Geological Survey of Canada
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PRECIOUS METAL MOBILITY DURING SERPENTINIZATION-DRIVEN REDOX REACTIONS

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1. Rationale

The behaviour of precious metals during serpentinization have implications for the source to ore pathways at ultramafic-hosted Au deposits and deep metal cycling during subduction, but are poorly understand because progressive hydration reactions typically obscure early-stage features.

Herein we report LA-ICP-MS results for a suite of sulphide (pentlandite, pyrrhotite, chalcopyrite), native metals and awaruite from variably serpentinized peridotite and pyroxenite from the Cache Creek terrane (Atlin, British Columbia, Fig. 1). Least serpentinized samples constrain metal mobility during early-stage serpentinization.

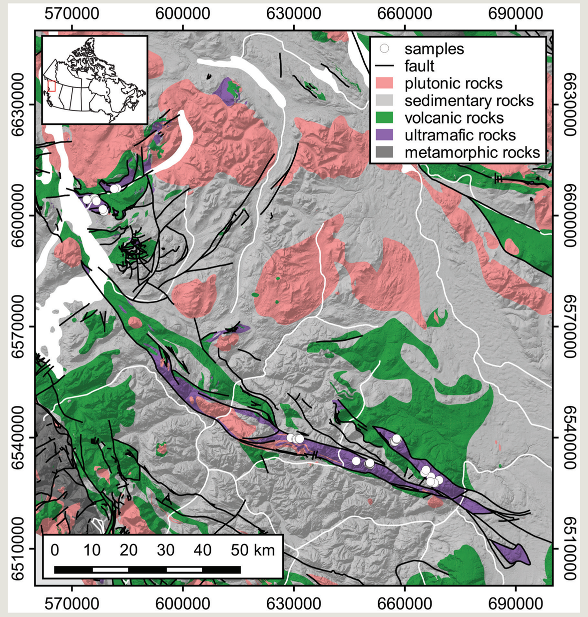


Figure 1 – Regional geologic map of northwestern British Columbia showing the distribution of mantle peridotites and sampling localities during the 2016 and 2017 field seasons. Shuttle radar topography mission (SRTM) elevation data shown for reference.

2. Petrography

Pentlandite and pyrrhotite occur as fine inclusions (few µm) and as coarser interstitial sulphides (1–200 µm), which are, in turn, replaced by native metals (Cu and Fe) and Ni-Fe alloy (awaruite; Fig. 2).

Native Fe- and awaruite-bearing mineral assemblages require super-reducing and/or S-poor conditions that were likely generated by H_2 fluids and/or gases during the conversion of olivine to serpentine and magnetite. Pentlandite occurs with magmatic clinopyroxene and Cr-spinel and is interpreted as a relict, base metal sulphide phase that escaped complete de-sulphidation.

