SUPERGENE DISPERSION OF ANTIMONY AND A GEOCHEMICAL EXPLORATION MODEL FOR ANTIMONY ORE DEPOSITS

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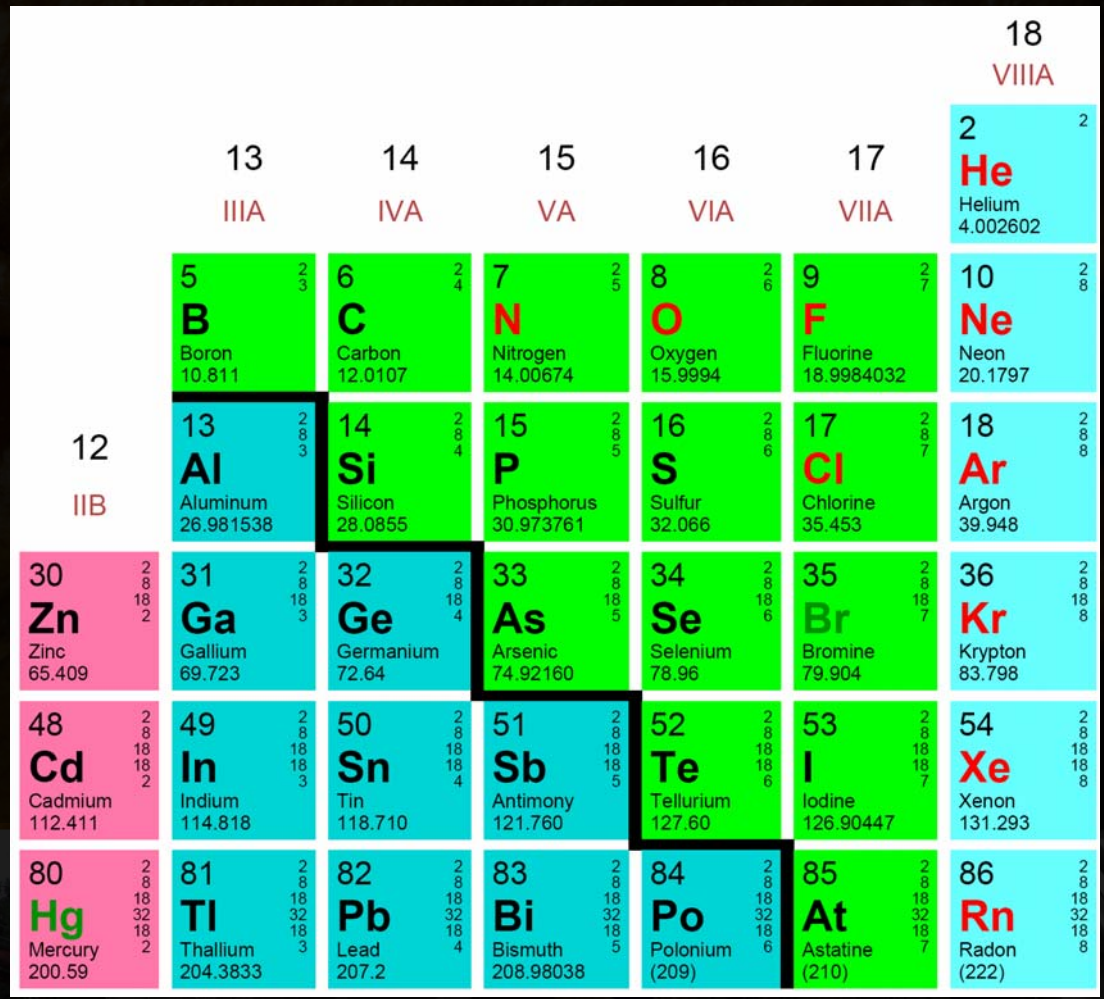
What is Antimony?



12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
						2 **He** Helium 4.002602
	5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
	13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
30 **Zn** Zinc 65.409	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.64	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.293
80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)

Ichinokawa mine, Shikoku Island, Japan
Stibnite, Sb_2S_3, is the most common primary Sb mineral.

