THE CHEMISTRY OF EXPLORATION GEOCHEMISTRY: WHAT'S THAT?

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Things fall down hills…

Fisher's antimony mine, Hillgrove

Bottinoite ($[Ni(H_2O)_6][Sb(OH)_6]_2$) on ullmanite (NiSbS); 6 mm; Dörnberg mine, North Rhine-Westphalia, Germany

- In the supergene zone, insoluble primary sulfides and the like weather to give much more soluble secondary minerals
- They buffer dispersion of elements in the regolith
- They control the extent and intensity of geochemical anomalies

But how do you read this?
That's the chemistry of exploration geochemistry!

- Antimony is a good example to pick to explore this
- Several hundred Sb-bearing primary sulfides and sulfosalts – all essentially insoluble in H_2O – stibnite (Sb_2S_3) is most common by far
- Some 40 secondary minerals formed by oxidation – all more soluble in H_2O
- Conflicting reports in the literature concerning mobility
- How soluble? Which are important? What environments?

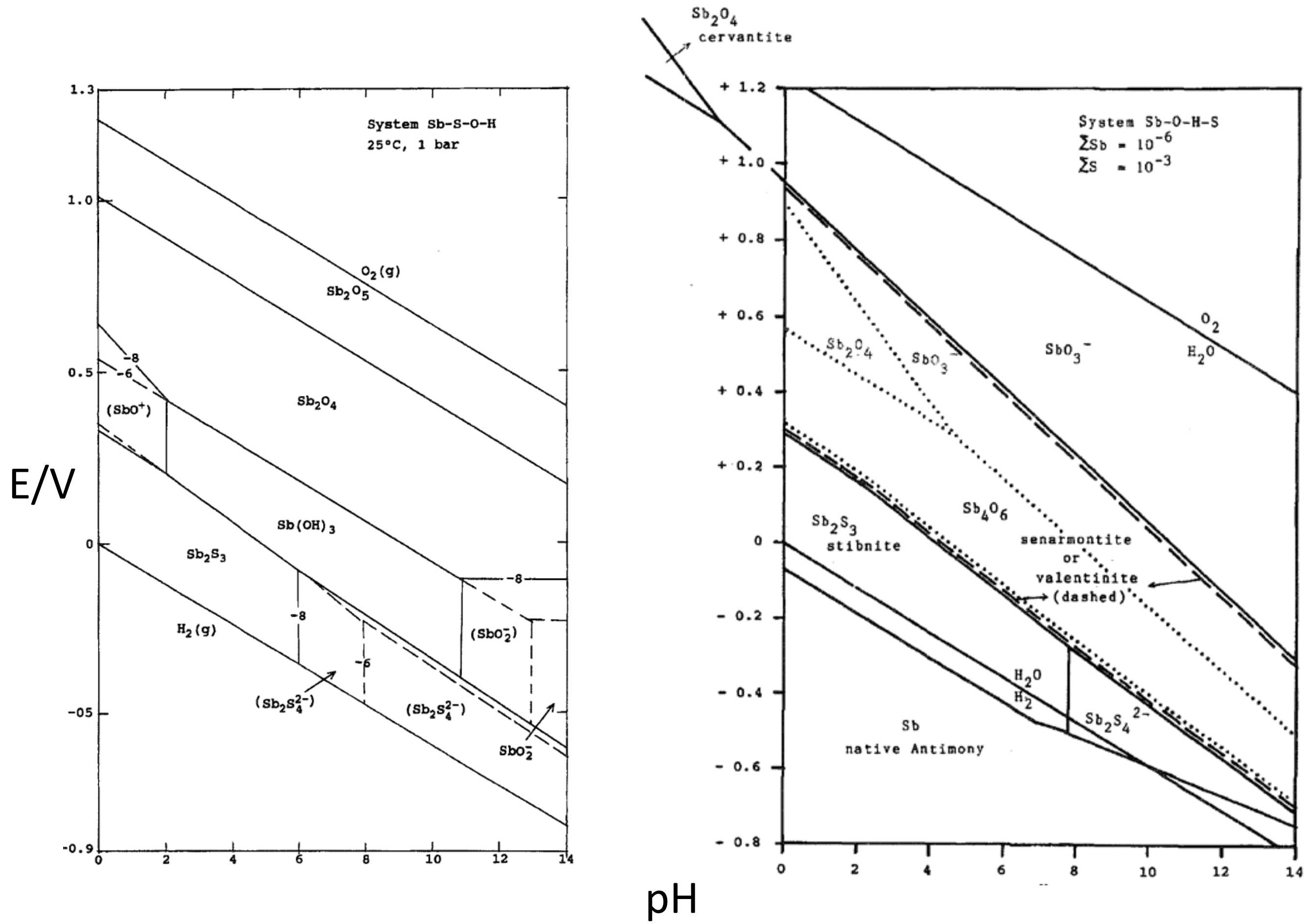
You pays your money and you takes your pick

- "…relatively high mobility of antimony under oxidizing conditions, be it acidic or alkaline." (Vink, 1996)
- "…relatively mobile in the environment, especially under oxic conditions." (Krupka and Serne, 2002)
- "…little is known about the environmental mobility of antimony…" (Filella *et al*., 2002)
- "…antimony is not readily mobilised into the environment…" (Wilson *et al*., 2004)

A “simple”, typical oxidation sequence would be stibnite (Sb_2S_3) → kermesite (Sb_2S_2O) → senarmontite/valentinite (Sb_2O_3) → cervantite (Sb_2O_4) → “antimonic acid” ($HSbO_3{\cdot}nH_2O$).

Natural salts of the latter are members of the roméite group; “stibiconite”, “bindheimite”, “bismutostibiconite”, “stetefeldtite”, etc.

