The Electrochemical Flocculation of Colloidal Gold by Semiconductive P-Type Pyrite at the Brucejack Deposit, NW British Columbia: a Solution to the Bonanza Gold Ore Paradox?

Insights from paragenetic observations, nanoscale imaging of electrum, and joint laser ablation ICP-MS–synchrotron x-ray spectroscopy analyses of pyrite

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I. Background & Research Motivation

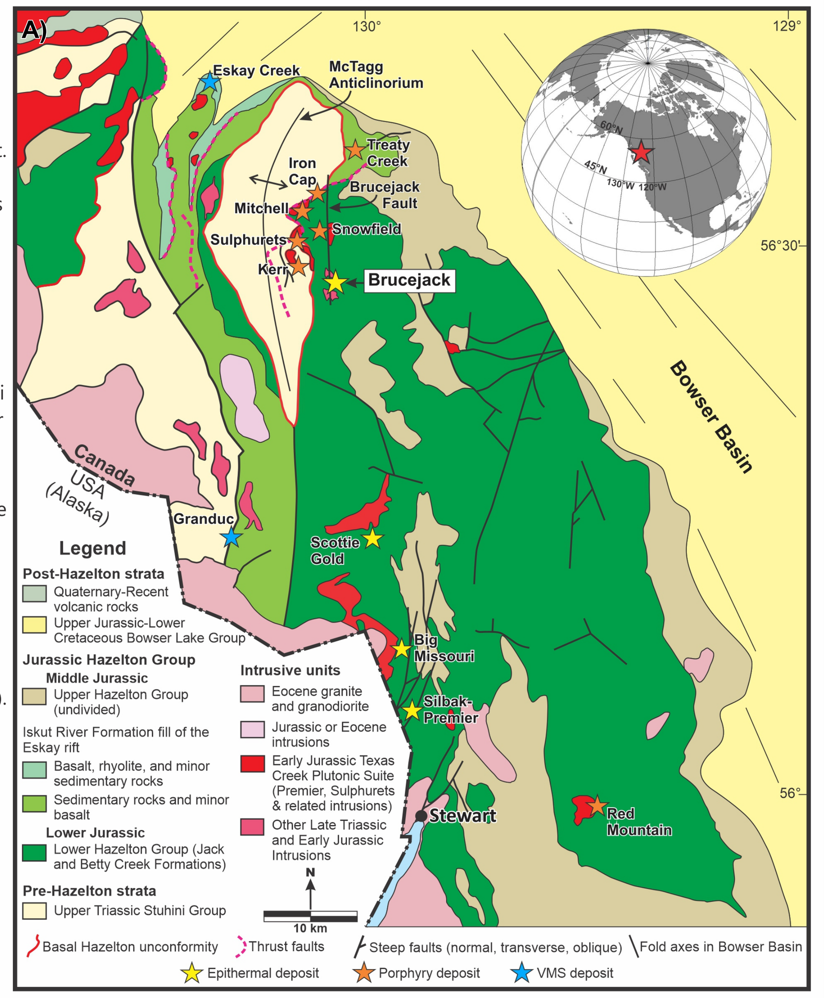
- A growing body of evidence suggests that bonanza-type hydrothermal gold deposits (e.g., Brucejack) are formed by the physical transport of gold as a colloid (i.e., a suspension of ≤ 10 nm, negatively-charged nanoparticles in an electrolyte solution) rather than direct deposition from dissolved, aqueous Au-complexes. While consensus is emerging that colloidal suspensions can explain how gold may be mobilised within hydrothermal systems at concentrations many orders of magnitude greater than those predicted by solubility models, there is little agreement regarding the processes by which colloidal gold suspensions flocculate to produce ultra-high-grade gold occurrences in hydrothermal veins.
- Solution-based models are problematic because laboratory experiments and measurements of active hydrothermal systems have shown that the solubility and concentration of gold in typical ore-forming fluids are exceptionally low. For example, gold concentrations in the fluids responsible for epithermal mineralisation are typically on the order of 10-30 ppb (Simmons & Brown, 2006), which are far too low to explain gold concentrations of 10's of thousands grams per tonne Au in veins in high-grade deposits like Brucejack. The formation of such bonanza-grade veins by direct precipitation of native gold or electrum from the ore fluids would require that individual fractures remain open for unreasonably long periods of time (e.g., >100,000 years) or that fluid fluxes be extraordinary.
- Our study is currently testing plausible models for ore formation at Brucejack, a high-grade epithermal Au-Ag deposit in NW BC, to gain insight into the origin and physicochemical evolution of the deposit, as well as to predict the potential locations of bonanza gold occurrences within its multi-generational network of hydrothermal veins.