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Fate of Stibnite and Other Sb Sulfosalts in the Supergene Environment

They oxidise; $S^{2-} + 2O_2 \rightarrow SO_4^{2-}$ with Sb(III) and Sb(V) depending on redox potential.

Secondary Sb minerals control solubility and dispersion.

40 secondary minerals known.

What is the extent of the dispersion?

Stibiconite, Sb_3O_6OH, after stibn

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Confusion Behind Antimony Geochemistry due to $Sb_2O_5(s)$

- "…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)
- Sb_2O_5 is not a mineral.
- Aging leads to precipitates of "antimonic acid"

Common Secondary Sb Minerals

Sénarmontite Sb_2O_3 $[Sb]_{TOT}$ = *ca* 1.3 ppm

Valentinite Sb_2O_3 $[Sb]_{TOT}$ = *ca* 6.4 ppm

- At neutral pH and 25°C
- Nearly always in small amounts
- Further oxidation gives rise to Sb(V) species

Cervantite Sb_2O_4

Stibiconite $Sb^{3+}Sb_2O_6OH$

Roméite $Ca_2Sb_2O_7$

Bindheimite $Pb_2Sb_2O_7$

Aqueous Species and Hydrolysis at 25°C

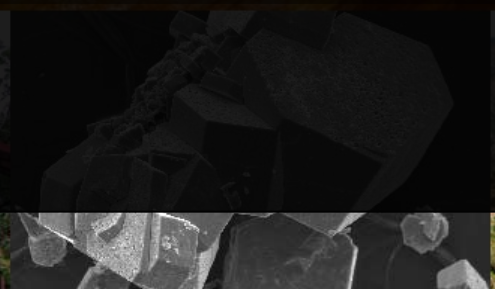
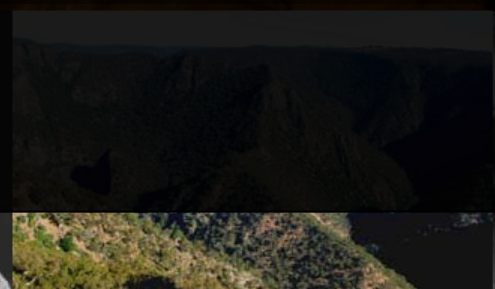
Antimony (III) pH 1-14