“stibiconite”, probably oxycalcioroméite, 5 cm, San Luis Potosí, Mexico (right); image from Mindat.org

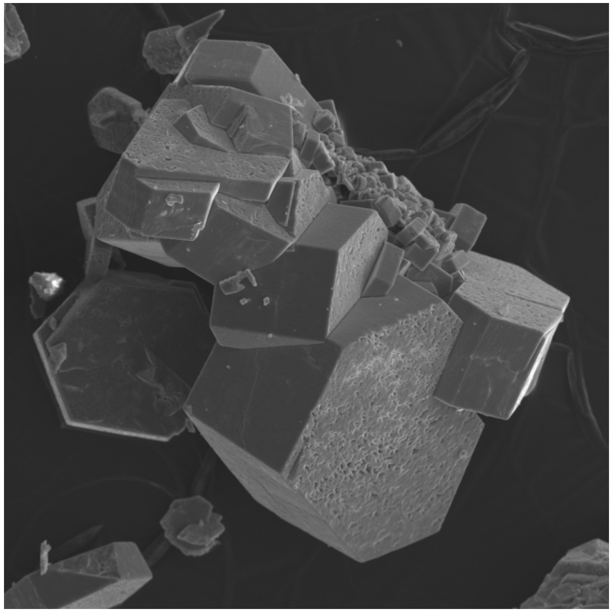


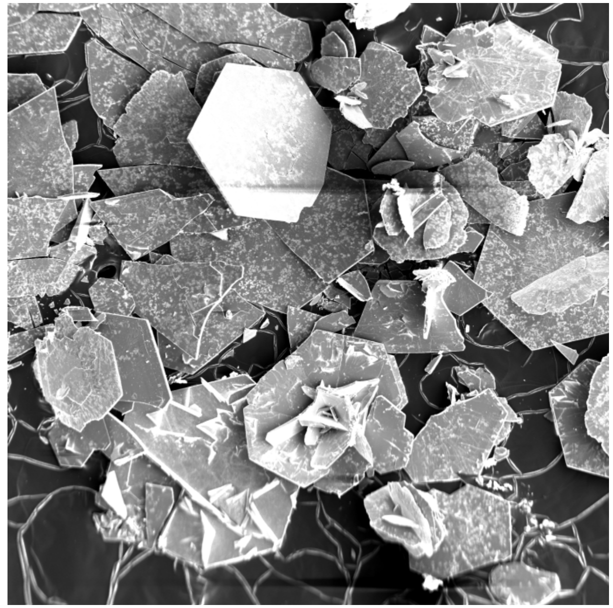
Vink (1996)

- Sb_2O_5 as a proxy; $Sb(OH)_6^-$ at all pH values; problems with thermochemical data – better now

“Simple” oxide solubilities at 25^{o}C, circumneutral pH

- Sénarmontite (Sb_2O_3): ***ca* 1.3 ppm dissolved Sb**
- Cervantite (Sb_2O_4): ***ca* 0.5 ppm dissolved Sb**





BSE images of synthetic brandholzite (left, FOV 1.7 mm) and synthetic bottinoite (centre, FOV 5 mm). The bottinoite crystals (blue) altering from ullmannite (NiSbS, dark grey) are *ca* 6 mm across.

Small cations with $Sb(OH)_6^-$ give species like

Bottinoite	$Ni[Sb(OH)_6]_2 \cdot 6H_2O$
Brandholzite	$Mg[Sb(OH)_6]_2 \cdot 6H_2O$
Mopungite	$NaSb(OH)_6$

Aqueous solubilities at 25^{o}C are
mopungite: ***ca* 390 ppm** Sb
brandholzite: ***ca* 480 ppm** Sb
bottinoite: ***ca* 80 ppm** Sb

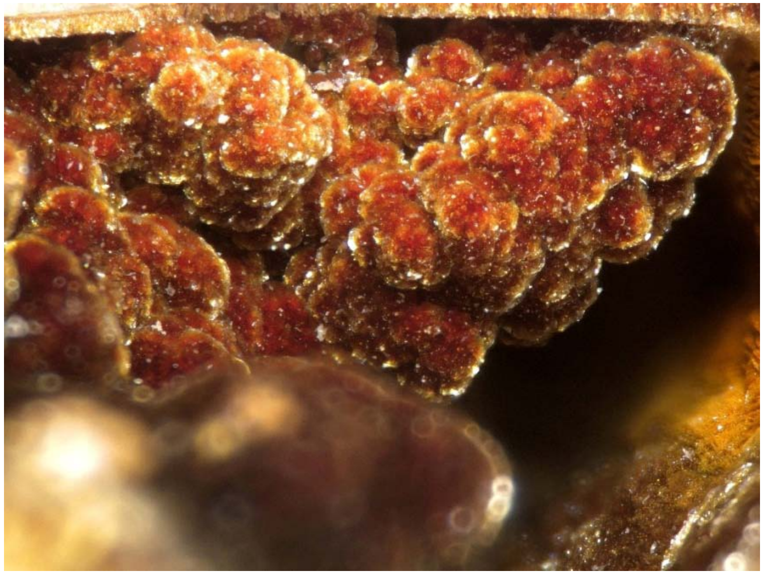
- "Antimonic acid" ($HSbO_3 \cdot nH_2O$): ***ca* 10 ppb dissolved Sb**, including hyperacidic environments
- "Bindheimite" ($Pb_2Sb_2O_7$), pH 2: ***ca* 9 ppb dissolved Sb**
- Oxycalcioroméite ($Ca_2Sb_2O_7$) pH 2: ***ca* 40 ppb dissolved Sb**

BUT WE ARE ON ANOTHER SLIPPERY THERMOCHEMICAL SLOPE!

