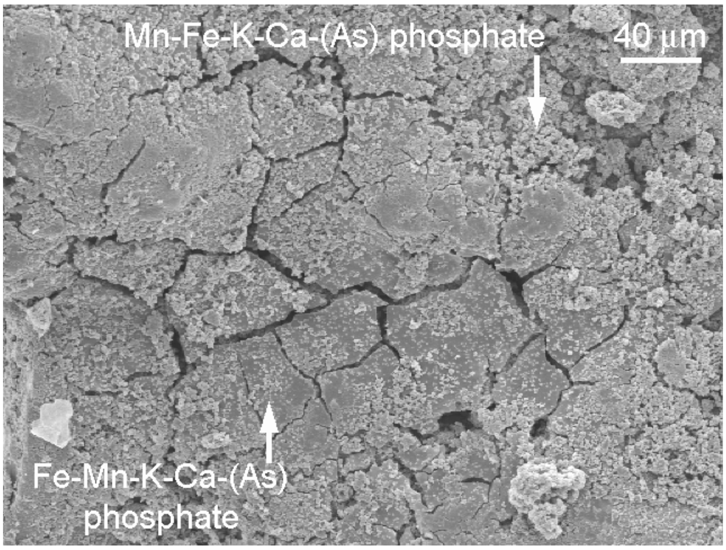
Botryoidal coalescence of Cu-Ca-(Cl) phosphate rosettes precipitated on quartz and chalcopyrite. Spherical Ca phosphate possibly a partially dissolved remnant fertiliser granule, column G post-coating stage.



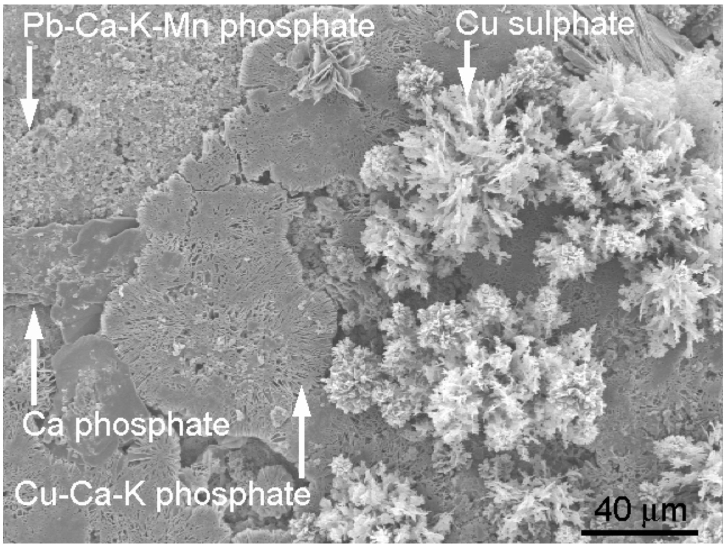
Prismatic Mn-Zn phosphate crystals precipitated on amorphous Mn-K phosphate coating with occasional desiccation cracks, column A post-dissolution stage.



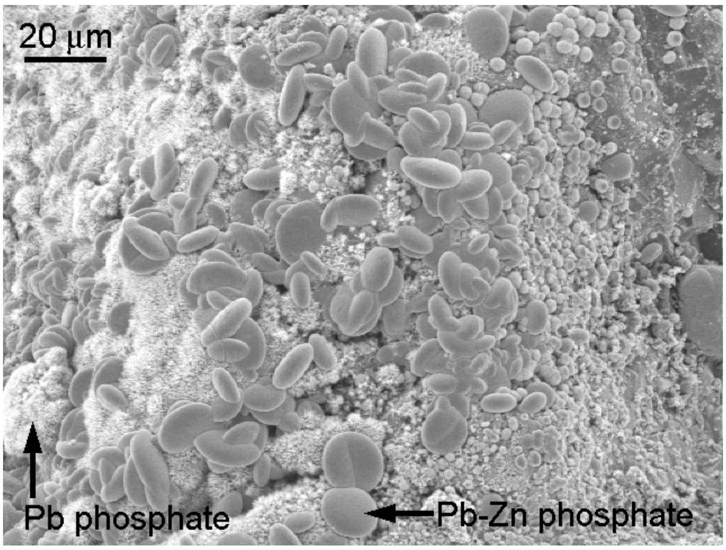
Globular to amorphous Mn-Pb phosphate coating on galena, column A post-dissolution stage.