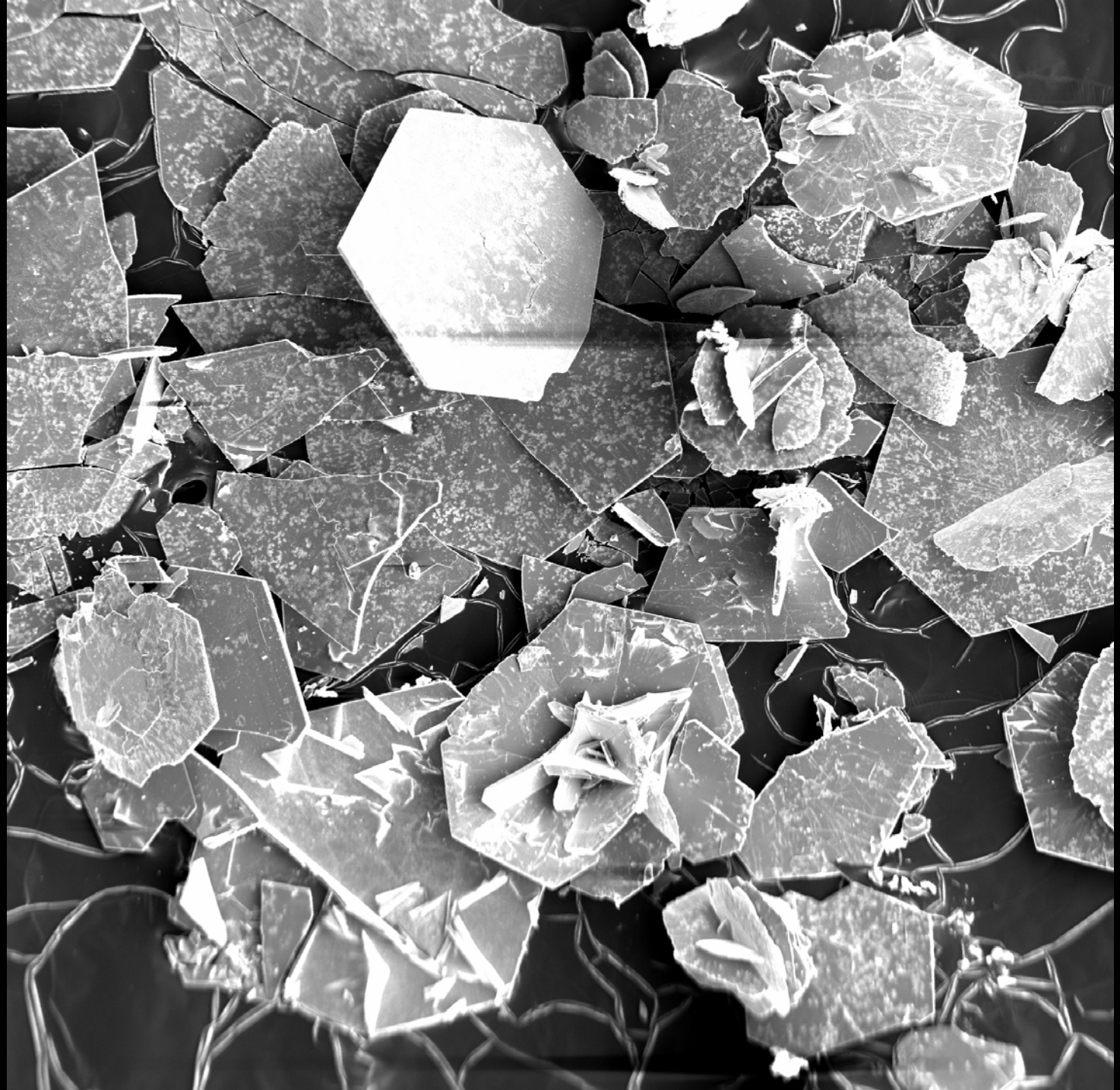
$Sb(OH)_2^+$, $Sb(OH)_3^0$, $Sb(OH)_4^-$