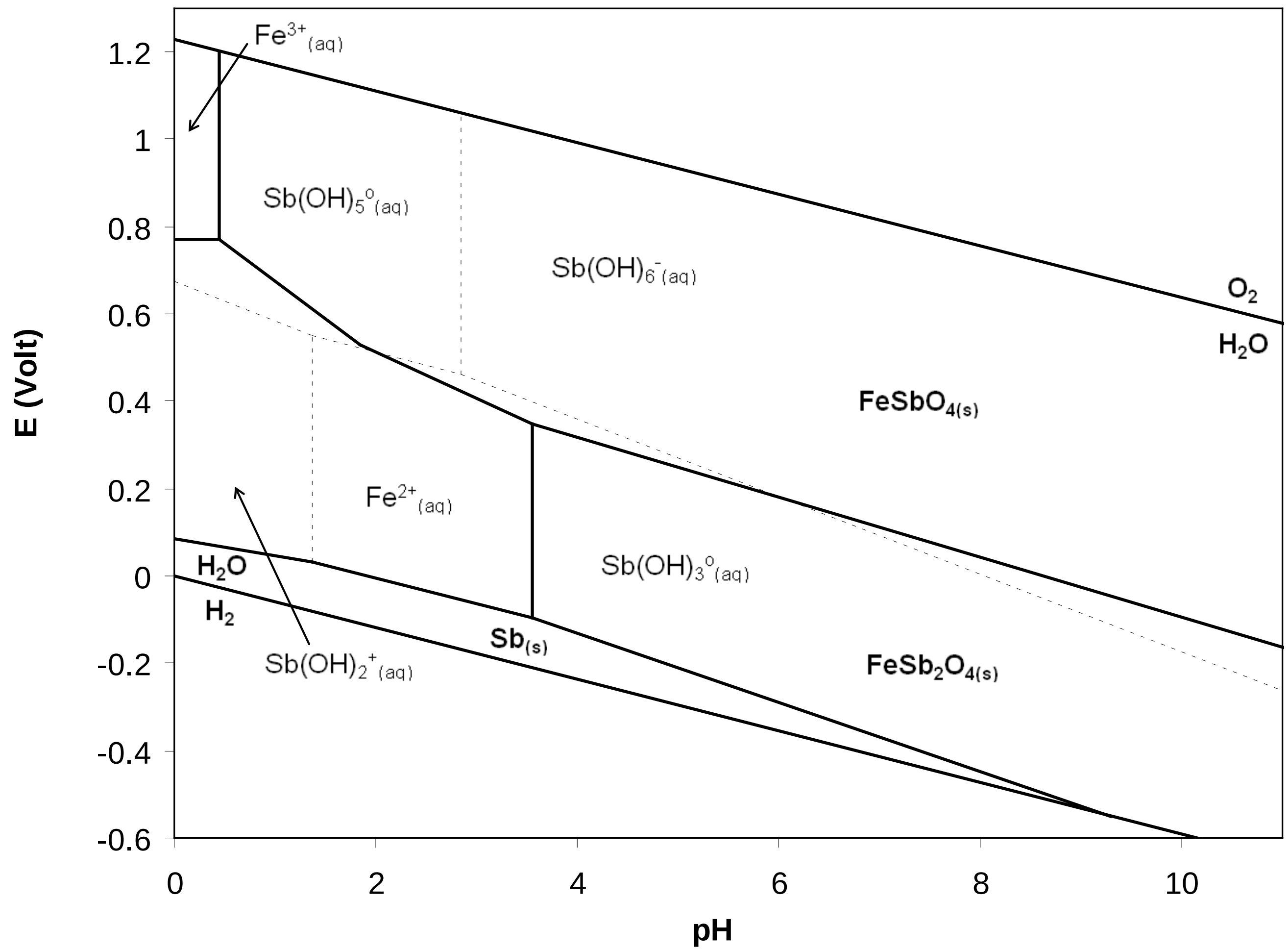
Other phases are worthy of attention

Tripuhyite, $FeSbO_4$, and schafarzikite, $FeSb_2O_4$

- Mindat lists 60 localities for tripuhyite and 12 for schafarzikite; many others are known



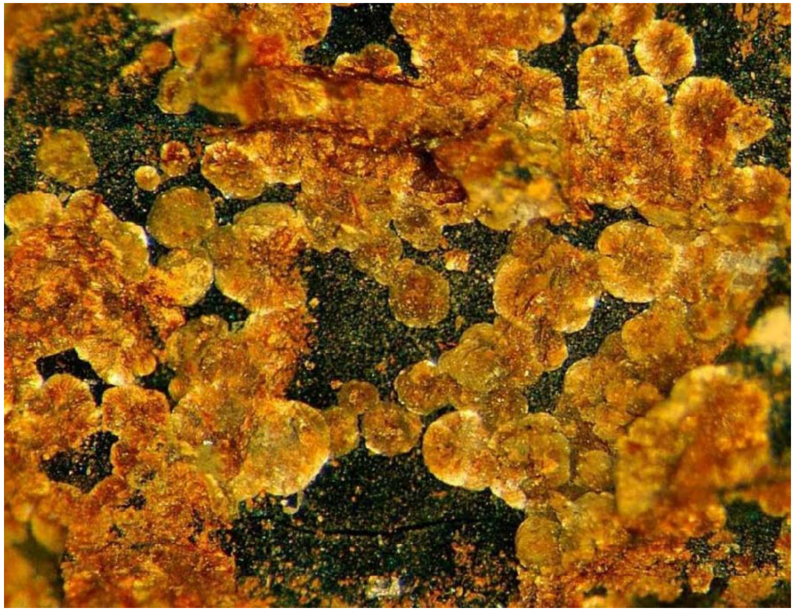
Tripuhyite (left), Clara mine, Oberwolfach, Germany, FOV 10 mm; schafarzikite (right), Krížnica, Slovakia; FOV 4 mm; images courtesy of Mindat.org.



25°C; total dissolved Sb and Fe = 10^{-6} M

- Derived $\Delta G_f^{\ominus}$(s, 298.15 K) values for $FeSb_2O_4$ and $FeSbO_4$ are –959.4 $\pm$4.3 and –836.8 $\pm$2.2 kJ mol^{-1}, respectively
- Goethite vanishes from considerations!
- $a(Sb(OH)_5^{o}) = 10^{-11}$ at 298.15 K reacts with goethite to form tripuhyite (***ca* 1 ppt Sb!**)
- Other “simple” Sb oxide minerals play a role at neutral to weakly alkaline pH