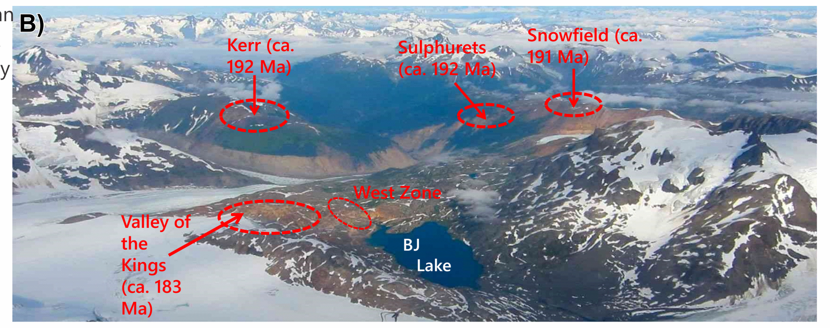
III. Location and Geologic Setting

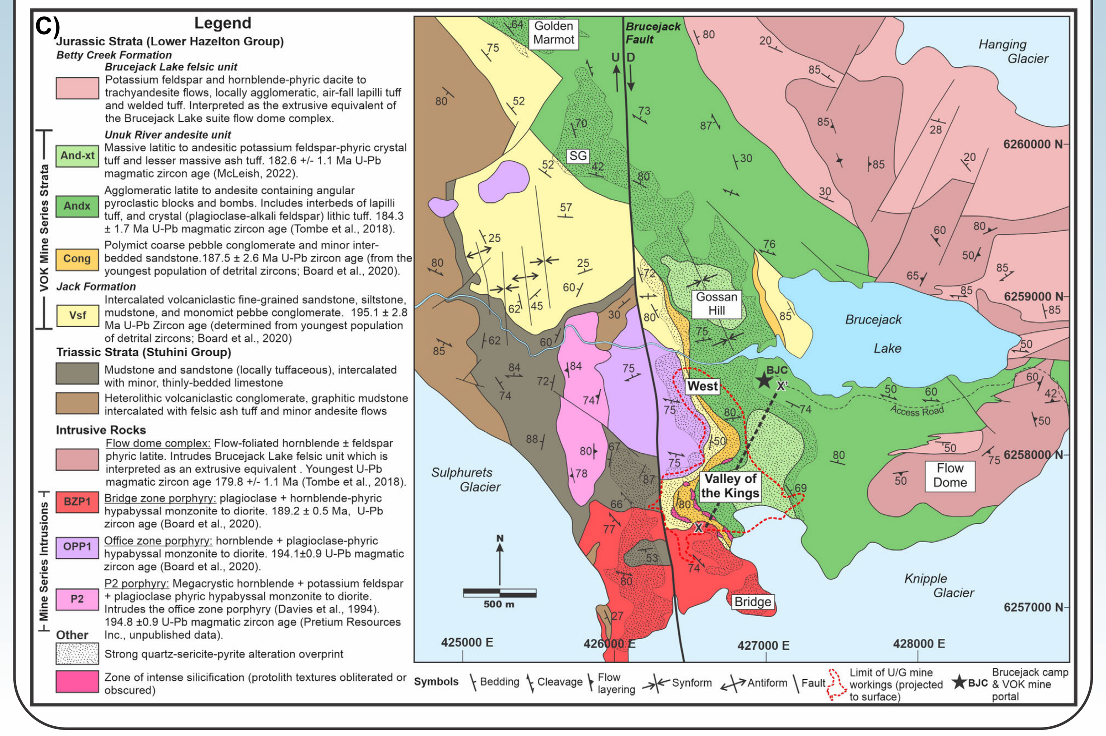
(A): Map showing the location of the Brucejack epithermal Au-Ag deposit in relation to the major deposits of the Stewart-Eskay Creek mining district. Brucejack is hosted within volcano-sedimentary rocks of the Lower Jurassic Hazelton Group on the western margin of the Middle Jurassic Bowser Basin, proximal to the regional-scale unconformity between the Stuhini and Hazelton groups (after Nelson and Kyba, 2014).

(B): Aerial photo of the Brucejack area showing the location of the main mining areas, the Valley of the Kings and West zones, relative to neighbouring world-class Cu-Au porphyry deposits (Kerr, Sulphurets, and Snowfield). Also visible are the well-developed phyllic alteration-related gossans which are characteristic of deposits in the Sulphurets camp.

(C): The geology of the Brucejack area showing main zones of mineralisation (VOK, West, Flow Dome, Bridge, Gossan Hill, and Golden Marmot), which are hosted generally within a strongly sericite-quartz-pyrite altered sequence of hornblende and feldspar-phyric volcanic flows, lapilli tuffs, and volcanic sedimentary rocks of the lower Hazelton Group (after Davies et al., 1994).







II. Key Results

- **Detailed paragenetic observations at Brucejack show that ore-stage epithermal carbonate-quartz-electrum veins commonly host bonanza gold where these veins cross-cut earlier mesothermal pyrite veins. This observation, coupled with the mapping arsenic-rich growth zones in pyrite by laser ablation (LA-) ICP-MS and synchrotron micro X-ray fluorescence (SR-µXRF), offers insight into how such flocculation might occur.**
- **Specifically, we propose that charged surfaces on arsenian pyrite, which behave as p-type semiconductors (due to As substitution in the sulphide structure), promote cationic bridging and electrochemically destabilise colloidal gold suspensions circulating in the epithermal carbonate-quartz veins. This destabilisation triggers flocculation (deposition) of the colloidal gold particles and explains why, at Brucejack, many spectacular gold occurrences appear to have been triggered by the intersection of ore-stage veins with earlier pyrite veins.**
- **This genetic model can be used to predict the potential locations of bonanza gold from the block-modelled distribution of As based on exploration and resource drill data, provided that the source of As anomalies can be confidently attributed to arsenian pyrite.**
- **Compared with standard LA-ICP-MS analyses of pyrite, SR-µXRF can be used to rapidly evaluate the presence/distribution of As in pyrite without the need for making thin sections (measurements can be done directly on drill core). In addition, synchrotron based analyses can determine the speciation of trace elements which is not possible by LA-ICP-MS. Such information is useful in characterising the nanoparticulate vs. lattice-bound nature of the trace element anomaly (e.g. metallic vs. refractory Au).**

IV. Brucejack Valley of the Kings Zone Vein Paragenesis

Hydrothermal veining in the Valley of the Kings comprises six stages, including two pre-mineral stages (Stage I and II), three syn-mineral stages (III-V) and one post-mineral stage (VI). Detailed petrographic, mineral chemistry, and fluid inclusion studies have interpreted the pre- and syn-mineral stages to have formed in a porphyry/mesothermal environment, whereas syn-mineral stages are characteristic of upper-crustal, low- to intermediate-sulphidation epithermal conditions (Tombe et al. 2018; Board et al., 2020; McLeish, 2022). The post-mineral stage likely formed during mid-Cretaceous contractional deformation associated with development of the McTagg anticlinorium / Skeena fold belt.