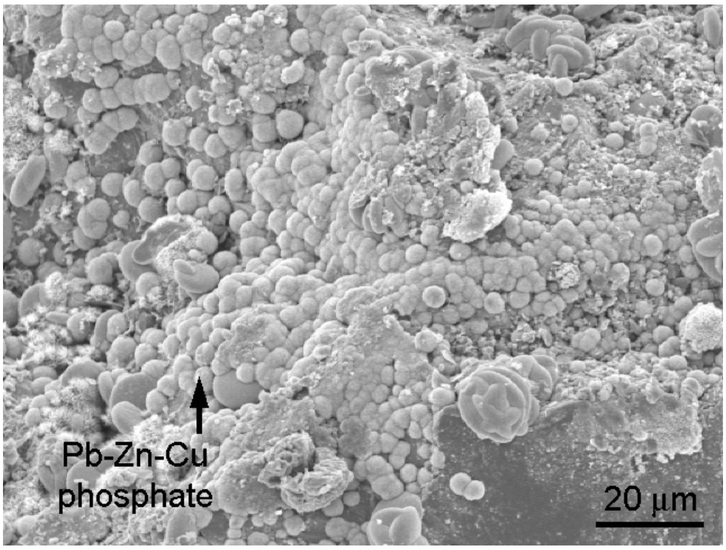
Granular Mn-Fe-Ca-(As) phosphate coating which becomes more amorphous with increasing Fe content, column E post-coating stage.



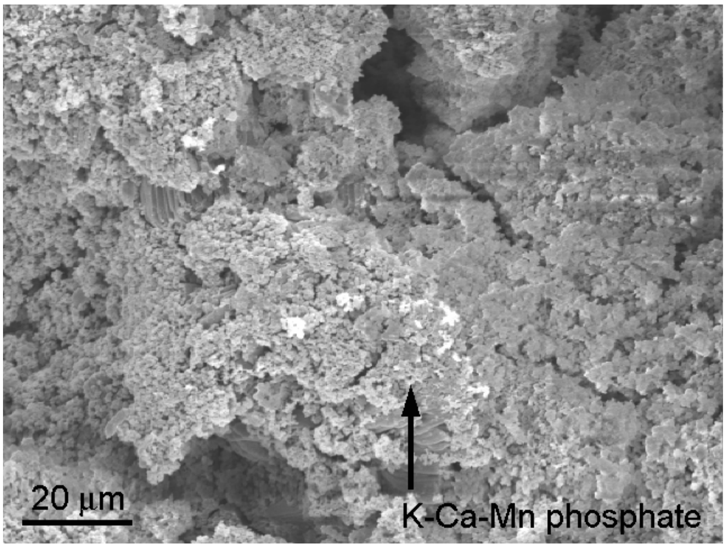
Cu sulphate rosettes precipitated on coalesced Cu-Ca-K phosphate rosettes which are precipitated on prismatic Ca phosphate crystals and Pb-Ca-K-Mn phosphate coating, column E post-coating stage.



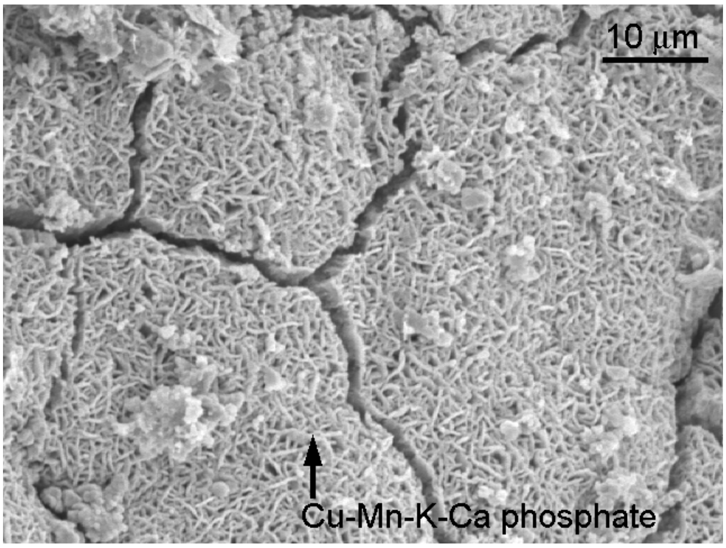
Bean-shaped Pb-Zn phosphate crystals precipitated on acicular Pb phosphate pincushions, column C post-dissolution stage.