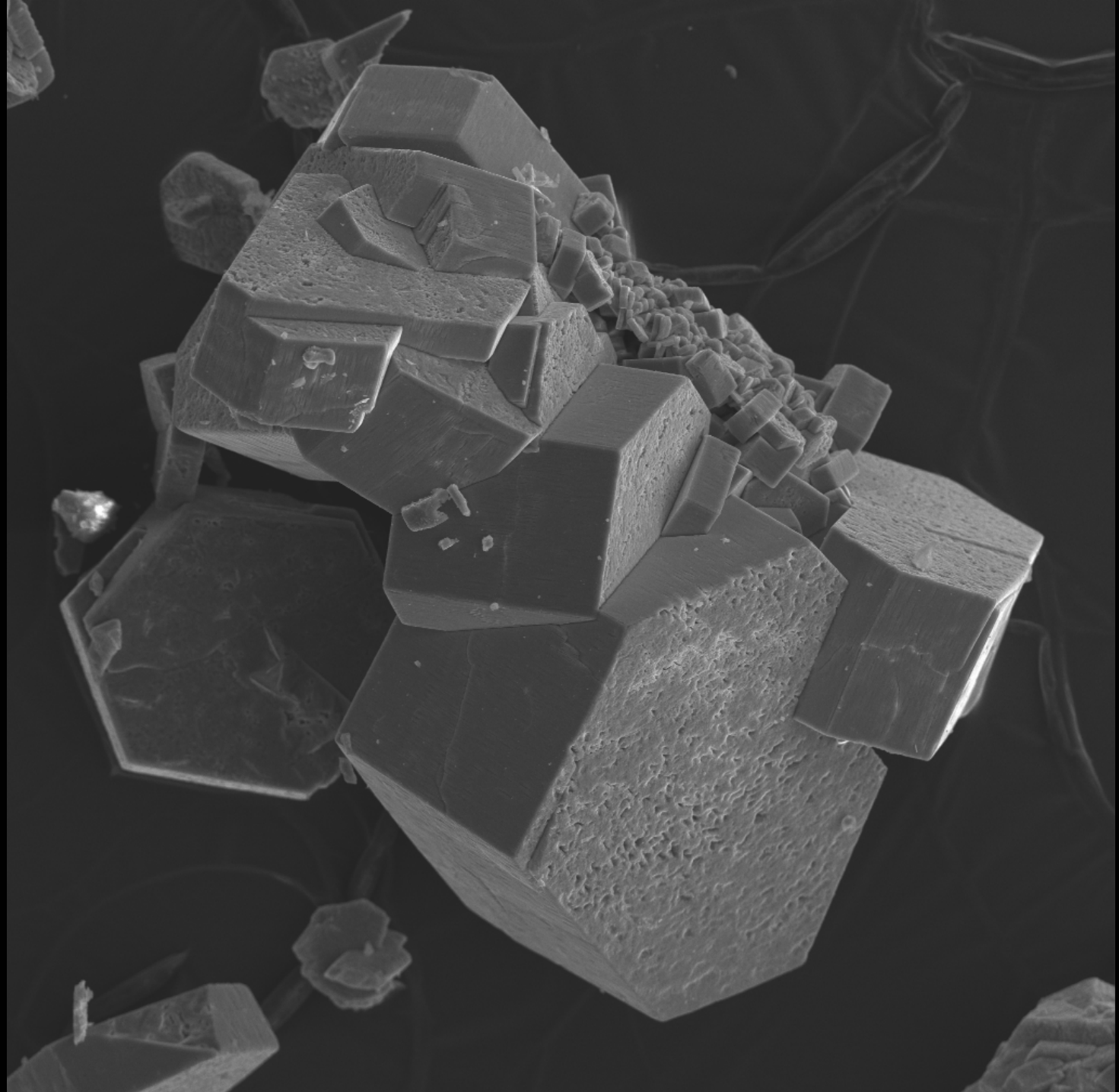
Antimony (V)