Stage I: Ductilely deformed, variably oriented, locally discontinuous pyrite-quartz ± calcite veins with sericite and weak chlorite alteration halos. Abundance can typically be corelated with wallrock phyllic alteration intensity.

Stage II: White to translucent, often discontinuous, microcrystalline quartz veins. Occurrence is generally limited to strongly silicified rocks.

Stage III: Electrum-bearing quartz-calcite ± dolomite ± sericite veins, which typically are sheeted (Stage IIIa), but also display dm- to m-scale brecciated (IIIb) and stockwork morphologies (IIIc).

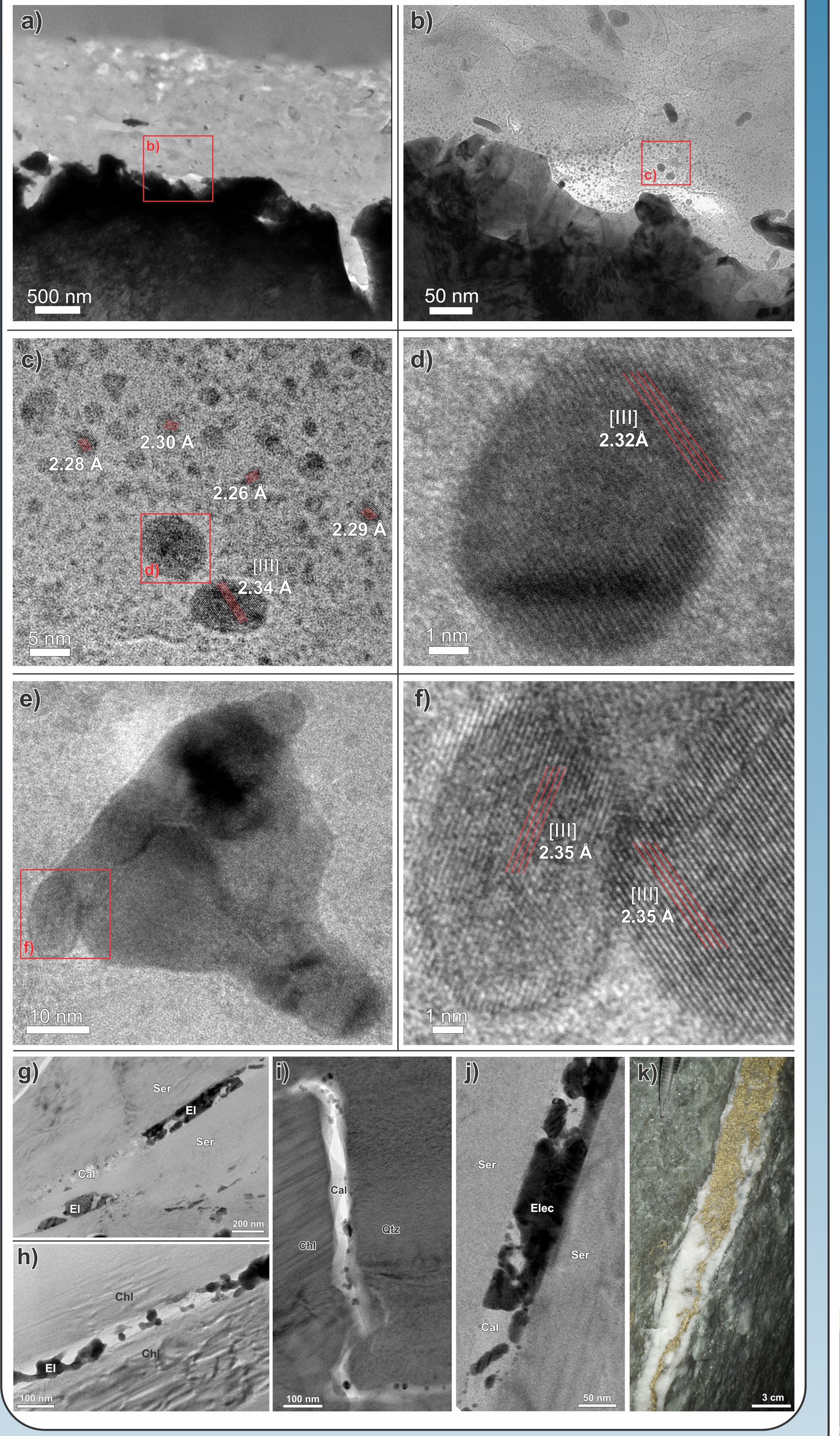
Stage IV: Sub-planar to uncommonly anastomosing quartz ± calcite veins containing base metal sulphides, Ag-sulphosalts, and Ag-rich electrum. See paragenetic table (lower right) for mineralogical detail.