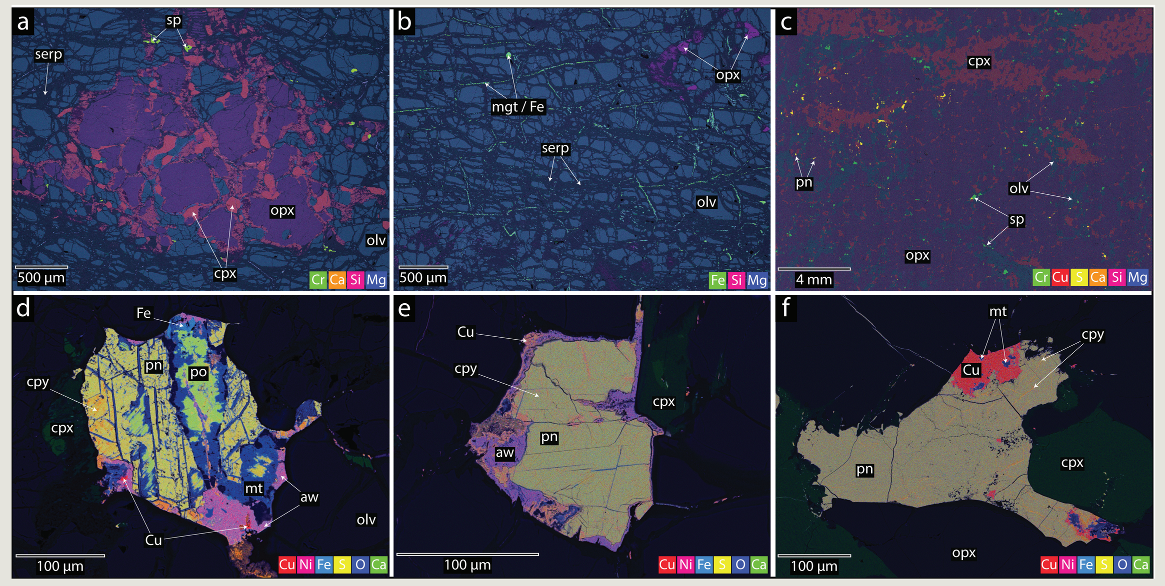


Figure 2. Scanning electron microscope energy dispersive spectroscopy (SEM-EDS) map results. Maps are colour coded to major element composition using the Oxford Instruments Aztec software package (aw = awaruite; cpx = clinopyroxene; cpy = chalcopyrite; mt = magnetite; olv = olivine; opx = orthopyroxene; pn = pentlandite; serp = serpentine; sp = spinel).

3. LA-ICP-MS spot results

Sulphide breakdown decoupled precious metals at the microscale, partitioning Au, Ag, and platinum-group PGE (PPGE; Pt and Pd) within awaruite and native metals (Cu and Fe) at concentrations up to 100s of ppm (Fig. 3). Other PGE, including iridium-group PGE (IPGE; Os and Ir) acted as conservative elements within relict pentlandite and pyrrhotite (0.1–100 ppm; Fig. 3).

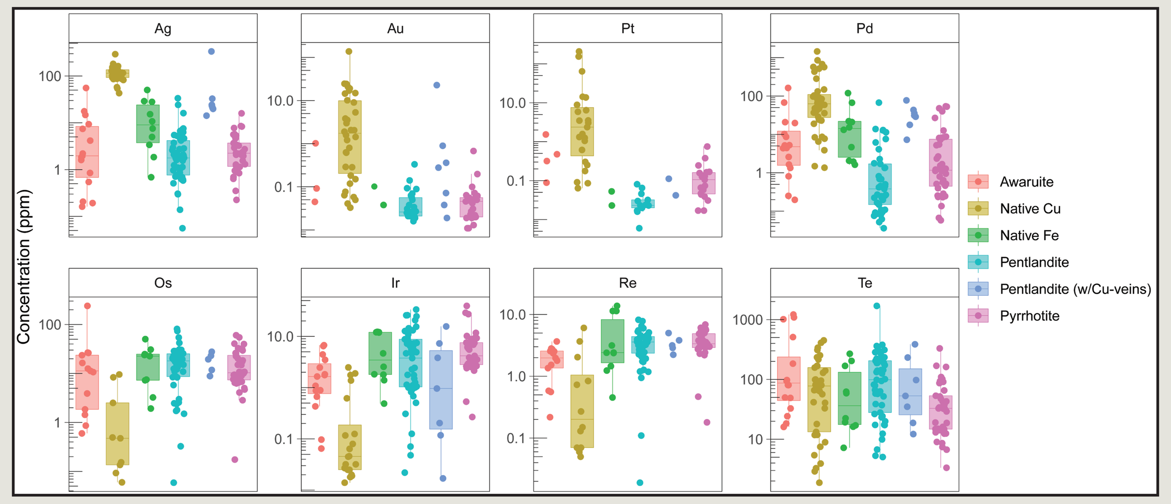


Figure 3. Boxplot summarizing LA-ICP-MS spot results. Concentrations are reported as ppm and processed using Glitter (Griffin et al., 2008).

4. Whole-rock NiS-FA PGE results

Peridotite and pyroxenite samples yield flat and postively-sloped whole-rock PGE profiles, respectively.

Estimated bulk sulphide compositions, calculated using typical modal abundances and median concentrations (LA-ICP-MS spot analyses) of each phase (Fig. 3), overlap with re-calculated whole-rock data for Os-Ir-Pd (Fig. 4d), suggesting that the model sulphide is the dominant host for these elements.

The flat PGE profile of the model sulphide composition and re-calculated whole-rock data are distinct from the expected composition of residual sulphides (Alard et al., 2000) and melt-depleted mantle peridotite, respectively.