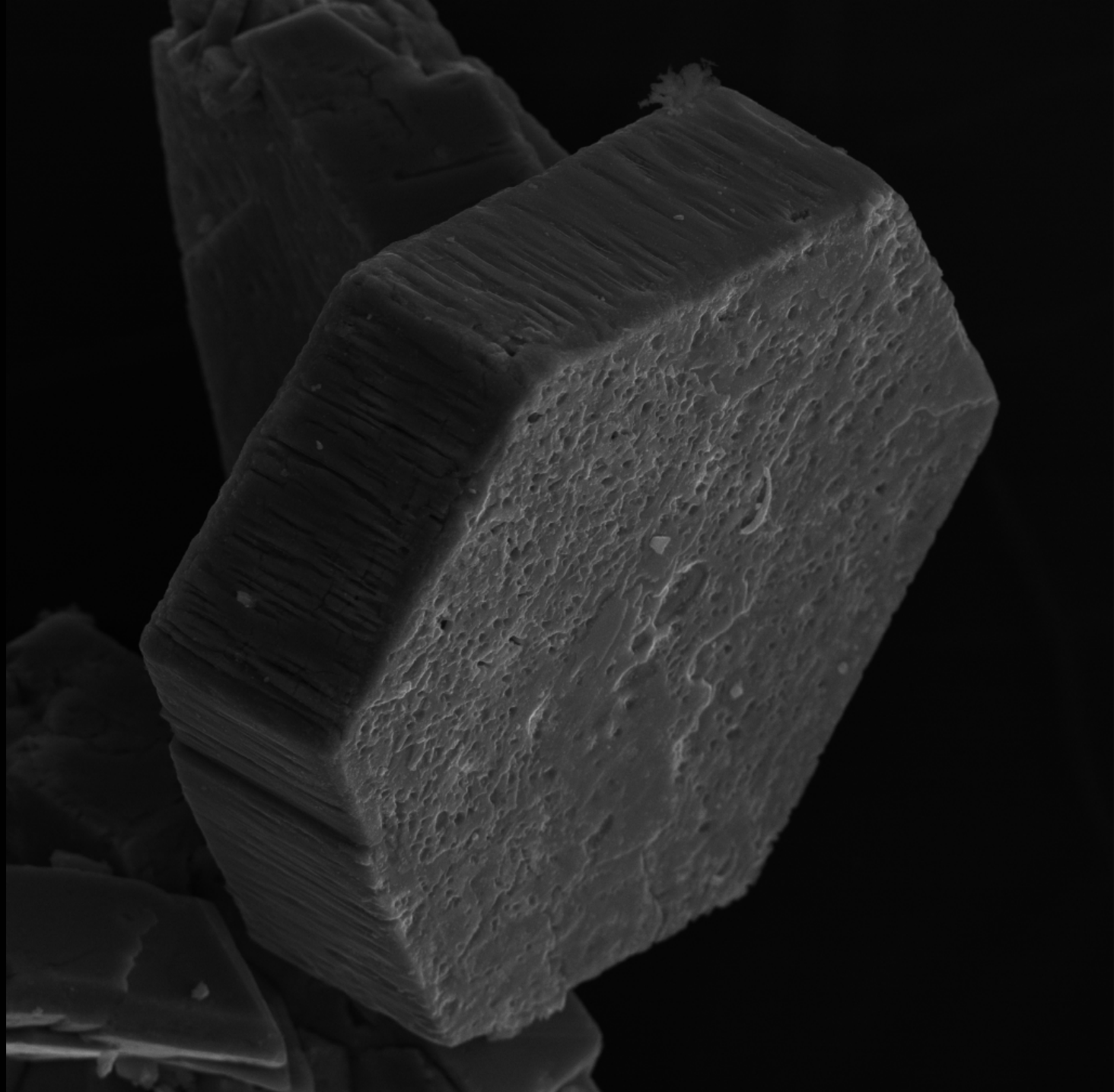
$Sb(OH)_5^0$ pH < 2.85,

$Sb(OH)_6^-$ pH > 2.85





Solubility at 25°C

Brandholzite

$[Mg(H_2O)_6][Sb(OH)_6]_2$ = 1.95 ± 0.04 x 10^{-3} mol dm^{-3} (n=4) $[Sb]_{TOT}$ = *ca* 873 ppm

Bottinoite

$[Ni(H_2O)_6][Sb(OH)_6]_2$ = 3.42 ± 0.11 x 10^{-4} mol dm^{-3} (n =4) $[Sb]_{TOT}$ = *ca* 153 ppm

Mopungite

$NaSb(OH)_6$ = 3.18 ± 0.2 x 10^{-3} mol dm^{-3}

$[Sb]_{TOT}$ = *ca* 712 ppm (Blandamer *et al.*, 1974)

These minerals are very rare.

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Fate of Sb(V)

$Sb(OH)_5^0 + H_2O \leftrightharpoons Sb(OH)_6^- + H^+$

pK_a = 2.85 at 25°C (Accornero *et al.*, 2008)

Aging of acidic solutions, except for very dilute ones, over hours to days leads to the formation of white precipitates of “antimonic acid”.

$(H_3O)_2Sb_2O_6 \cdot H_2O$ = “$Sb_2O_5 \cdot 4H_2O$”