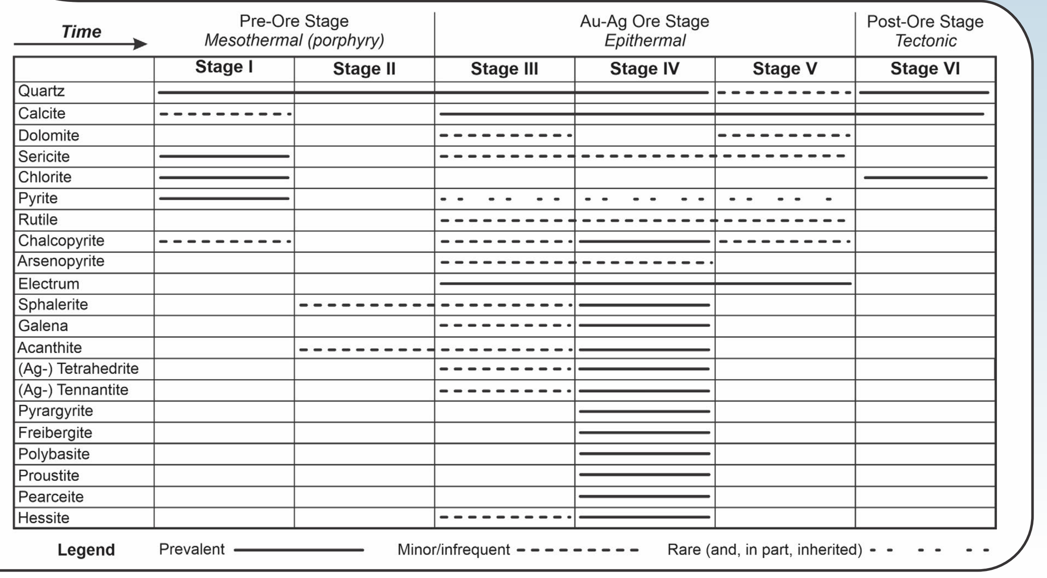
Stage V: Sub-planar to planar carbonate ± quartz veins locally containing abundant grey, and less frequently, orange-coloured calcite, and electrum.

Stage VI: Shallow-angle quartz veins with very rare, remobilised mineralisation filling thrust fault planes and contractional shear zones. Also found as barren, white quartz tension-gash veins with adjacent chlorite.

V. Evidence for Colloidal Transport & Flocculation of Gold

(A-F): Transmission Electron Microscopic (TEM) images of mineralised Stage III veins at Brucejack reveal the presence of ~ < 1 to 10 nm wide spheres of electrum (A & B (low-magnification) and C-F (high-resolution)). The atomic lattice fringe spacing within these spherical nanocrystals varies between 2.2 and 2.4 Å (C & D), which is consistent with the lattice spacing for electrum. Larger particles (E & F) display multiple lattice orientations (red lines) suggesting that they may have formed through the flocculation of numerous, smaller nanocrystals. **(G-K):** In a Stage V vein sample, individual and flocculated electrum nanoparticle masses can be seen clogging nano-scale calcite veins (G-J); (K) photo of electrum mineralisation from underground workings at Brucejack showing near-identical textures of massive electrum at the marco-scale (McLeish et al., 2021).