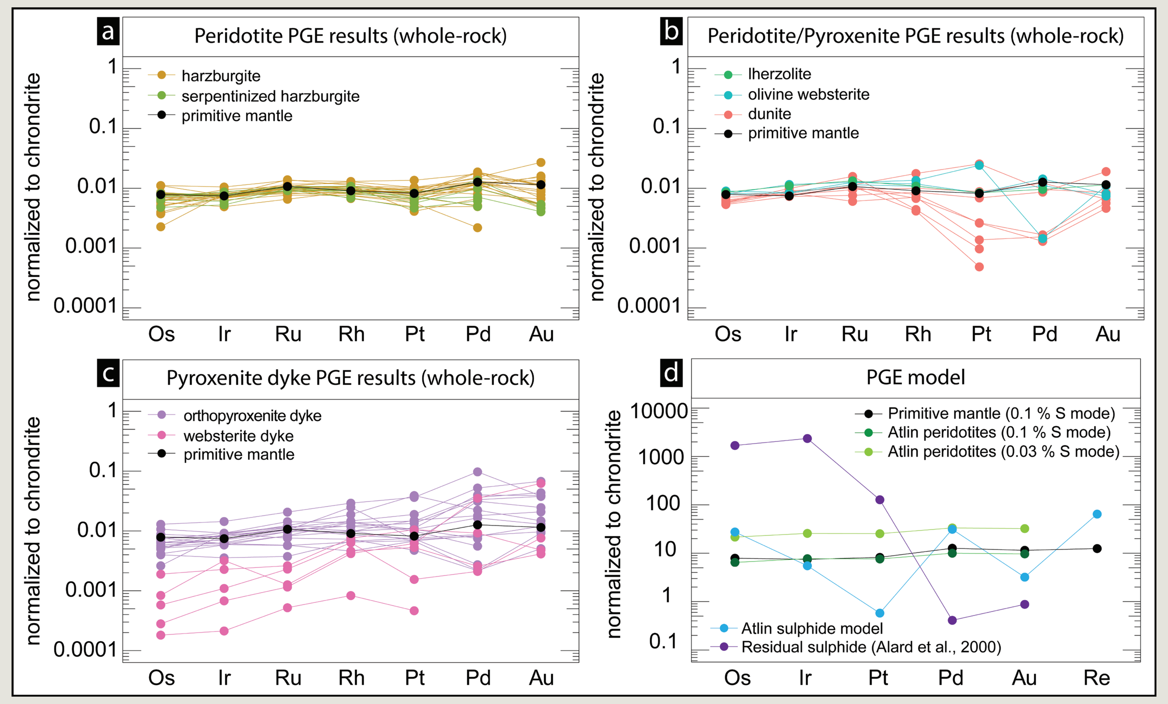


Figure 4. (a–c) Chondrite normalized (Palme and O'Neill, 2014) PGE plots showing new NiS-FA PGE results for Atlin peridotites and pyroxenite. Primitive mantle (Palme and O'Neill, 2014) shown for reference; (d) Median Atlin peridotite (assuming 0.3% and 0.1% modal sulphide abundance) and primitive mantle (Palme and O'Neill, 2014) re-calculated to 100% sulphide.

5. LA-ICP-MS mapping results

Mapping results for IPGE (Os and Ir) are homogenously distributed within the pentlandite, suggesting that these elements were mostly immobile during de-sulphidation reactions (Fig. 5).

Other metals, including PPGE and Au, yield heterogeneous spatial distributions at the micro-scale, suggesting that they may occur as ultrafine (sub-micron) inclusions.

Remobilization of metals within the super-reduced, native Fe-bearing assemblage is highlighted by the spectacular distribution of Cu within the serpentine mesh. However, primitive mantle-like whole-rock PGE results (Fig. 4) suggest that Au and PGE remobilization was mostly limited to the micro-scale.