Roméite and Bindheimite Solubility 1

Solubility of near end-member roméite, $Ca_2Sb_2O_7$, in 0.010 M HNO_3 at 25°C gives (n = 6):

pH = 2.232 ± 0.008

$[Ca^{2+}]_{TOT}$ = 2.11 ± 0.05 x 10^{-3} M

$[Sb^{5+}]_{TOT}$ = 3.10 ± 0.26 x 10^{-7} M; *ca* 38 ppb

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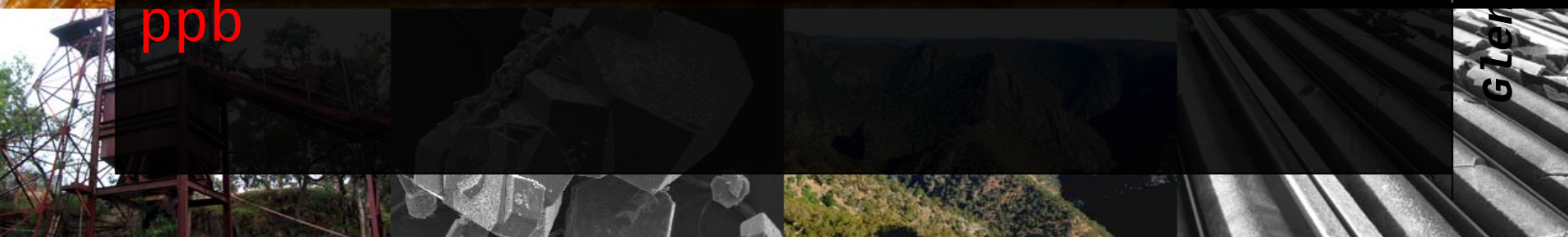
Roméite and Bindheimite Solubility 2

Solubility of near end-member bindheimite, $Pb_2Sb_2O_7$, in 0.010 M HNO_3 at 25ºC gives (n = 6):

pH = 2.053 ± 0.047

$[Pb^{2+}]_{TOT}$ = 4.12 ± 0.13 x 10^{-5} M

$[Sb^{5+}]_{TOT}$ = 7.66 ± 0.64 x 10^{-8} M; ca 9 ppb



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Field Studies – Water Sampling

Underground Hillgrove Sb mine
1740 level

$[Sb]_{TOT}$ = 3.46 and 0.
$[As]_{TOT}$ = 215 and 13

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Antimonic ochres - amorphous Sb rich stalactites.

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Field Studies – Mineral Sampling

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Field Studies – Mineral Sampling

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Field Studies – Mineral Sampling

Fishers antimony mine, Hillgrove

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The mineralogical evidence shows that Sb is not very mobile in the supergene environment.

Dimorphous valentinite and sénarmontite Sb_2O_3 replacing stibnite.