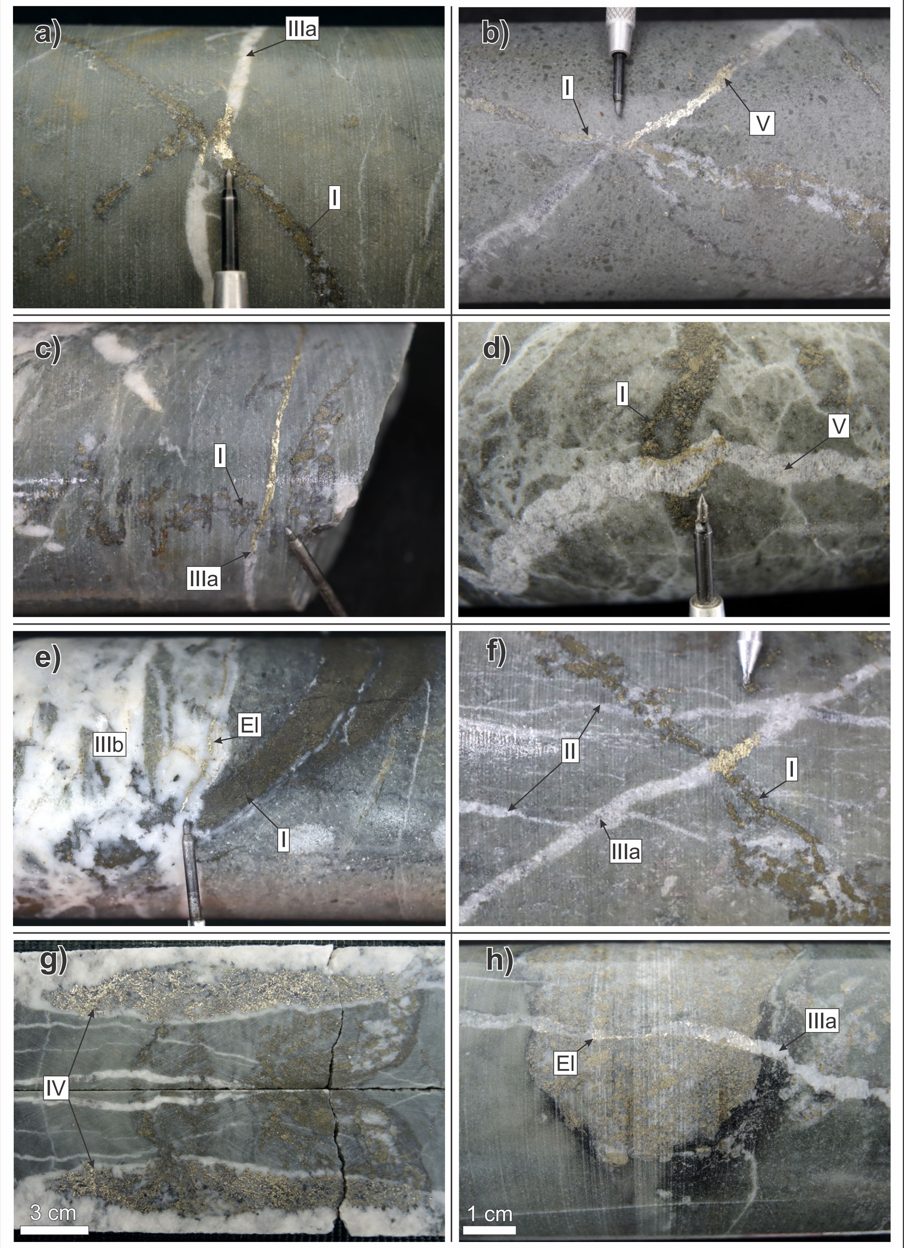




VI. Early Pyrite-Electrum 'Trigger' relationship

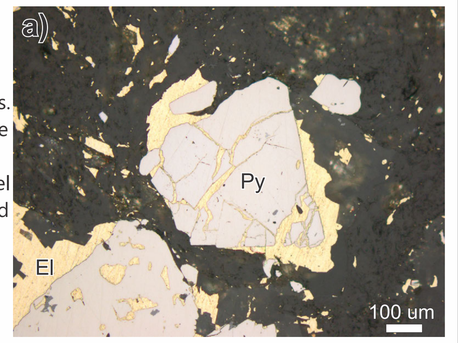
Macro-scale observations

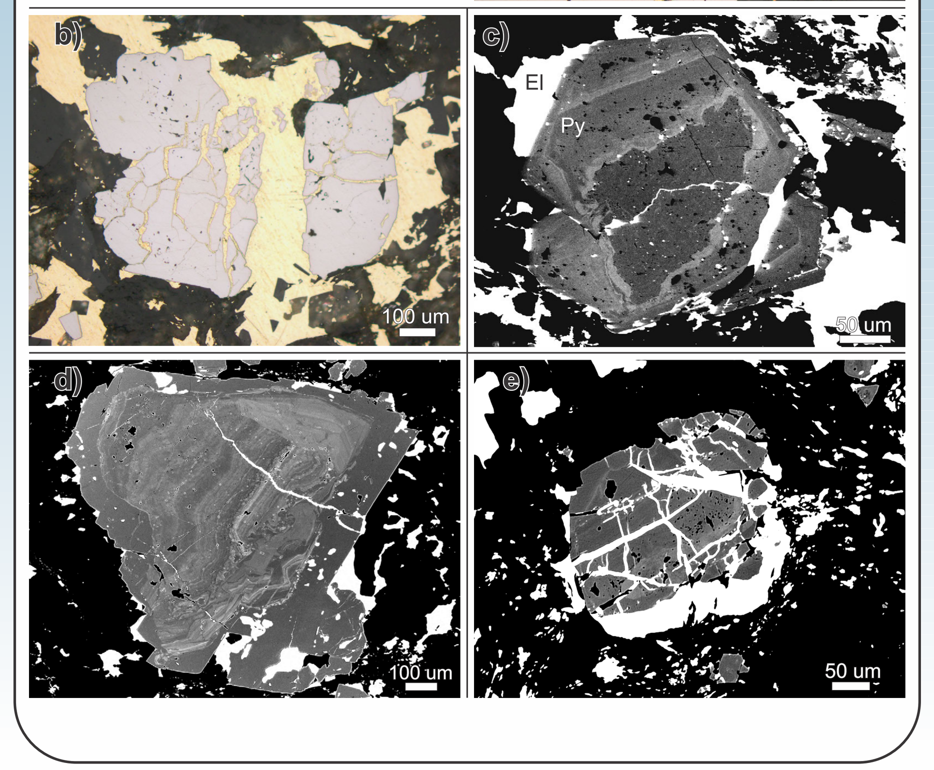
(A-F): Representative drill core photographs illustrating the close spatial relationship between bonanza gold occurrences in Stage III-V veins and Stage I pyrite veins. The intersection of the Au-Ag nanoparticle-bearing epithermal carbonate-quartz veins with the earlier pyritic veins appears to have triggered the flocculation Au-Ag nanoparticles, resulting in the development of high-grade electrum mineralisation at the intersection sites. **(G & H):** Preferentially pyritised conglomerate/ agglomerate (cong) clasts in phyllically-altered wallrock display a similar trigger relationship with electrum.



Micro-scale observations

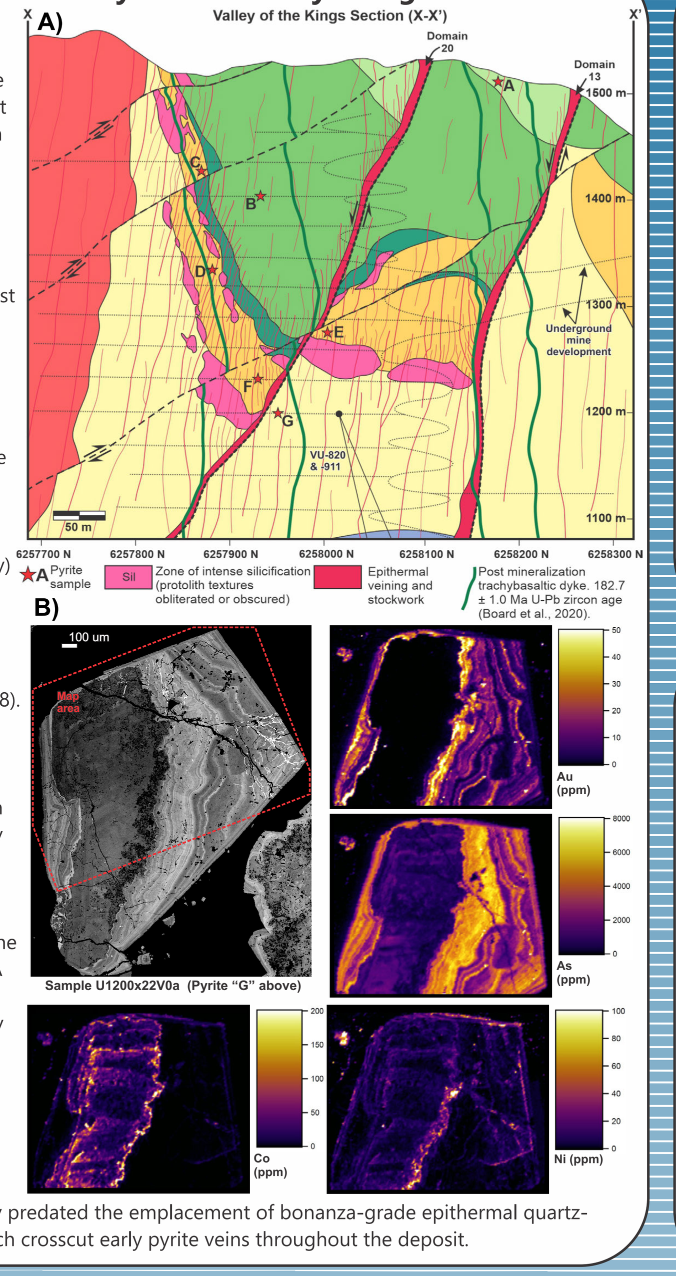
(A & B): Reflected light photomicrographs of electrum filling fractures and nucleating on the surface of pyrite in Stage III (A) and V (B) veins, proximal to intersections with Stage I pyrite veins. Based on the fractured and disaggregated nature of the pyrite grains and similarities in their trace element zonation patterns to Stage I pyrite (Panel VIII, right), they are interpreted as being inherited from Stage I veins. **(C-E)**: BSE images of pyrite and electrum from Stage III (C), Stage IV (E) and Stage V (F) veins showing multi-generational growth zonation patterns cut by electrum.