Botryoidal Pb-Zn-Cu phosphate precipitates on quartz, column C post-dissolution stage.



Granular K-Ca-Mn phosphate which forms the induration cementing grains together at the top of columns E and F (column E post-dissolution stage).



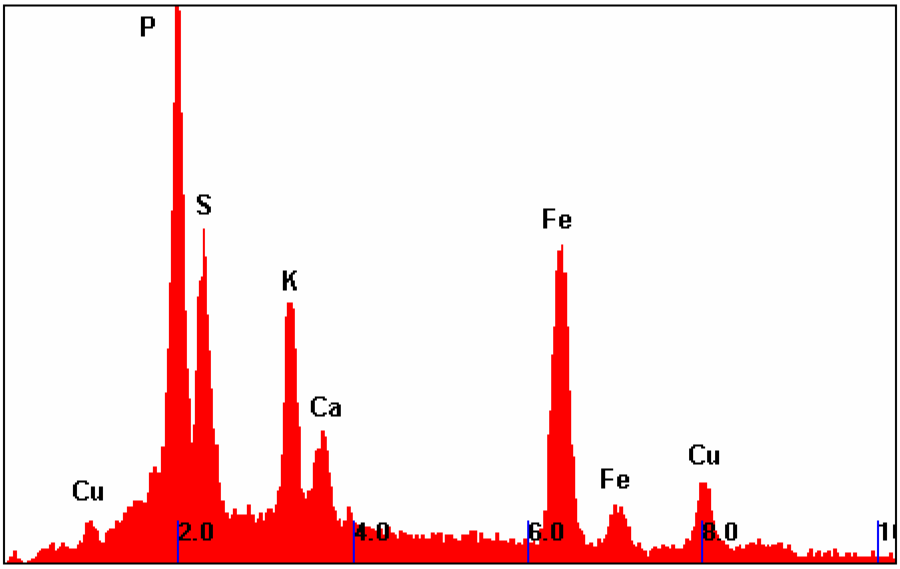
Detail of Cu-Mn-K-Ca phosphate coalescence showing desiccation cracks, column B post-dissolution stage.

Appendix B8

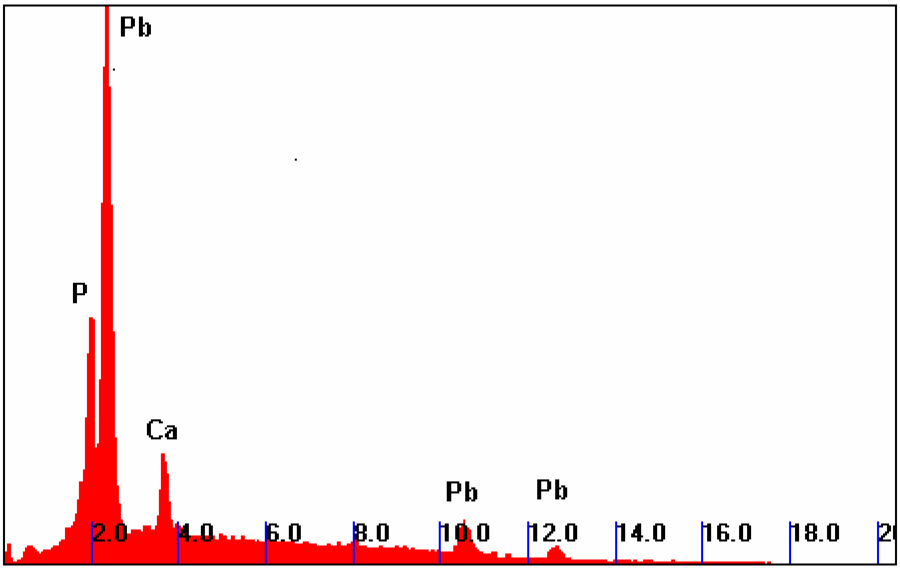
Phosphate coating and precipitate phase characterisation

Representative EDS traces of common phosphate phases formed in the coated columns