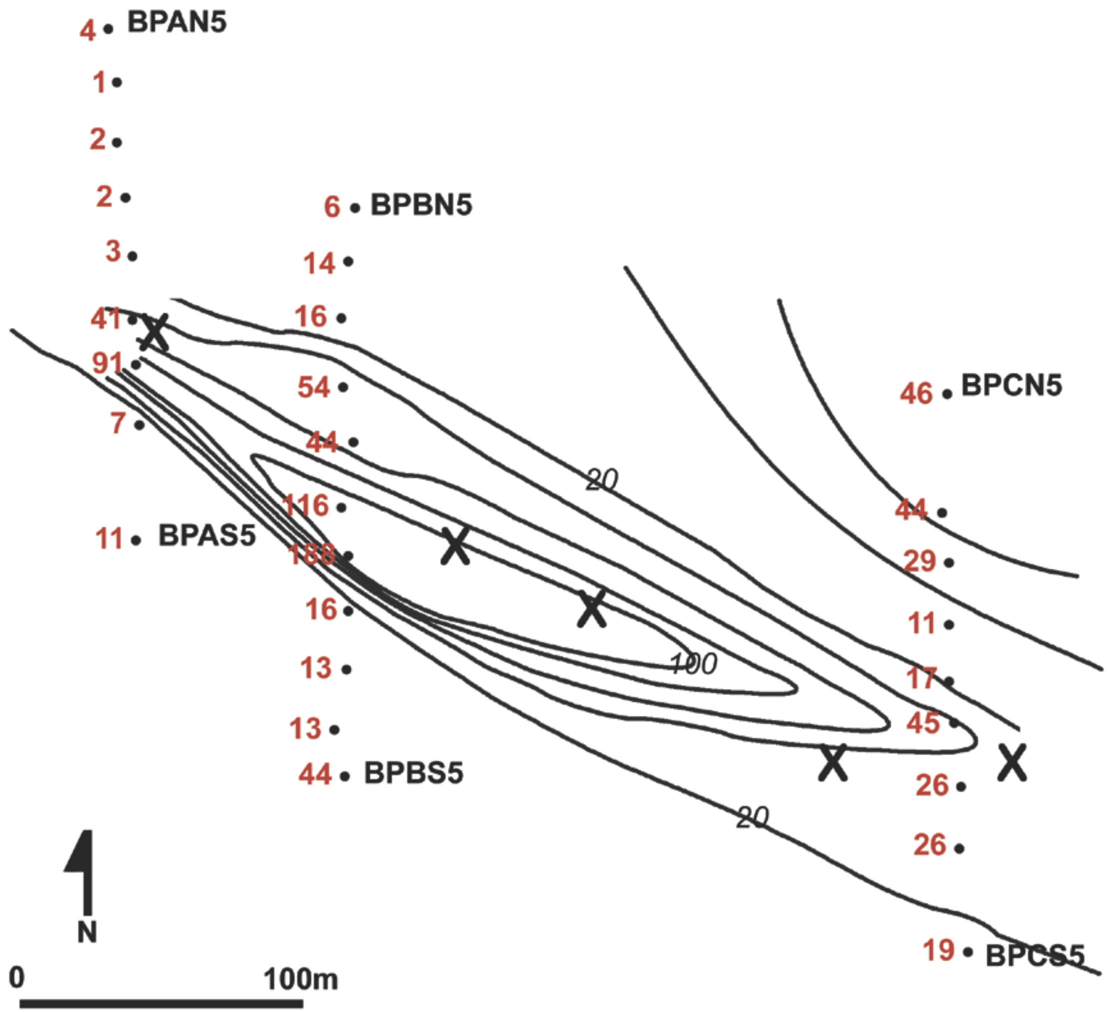
- Why has tripuhyite been overlooked?
- Physical characteristics



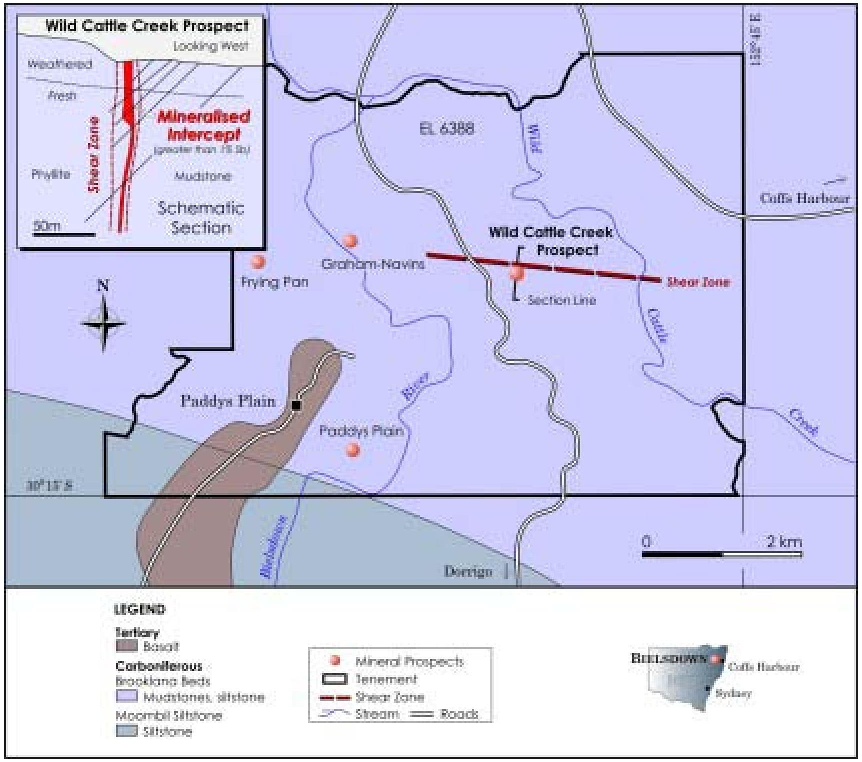
Tripuhyite rosettes up to 0.5 mm across, Clara mine, Oberwolfach, Germany; images courtesy of Mindat.org.

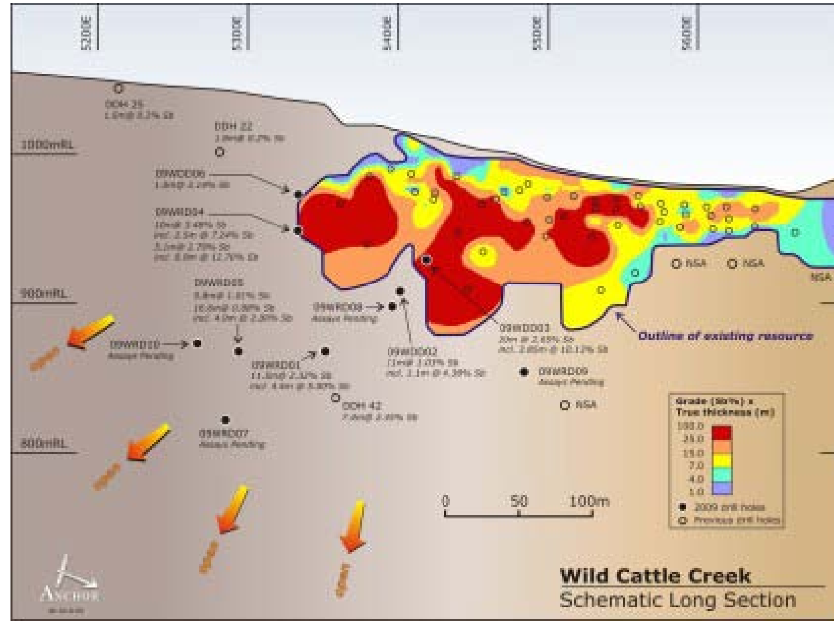
- So where do we stand?
- **Sb is not going anywhere in solution**
- “Reverse” modelling gives total dissolved Sb load for any ground water composition
- Colloids, suspensions, organics, adsorption – Montserrat Filella, Juraj Majzlan, and others
- In the geochemical world, soil is a wonderful “filter” and Sb geochemical anomalies are very “tight”

The Bayley Park prospect, Hillgrove, NSW, Australia.