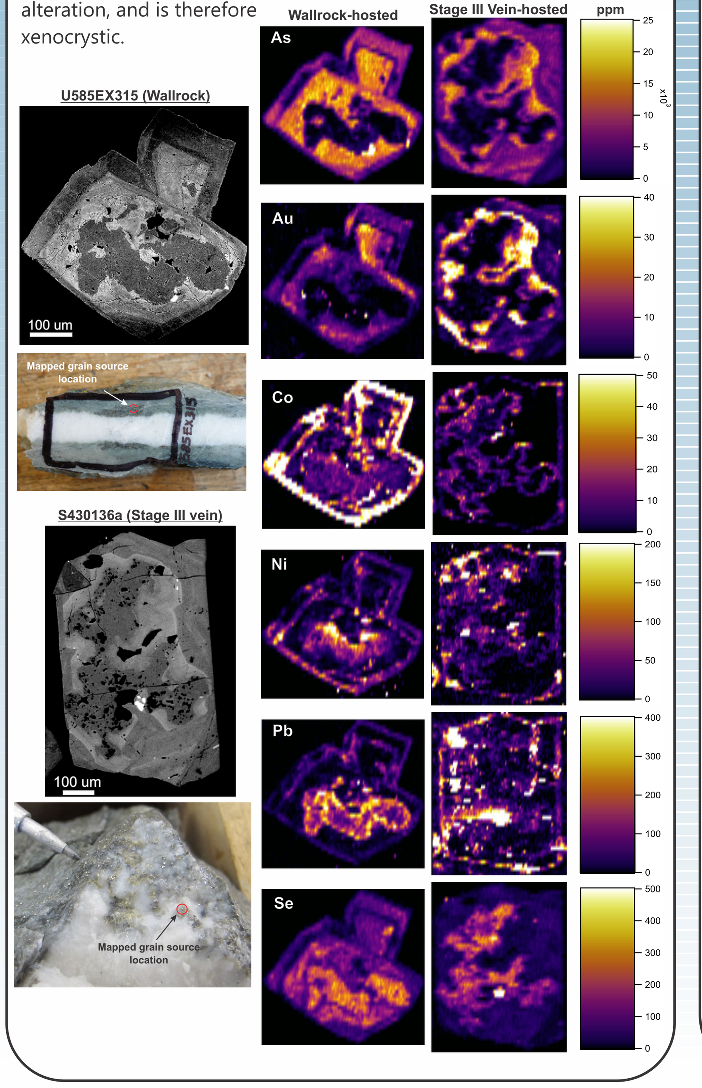
VII. LA-ICP-MS Pyrite Chemistry - Stage I Veins

(A): Geologic cross-section through the Valley of the Kings zone of the Brucejack deposit (see Panel III for section trace) showing the location of Stage I vein pyrite samples mapped compositionally by LA-ICP-MS. All mapped grains, regardless of host rock lithology, display chemical zonation patterns similar to **(B)** sample U1200x22V0a see McLeish, 2022, for complete results). These data suggest that the early Stage I vein fluids were of magmatic hydrothermal (porphyry) origin, as indicated by pyrite cores that are cubically zoned and relatively rich in Co and Ni (cf. Sykora et al., 2018). The Co-Ni pyrite cores are mantled by oscillatory, locally colloform pyrite growth zones that are relatively rich in Au and As and record an evolution to epithermal-type fluids during telescoping of the hydrothermal system. A narrow, outer Co-Ni growth zone commonly mantles the As-Au oscillatory zones in the early pyrite crystals, indicating a possible localised reversal in telescoping. All of this hydrothermal activity predated the emplacement of bonanza-grade epithermal quartz-carbonate veins, which crosscut early pyrite veins throughout the deposit.