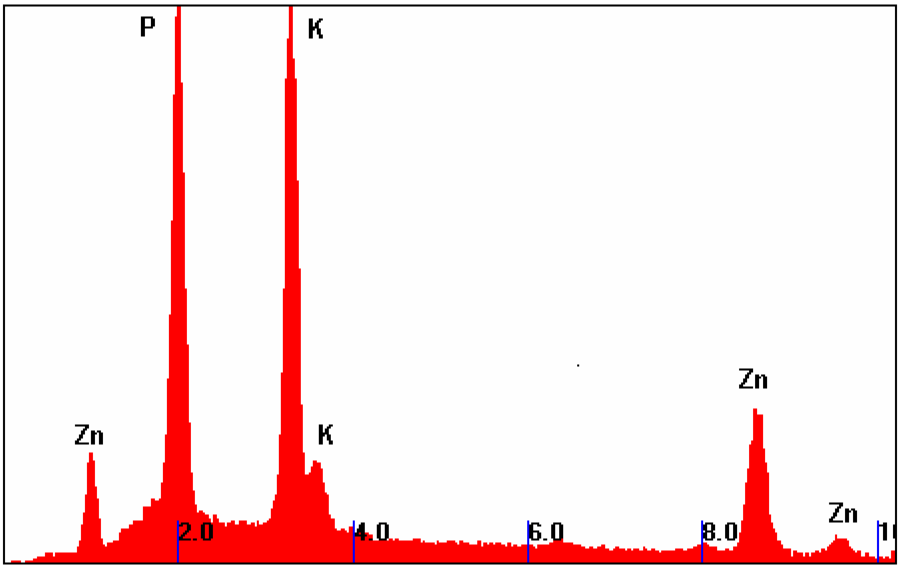
X-axis in keV.



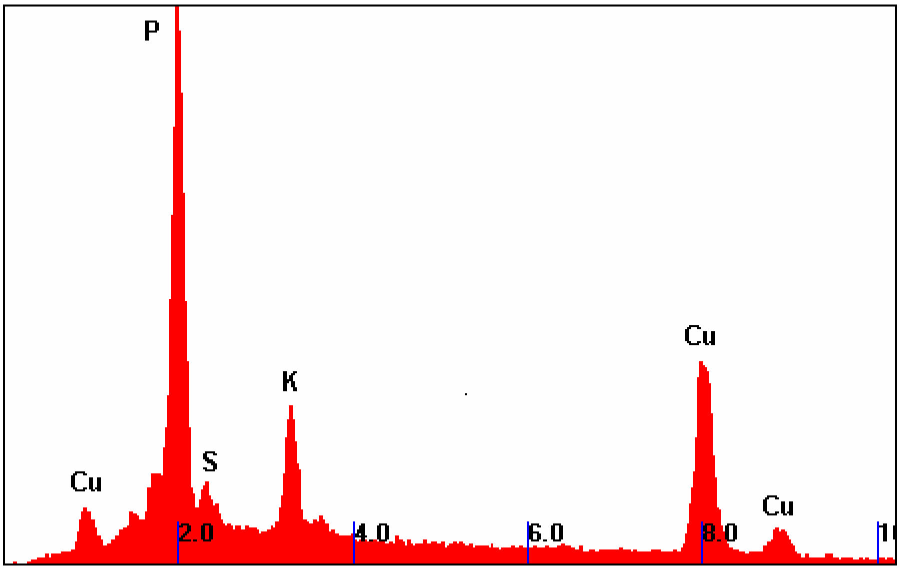
Fe-K-Ca-(Cu?) coating on chalcopyrite, experiment 1 post-coating stage. Similar to material shown in Fig 3.4a,b,d.