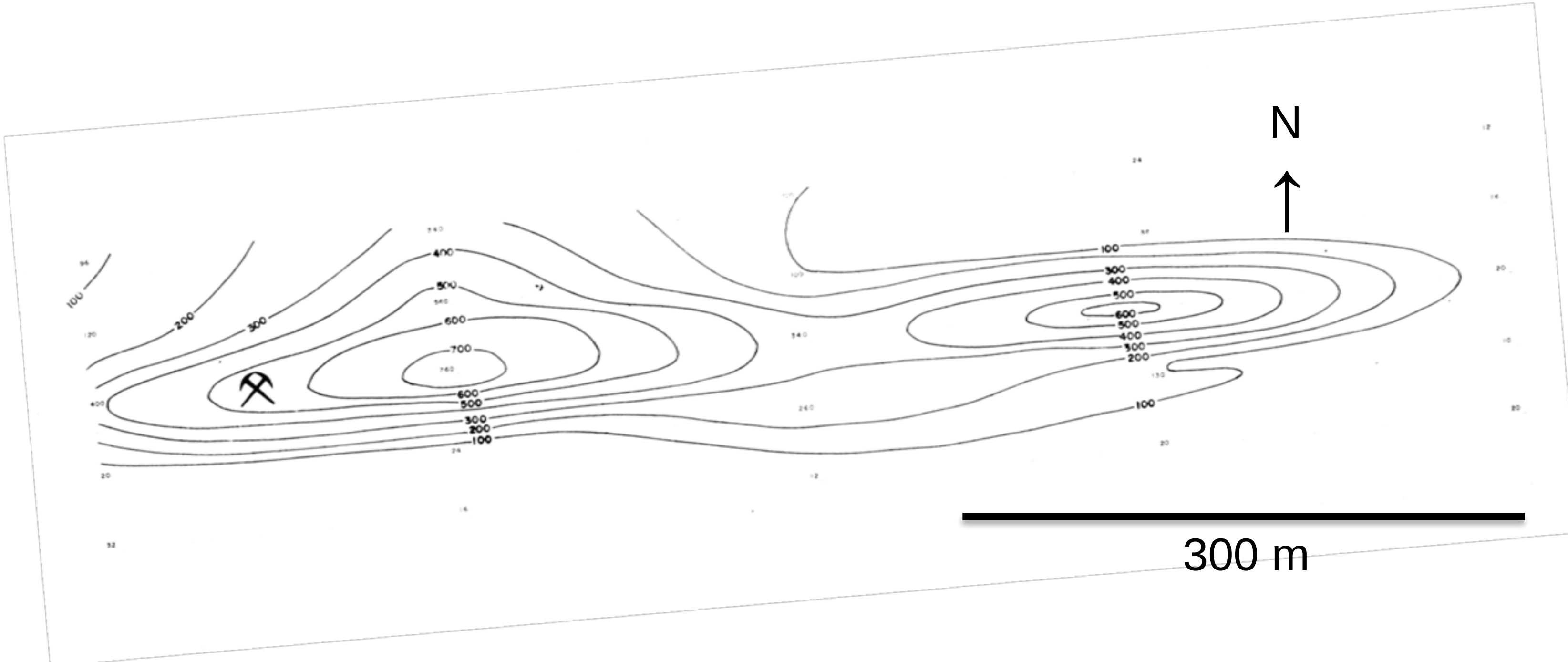


Bayley Park soil Sb (C); 20 ppm contours; X = shallow prospecting pit.