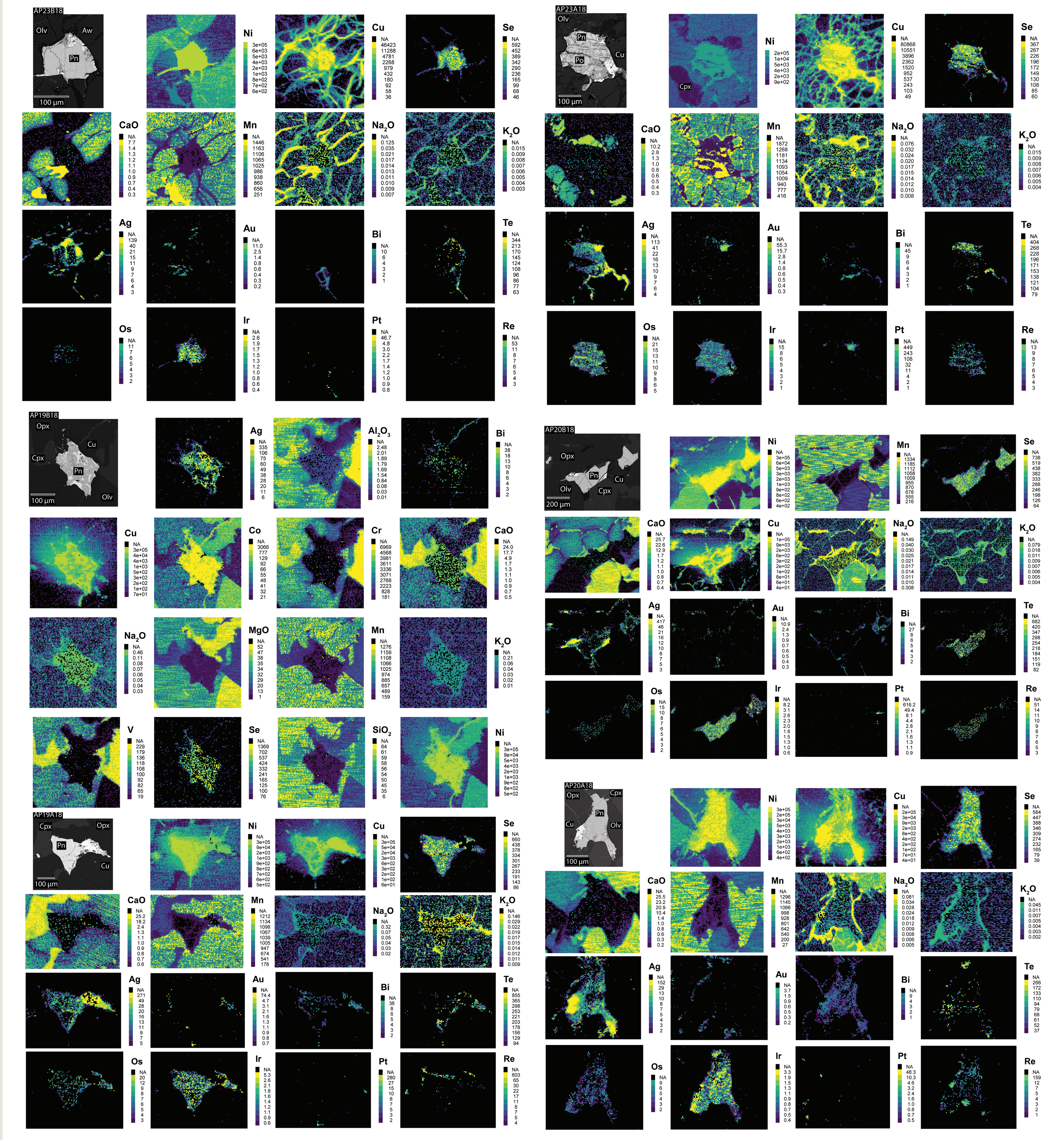


Figure 5. LA-ICP-MS mapping results for coarse, interstitial pentlandite crystals enveloped by awaruite and/or native metals (Cu and Fe). Concentrations are reported in ppm (wt.% for oxide) using decile scaling. Element concentrations below the analytical detection limit are reported as NA. Mapping was completed at the GSC using (4–6 µm spots). Data was calibrated (GSE-1G, Po726; 100% normalization) and processed in R.

6. Machine learning results

LA-ICP-MS mapping coupled with machine learning tools define the mineral phases that control trace elements across multiple maps (Fig., 6). Clustering of log ratio-based PCA scores, was validated and iteratively adjusted until the spatial distribution of the clusters closely matched, as much as possible, the observed mineralogy.

Map pixels classified as pentlandite (pn) are the dominant mineral host for IPGE (Os and Ir). Other elements, such PPGE and Au, are hosted by a variety of mineral phases, including fractures and grain boundaries corresponding to a mixed mineral assemblage (mix).