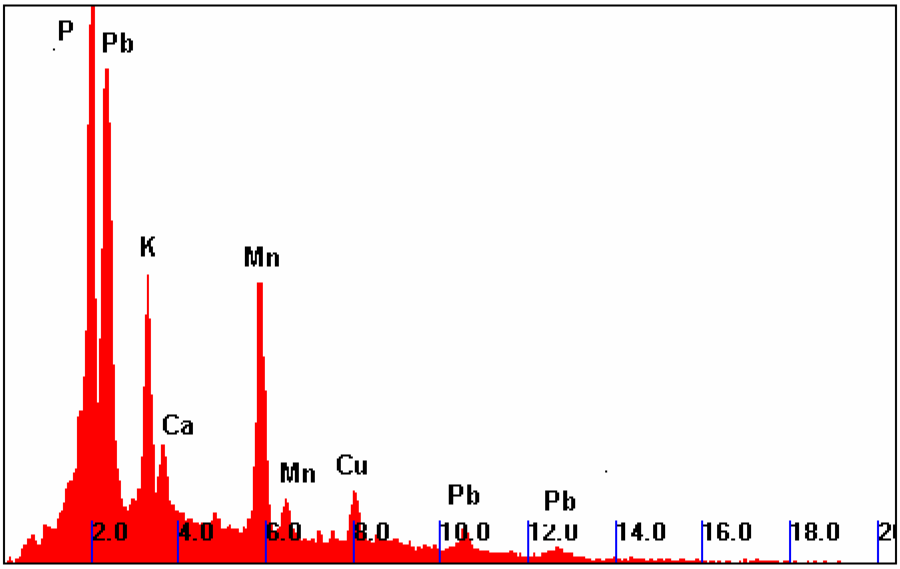
Pb-Ca phosphate, column D, experiment 1 post-coating stage.



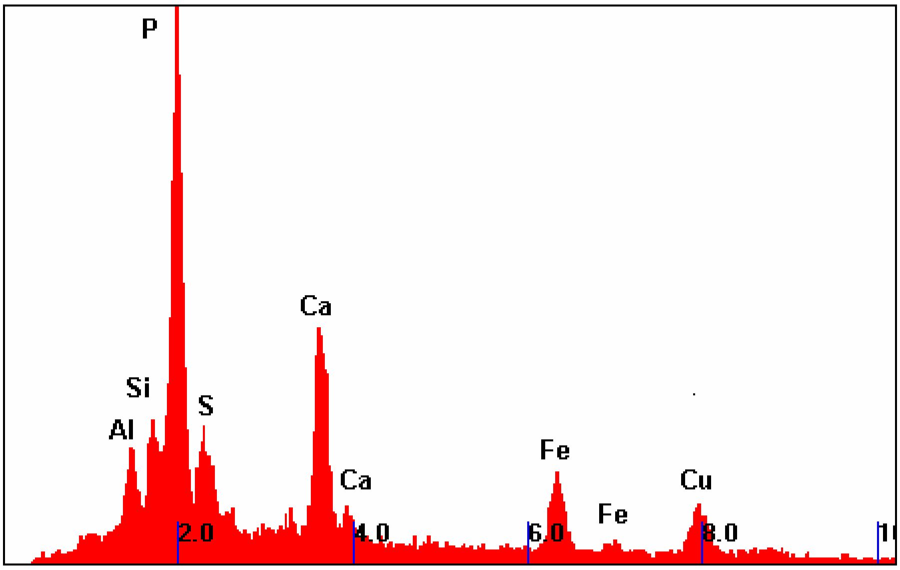
Flow-like Zn-K phosphate, column C, experiment 1. Shown in Fig. 3.4b and appendix B5



Coalescence of Cu-K phosphate rosettes, column A, experiment 2 pre-$Ca(OH)_2$ addition. Note absence of Ca. Shown in Fig. 3.10b