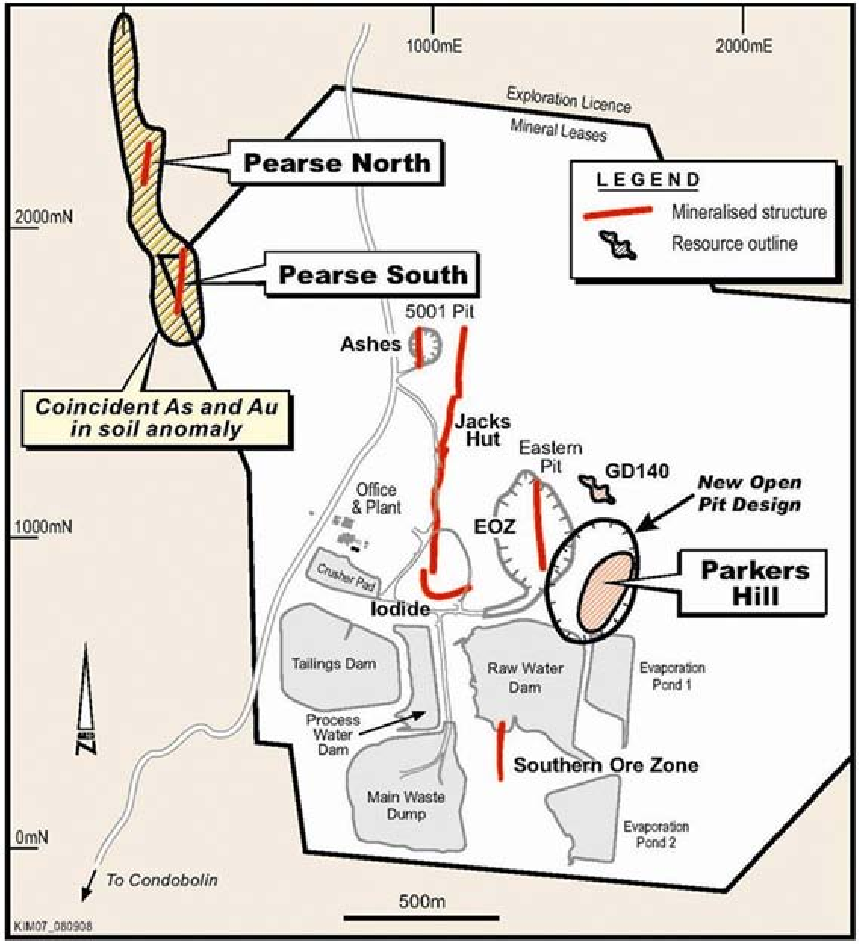




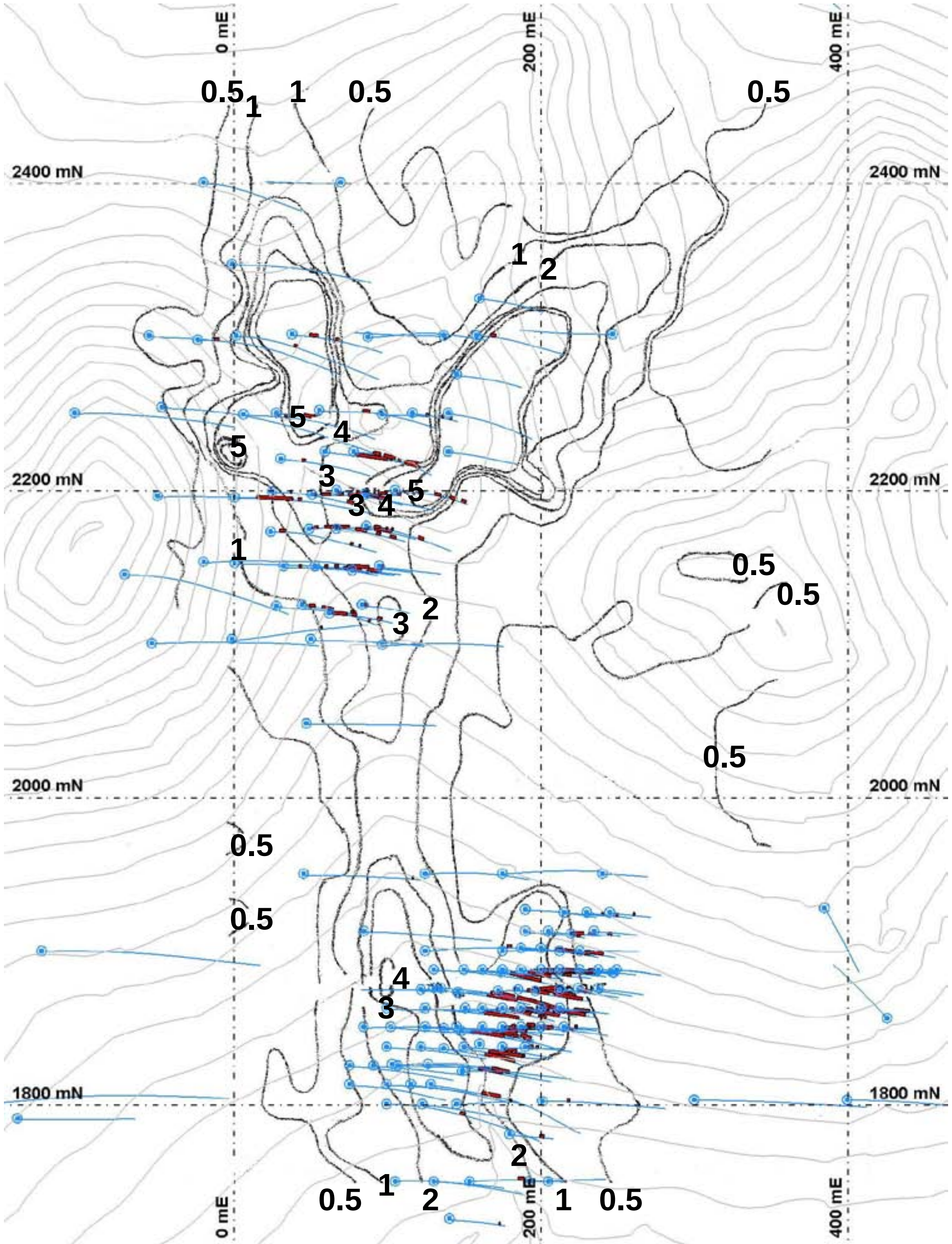
The Wild Cattle Creek deposit, Dorrigo, NSW – the mineralization is confined to the shear zone (left) and sections in red (right) carry >1% Sb as stibnite; images courtesy of Anchor Resources Limited.



- A 700 m soil Sb anomaly to the E of the Wild Cattle Creek mine (contours to 700 ppm; cut–off 100 ppm; A horizon, 0–25 cm)
- Subsequent drilling (1972) confirmed the continuation of mineralization in the sub–vertical structure



Pearse South Au-Ag-Sb deposit, Mineral Hill, NSW, Australia; images courtesy of KBL Resources



Pearse South soil Sb (ppm)

- Sample at point of refusal of auger
- Drill holes in blue; high grade Au intersections in red
- Soil Au and Ag anomalies are confined to the same trend but do not overlay perfectly
- Lots of tripuhyite

So, Boyle and Jonasson (1984) *J. Geochem. Exploration,* **20**, 223-302 guessed correctly:

- "Soil anomalies related to antimoniferous mineralization are usually well developed and have a high contrast, features related to the relatively low mobility of antimony during most soil-forming processes."

Bismuth and Molybdenum

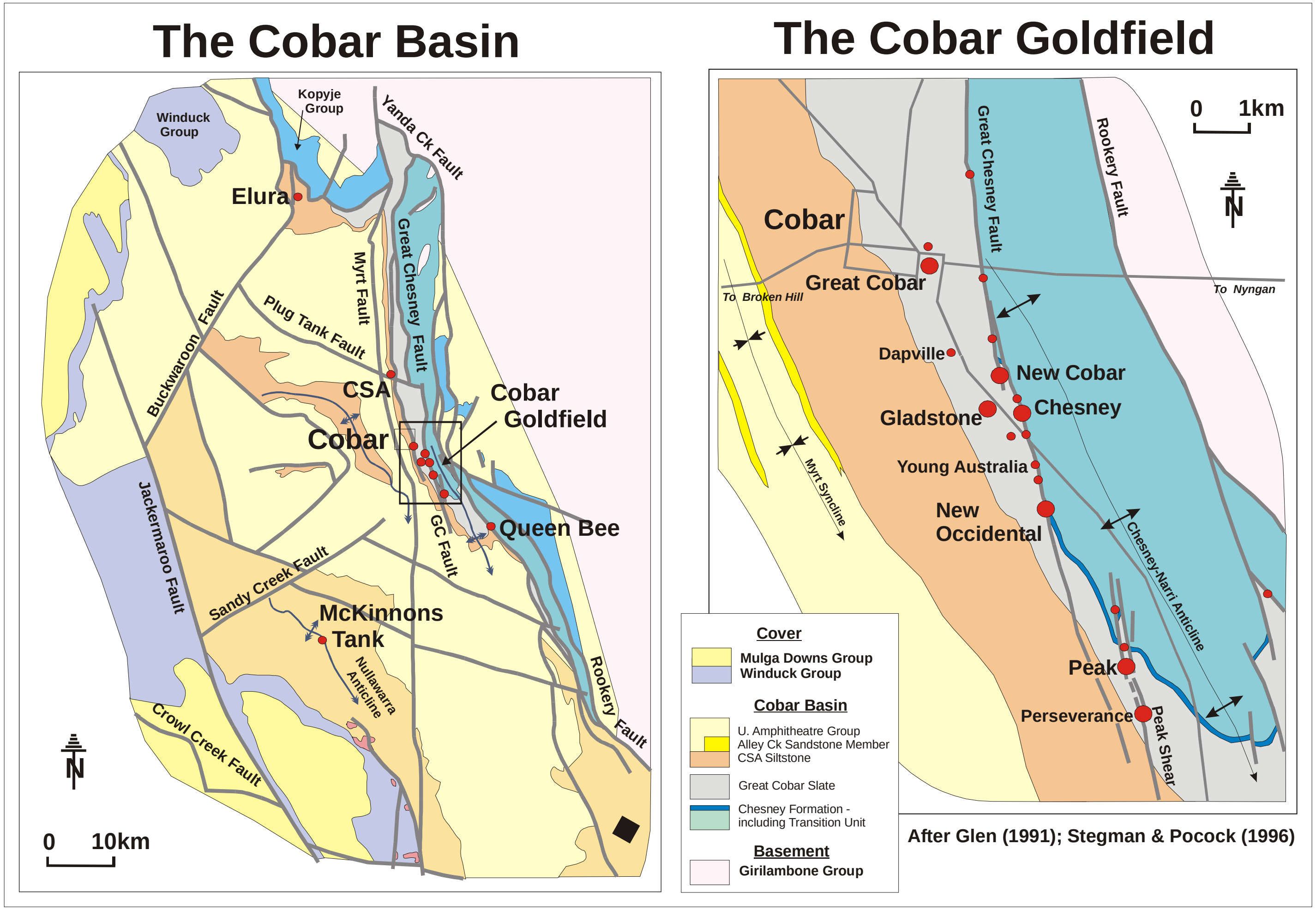
Ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 7H_2O$); Kingsgate, NSW; 7 mm