Field of view aprox 5 mm

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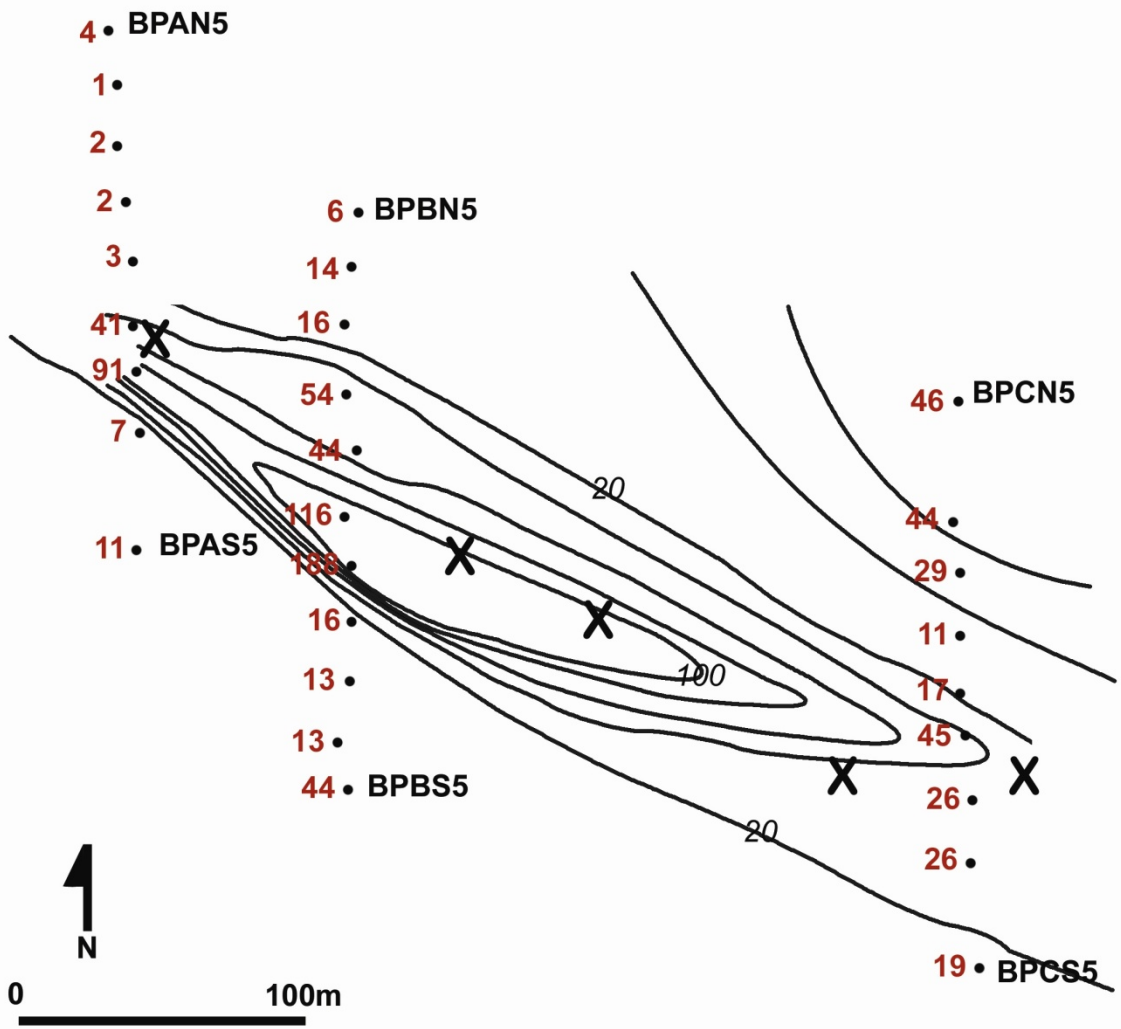
The experimental solubility evidence bears this out.

These conclusions can be applied to the search for new Sb ore deposits.


4 BPAN5
1
2
2
3
41
91
7
11 BPAS5
6 BPBN5
14
16
54
44
116
188
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13
44 BPBS5
46 BPCN5
44
29
11
17
45
26
26
19 BPCS5
20
100
20
N
0
100m

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Concluding Comments

Finally, it is pleasing to note that the results of this investigation have been incorporated in the exploration strategy of Straits Hillgrove Gold Ltd.

Led to a submission to the IMA for a new mineral.

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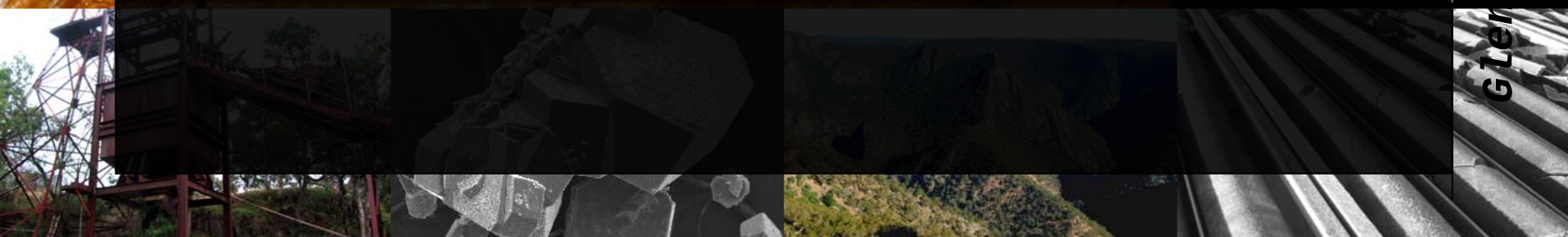

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Hopefully we can find a bull market at the end of the rainbow.

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