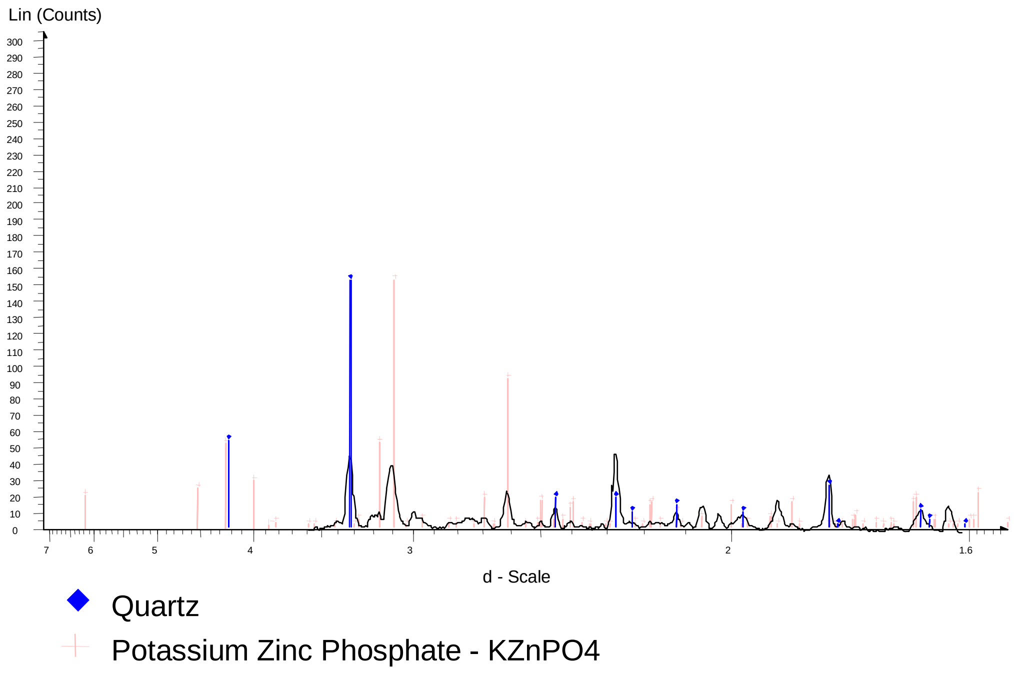


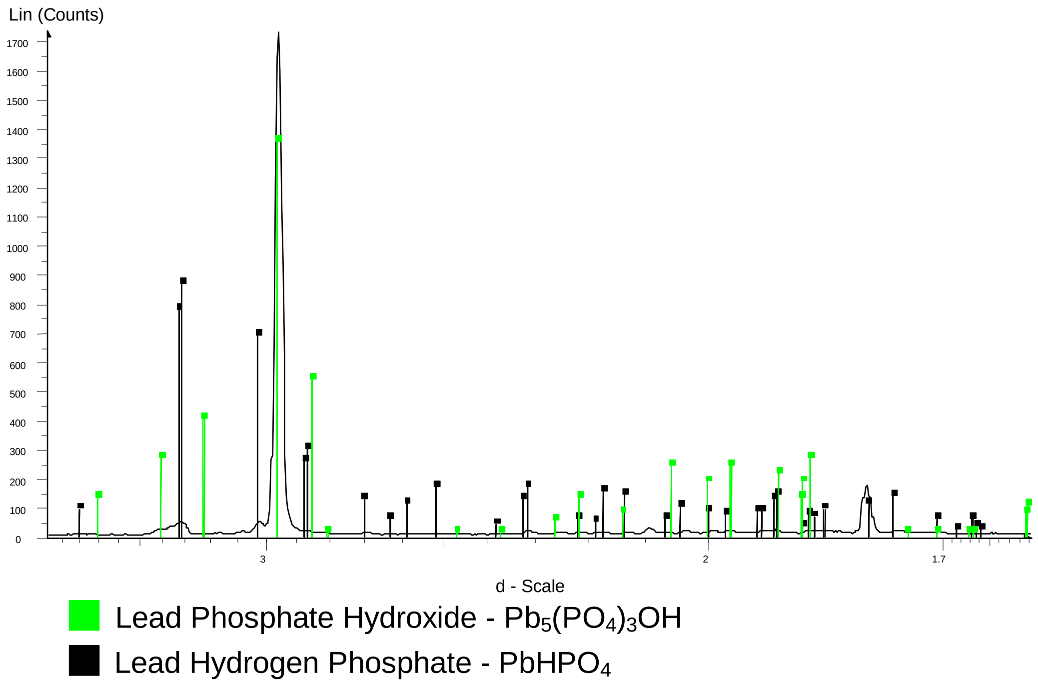
Globular Mn-K-Pb (Ca-Cu) phosphate coating, column A, experiment 3. Similar to material shown in Fig 3.16a.



Granular precipitate of Ca-Fe-Cu-(Si-Al-S) phosphate, column G, experiment 3. Similar to material shown in Fig. 3.16c.

GADDS traces of selected phosphate precipitates





Note: GADDS analyses were performed on only two or three samples. As the technique only reads the surface of the sample crystal not all diffraction peaks may show on each trace (A. Chappell pers comm 2002). This may explain the apparent poor fit for the lead phosphate hydroxide in the above trace. The phases listed above represent the best fit for any phase containing the correct chemistry (known through SEM-EDS).