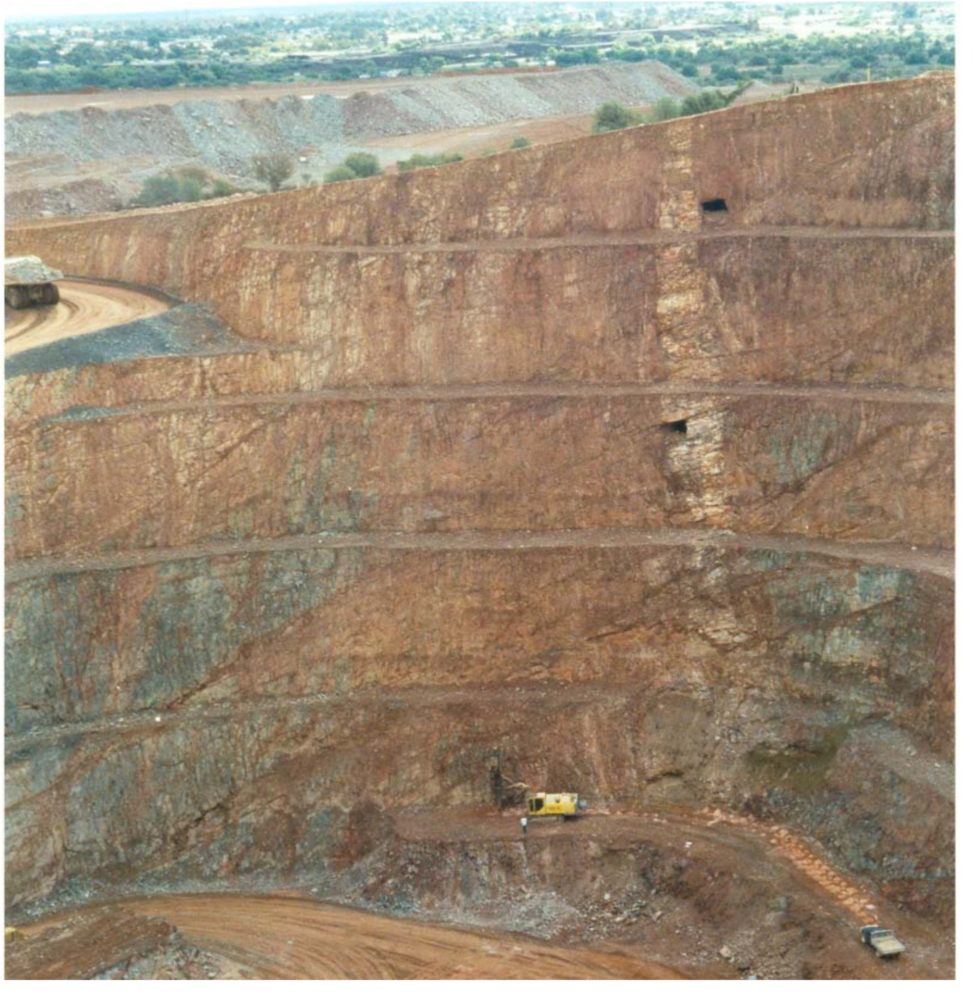
Goodwin's pipe, Kingsgate, NSW

- Not everything yellow is ferrimolybdite
- Ferrimolybdite is rare at Kingsgate
- Yellow secondaries are dominated by koechlinite (Bi_2MoO_6) and russellite (Bi_2WO_6)
- This pattern is common from N QLD to VIC where Bi, W and Mo are found together
- So, what controls the chemical dispersion of Bi?

- Bismoclite (BiOCl), bismutite ($Bi_2O_2CO_3$), koechlinite (Bi_2MoO_6) and russellite (Bi_2WO_6)
- Other phosphates and arsenates (much rarer)
- Reverse solubility modelling from pH 0 to 9: **total dissolved Bi never exceeds 8 ppm (pH 0); < 0.1 ppm pH 1-9; 12 ppt at pH 4!**
- Bi isn’t going anywhere either
- Geochemical exploration (Mo, Bi) in E Australia over the last 50 years is of little to no use and the area remains essentially untested