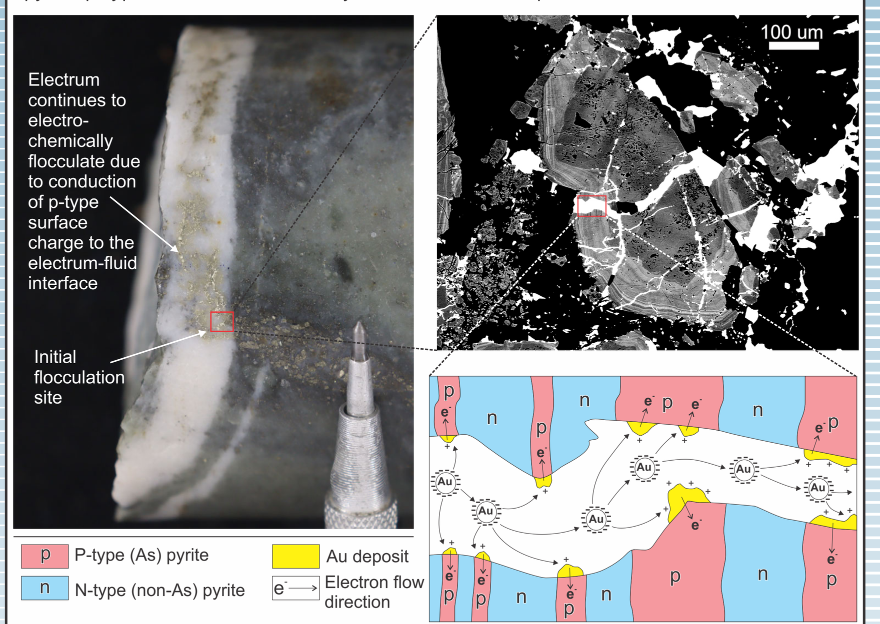
VIII. LA-ICP-MS Pyrite Chemistry - Wallrock vs. Bonanza Epithermal Veins

Below: A comparison between the intracrystalline trace element growth zonation patterns of wallrock- vs. bonanza epithermal vein-hosted pyrite. Stage III vein-hosted pyrite displays chemical and textural growth zoning indistinguishable from that in the wallrock, indicating that the vein-hosted pyrite was inherited from earlier, wallrock-hosted phyllic alteration, and is therefore xenocrystic.



IX. Model: Electrochemical Flocculation by P-Type Pyrite

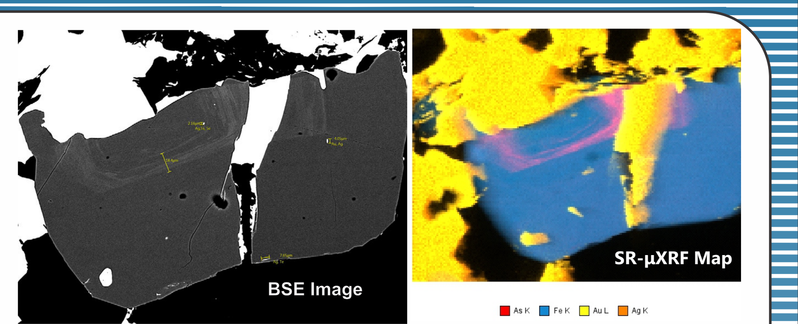
The intimate spatial relationship between later electrum and earlier pyrite offers insight into a mechanism for the formation of bonanza gold at Brucejack. The ability of pyrite to electrochemically attract and, through absorption and/or reduction, precipitate gold on crystal surfaces has been widely documented in laboratory experiments (e.g. Hyland & Bancroft, 1989; Mikhlin & Romanchenko, 2007). This electrochemical attraction is due to the semiconductive properties of pyrite (Skey, 1871), which can be classified by its n-type (electron donor) or p-type (e- acceptor) characteristics (Shuey, 1975). These characteristics are controlled by trace element impurities in the sulphide structure and, in the case of pyrite, p-type behaviour is caused by the addition of acceptor cations such as As.



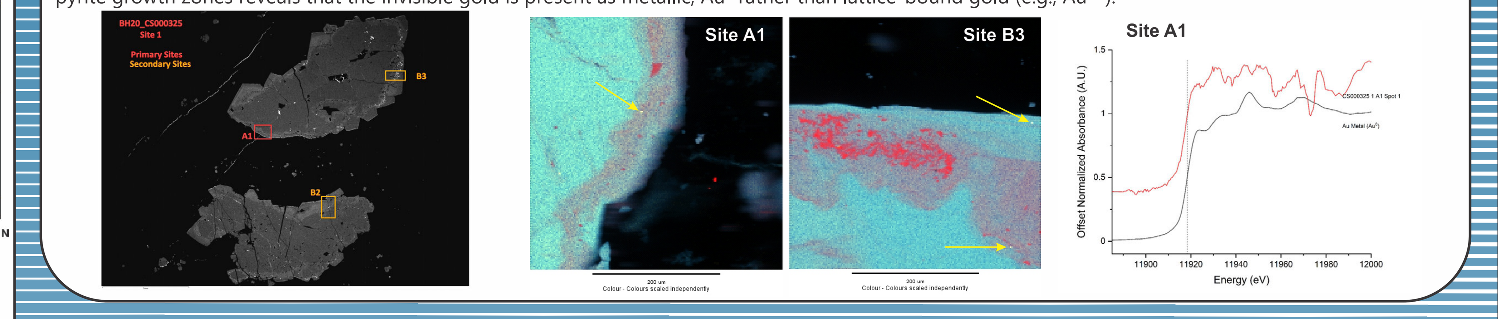
Above: We propose a model for the electrochemical flocculation of colloidal gold suspensions by pre-existing arsenian pyrite at Brucejack (illustrated by a drill core photograph and BSE image of the pyrite-electrum 'trigger' relationship). In this model, colloidal suspensions of gold (electrum) in a hydrothermal fluid are attracted to p-type arsenian pyrite surfaces, whereby positive surface charges of the pyrite overcome the negative surface charges of gold nanoparticles, and through cationic coagulation, or 'bridging', cause flocculation of the colloid. The flocculated gold is deposited on p-type arsenian pyrite surfaces. Owing to the high conductivity of gold, the p-type electronic characteristics of the pyrite surface that initially induced flocculation would be transmitted to the gold-fluid interface during gold deposition (Starling et al., 1989), thereby inducing further flocculation of the gold colloid and ultimately gold (electrum) crystal growth beyond the original pyrite surface. This electrochemical flocculation model for bonanza gold deposition explains why, at Brucejack, many spectacular gold occurrences appear to have been triggered by the intersection of ore-stage veins with pyritic Stage I veins.