Appendix B9

Phosphate fertiliser dissolution experiment and characterisation

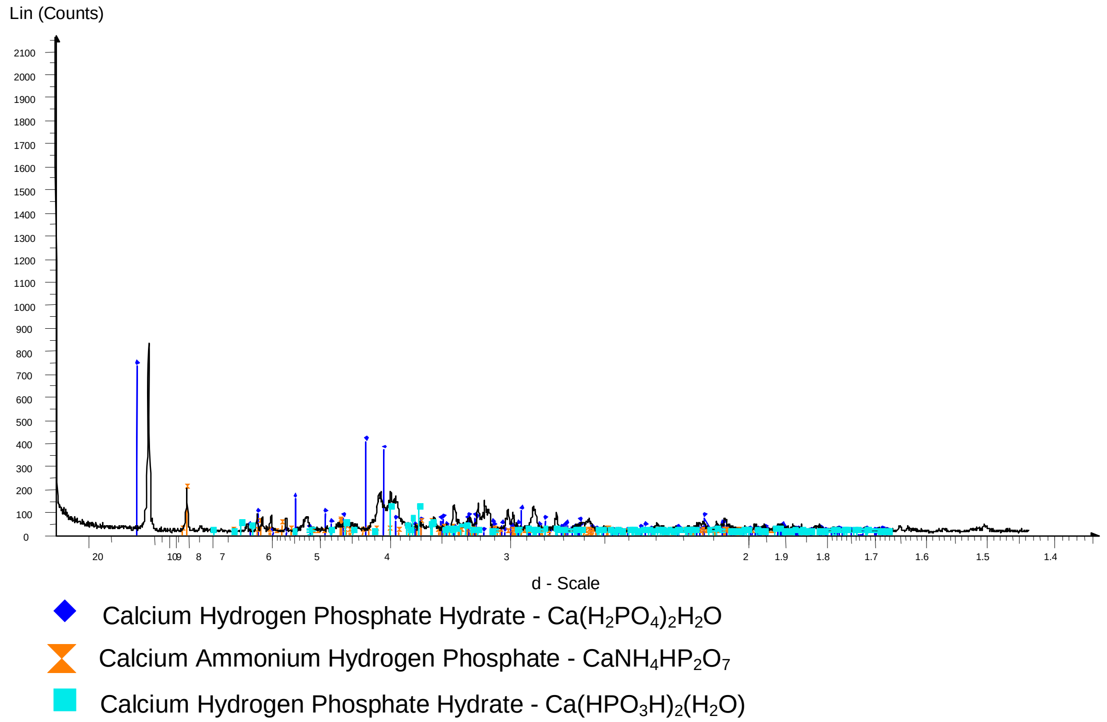
Dissolution experiment methodology

The aim of the dissolution experiment was to determine the chemistry of any impurities released into solution by the dissolution of the fertilisers. Sufficient fertiliser was immersed into 1 litre of distilled water to ensure saturation of the solution was attained. Thus, 500 g of MKP and 100 g of Trifos were each immersed into a beaker containing 1 litre of distilled water which was sealed using plastic food wrap. The beakers were kept at room temperature (25 ^{o}C) for 14 days. 100 ml of solution was then decanted from each beaker and submitted to the AAC, JCU for analysis by ICP-MS. The results give an estimation of the total amount of elemental release through fertiliser dissolution during the coating stage of experiment 3.

Dissolution experiment ICP-MS results

	MKP	Trifos
Ag µg/l	<0.05	1.58
Al mg/l	4.17	42.70
As µg/l	17300.00	385.00
Ca mg/l	7.97	3870.00
Cd µg/l	<0.50	212.00
Cu µg/l	119.00	386.00
Fe mg/l	6.66	101.00
Hg µg/l	<0.50	<0.50
K mg/l	58400.00	249.00
Mg mg/l	3.37	182.00
Mn µg/l	321.00	18800.00
Na mg/l	1310.00	183.00
P mg/l	43300.00	13400.00
Pb µg/l	12.30	<0.05
SO_4^{2-} mg/l	66.80	219.00
Sb µg/l	1010.00	43.20
Si mg/l	2.95	39.30
Zn µg/l	131.00	5630.00

Trifos fertiliser XRD trace



Note: The chemical with the peak closest to that on the trace is the same as the major ingredient listed in the fertiliser by the manufacturer – $Ca(H_2PO_4)_2H_2O$. There has possibly been a shift in the peak trace or the fertiliser chemicals have a slightly different crystallography to the chemical used to create the standard, explaining the poor fit of the XRD trace.