“Cobar – style” mineralisation

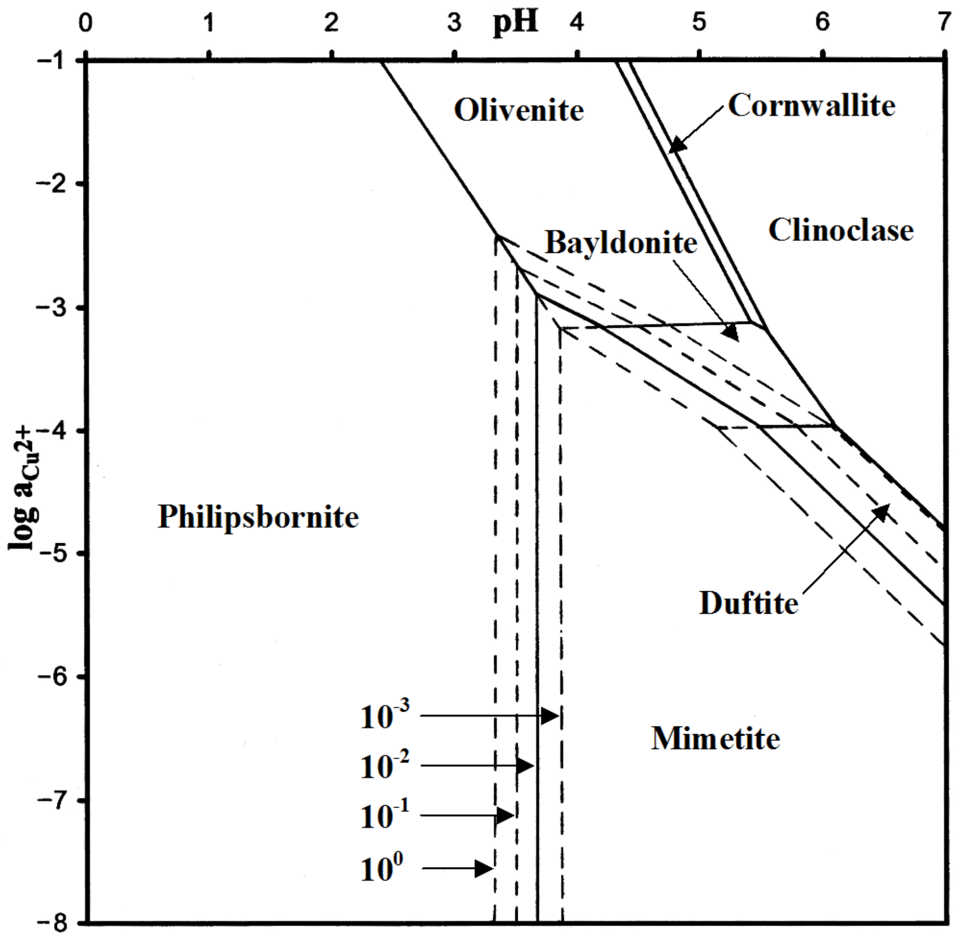




View facing northwest at the New Cobar mine (June, 2003). Mineralisation is associated with the steeply dipping fault visible in the in the wall of the open cut.

An As-rich suite (primary arsenopyrite, FeAsS) was deposited early in the oxidized lode under acidic conditions

Agardite-(Y)	$(Y,LREE,Al)Cu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$
Agardite-(Nd)	$(Nd,LREE,Al)Cu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$
Mimetite	$Pb_5(AsO_4)_3Cl$
Olivenite	Cu_2AsO_4OH
Duftite	$CuPbAsO_4OH$
Bayldonite	$Cu_3Pb(AsO_4)_2(OH)_2$
Chenevixite	$Cu_2Fe_2(AsO_4)_2(OH)_4 \cdot H_2O$
Gartrellite	$PbCuFe(AsO_4)_2(OH) \cdot H_2O$
Segnitite	$PbFe_3(AsO_4)(HAsO_4)(OH)_6$
Philipsbornite	$PbAl_3(AsO_4)(HAsO_4)(OH)_6$
+Plumbogummite	$PbAl_3(PO_4)(HPO_4)(OH)_6$
+Osarizawaite	$PbCuAl_2(SO_4)_2(OH)_6$



Stability field diagram for the Cu(II) and Pb(II) arsenates at 298.2 K, with $a(Pb^{2+}) = 10^{-8}$ and $a(Cl^{-}) = 10^{0}, 10^{-1}, 10^{-2}$ (bold), and 10^{-3} (as indicated)

- A later carbonate–rich event developed malachite, azurite and cerussite
- Pattern is repeated over the whole basin
- Reverse modelling again predicts solubilities and dispersion (use ground water geochemistry as a proxy for major ion ratios)
- Total **Cu**, **Pb** and **As** solution loads for the arsenate suite are **33**, **0.2**, and **1.1** ppm, respectively.

- Cobar basin – predict broader Cu soil anomalies and tight Pb ± As anomalies
- Intuitively as expected (Cu > Pb dispersion)
- Now we have the chemistry of the geochemistry we can be confident

- Much remains to be done
- The chemistry of geochemistry permits a much more rational approach for exploration methods and interpretation of data

THANKS

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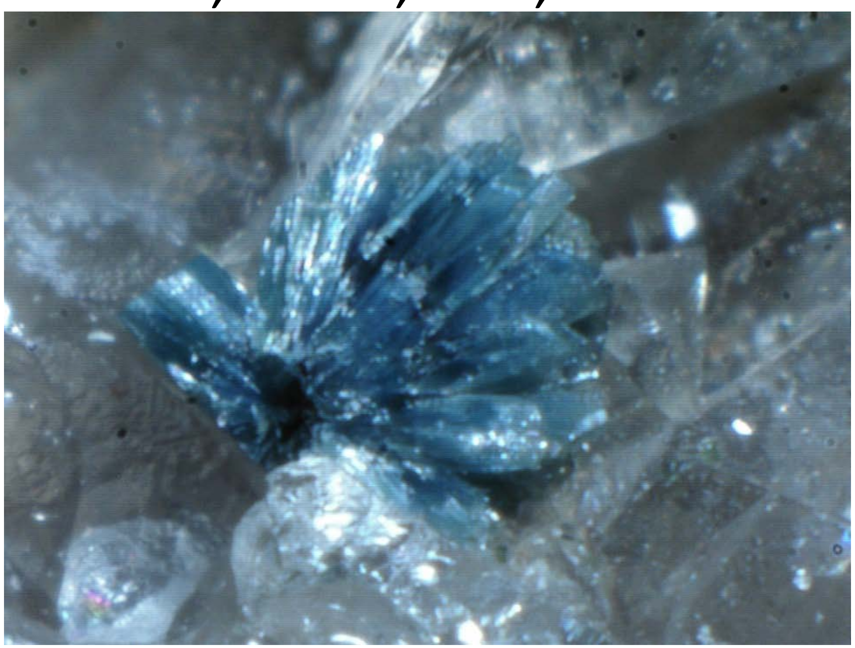

Gelosaite, $BiMo^{VI}_{(2-5x)}Mo^{V}_{6x}O_7(OH)\cdot H_2O$ Old 25 pipe, Kingsgate, NSW. FOV 2.5 mm.
Photo: John Haupt. Specimen:
Merv and Lil Legg