X. SR-µXRF Pyrite Chemistry - Bonanza Epithermal Veins

Right: High resolution synchrotron micro X-ray fluorescence (SR-µXRF) mapping of pyrite hosted in high-grade epithermal veins confirms that the early pyrite in contact with electrum contains oscillatory arsenian zones similar to those imaged and mapped in Stage I veins. Note that it is typically not possible to map pyrite surrounded by bonanza concentrations of electrum by LA-ICP-MS due to Au contamination of the laser ablation cell. The SR-µXRF map also resolves finer arsenian/ auriferous banding compared to LA-ICP-MAS (2 vs. ~20 µm resolution).

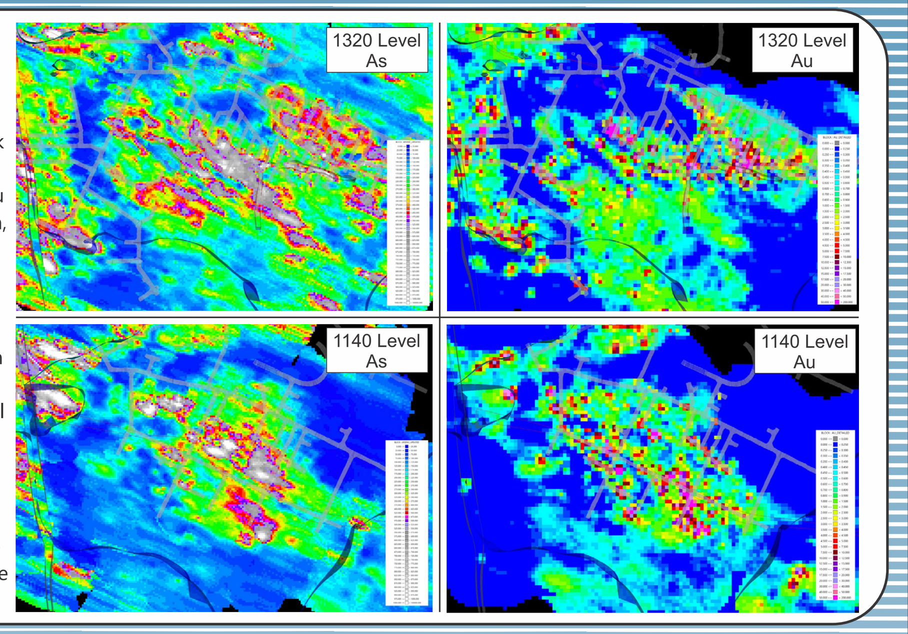


Below: X-ray absorption near-edge structure (XANES) spectroscopy analysis of invisible gold (yellow arrow) contained within, and just outside, the arsenian pyrite growth zones reveals that the invisible gold is present as metallic, Au^0 rather than lattice-bound gold (e.g., Au^{1+}).



XI. As-Au Association in the Valley of the Kings Block Model

Right: Comparisons between block modelled As and Au concentrations for the 1320 and 1140 levels of the Brucejack mine, VOK zone (Tetra Tech, 2020). A clear correlation is evident between areas with elevated As (> 200 ppm) and Au (> 1 ppm). High-grade blocks (> 5 ppm Au) lie exclusively in, or along the margins of, blocks having As concentrations of > 500 ppm. These associations occur irrespective of host rock lithology (e.g., the 1320 level lies largely within agglomeratic andesite whereas the 1140 level lies largely within sedimentary rocks). We submit that the early arsenian pyrite-electrum 'trigger' relationship, which is a direct manifestation of the electrochemical flocculation of colloidal gold suspensions by semiconductive p-type pyrite, is responsible for this As-Au relationship in the block model. Given the challenges of accurately modelling Brucejack's nuggety, bonanza-type Au mineralisation, As distribution data is being integrated into mine development planning to help optimise stope designs and thereby potentially improve Au recoveries.



XII. Concluding Remarks

- Bonanza-style gold mineralisation at Brucejack commonly occurs as coarse (cm- to dm-scale) dendritic clots of electrum in epithermal carbonate-quartz veins stages with generally low to very low native sulphide mineral content. Although this simple vein mineralogy explains the free-milling, high-value nature of the ore, it also poses a challenge for explaining gold transport and deposition using solution-based models. Considering that gold is transported in solution typically as a bisulphide complex under low- to intermediate-sulfidation epithermal conditions (Williams-Jones et al., 2009), the overall paucity of sulphide minerals in textural equilibrium with electrum is problematic for explaining the hyper-enrichment of gold in the deposit.
- Detailed petrographic analyses show that epithermal carbonate-quartz veins at Brucejack commonly contain bonanza gold where these veins cross-cut earlier pyrite veins. This relationship, when considered together with LA-ICP-MS and SR-µXRF trace element data for pyrite from early Stage I veins, and TEM imaging results from mineralised Stage III to V veins, indicates that bonanza gold occurrences formed through electrochemically-triggered flocculation of colloidal gold suspensions by interaction with semiconductive p-type arsenian pyrite.
- Beyond understanding the controls on mineralisation in a deposit-specific context, our findings from Brucejack offer a new model for the formation of bonanza gold veins. This model builds on previous colloidal Au studies by proposing a novel mechanism for gold colloid flocculation, namely, the deposition of bonanza gold in hydrothermal veins by sulphide mineral-induced cationic coagulation of Au nanoparticles. This mechanism offers a unique explanation for why, in many deposits, bonanza gold forms paragenetically late compared to sulphide minerals. Moreover, given that it does not require phase separation (boiling) or the existence of steep physicochemical gradients, this mechanism may explain the occurence of bonanza gold, and possibly other metals, in a variety of other deposit types.

XIII. Acknowledgements & References

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