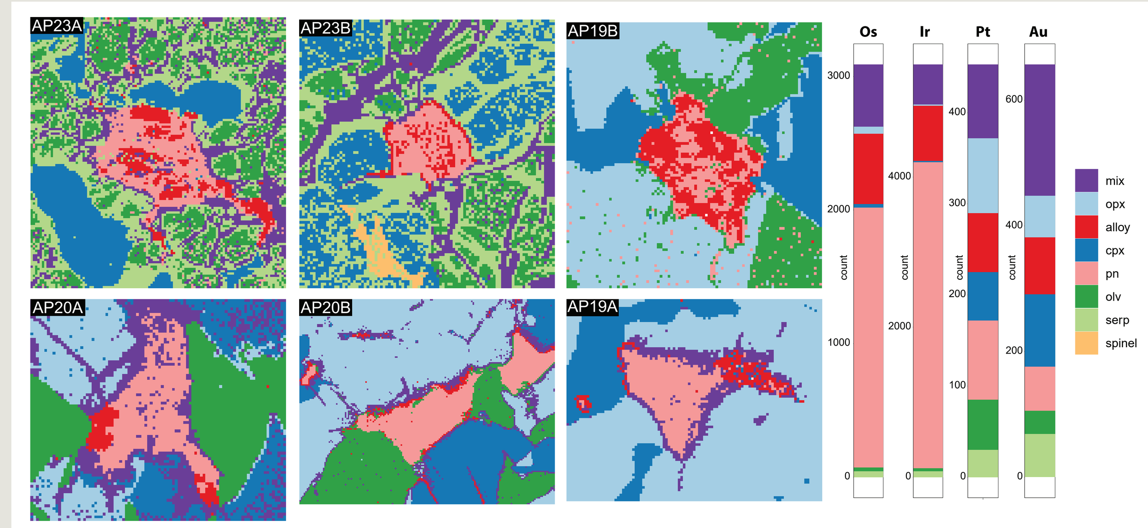


Figure 6. "Model Mineral Maps" showing the spatial distribution of classified pixels. Mineral classifications are based on robust PCA (log-ratio transformed) and a k-means clustering algorithm (R Core Development Team, 2018). Bar plots show counts of pixels that contain ≥ 1 ppm Au, Pt or Ir and are colour coded to modelled mineralogy.

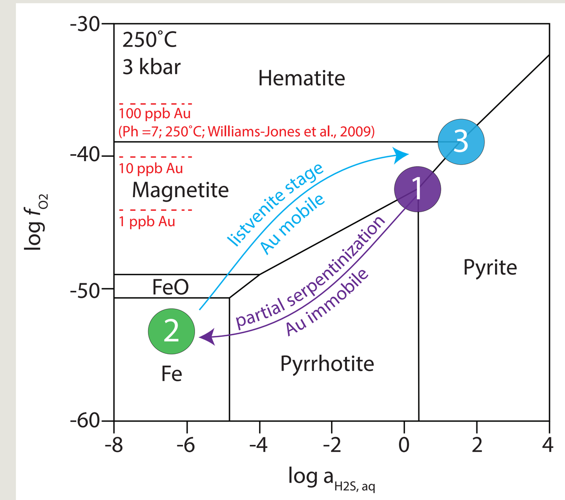
7. Conclusions

Base metal sulphide at Atlin are enveloped by a native Fe-bearing mineral assemblage. Precious metal mobility was limited to the micro-scale during the earliest, super-reduced and S-poor stage of serpentinization (1 to 2; Fig. 7).

Fluids associated with more advanced stages of serpentinization (e.g., listvenite; 2 to 3; Fig. 7) are relatively oxidising and more amenable for the transport of Au (Williams-Jones et al., 2009).

Circulating auriferous fluids ultimately deposit free gold along favourable faults and/or lithologic assemblages during pyrite-bearing sulphidation reactions at ultramafic-hosted gold deposits (2 to 3). Our results suggest that alloys and native metals are the primary host for Au within partially serpentinized mantle peridotite rather than mantle sulphides (1 to 3).

Figure 7. Activity diagram showing the stability of Fe-bearing mineral phases at varying $fO2$ and H_2S at 250°C and 3 kbar. Mineral stability boundaries are taken from Tominaga et al. (2017). Solubility estimates for Au within S-bearing fluids at 250°C and varying oxygen fugacity are shown for reference (Williams-Jones et al., 2009).



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