Calc-silicate Alteration and Ore Characterization, ASARCO Mission Complex, Pima County Arizona: Implications for the Optimization of Molybdenum Recovery

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Klondike Mountain Geological Services

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Introduction

- Porphyry-related hydrothermal systems are some of the most important Cu ± Mo deposits worldwide
- In SW US, a vast majority of these systems occur in carbonate-rich sedimentary host rocks, known as skarns
- Skarn deposits are economically important ore deposits
  - Complex mineral assemblages present many challenges to ore processing and mineral recovery at many skarn deposits worldwide
  - Identifying and understanding these challenges is essential to the success of taking a greenfield exploration project into production and laying the groundwork for a profitable operation

Objectives

- The primary objective of this study was to increase understanding of calc-silicate alteration and Cu-Mo mineralization zonation in three different parts of the ASARCO Mission Complex:
  - San Xavier South
  - East Mission
  - Mission-Pima ("Pima South")
- The secondary objective of this study was to document alteration occurring with Mo to help with molybdenum processing optimization
- The ultimate goal: Assist with future ore control and processing

How the objectives were met

Implement a modified Anaconda method of mapping calc-silicate alteration and sulfide mineralogy to:

1. Understand the [possible] ore body
2. Highlight favorable exploration targets
3. Identify areas for possible expansion at current operations
4. Identify future [or current] production challenges
5. Assist in optimizing recovery of sulfide ore minerals

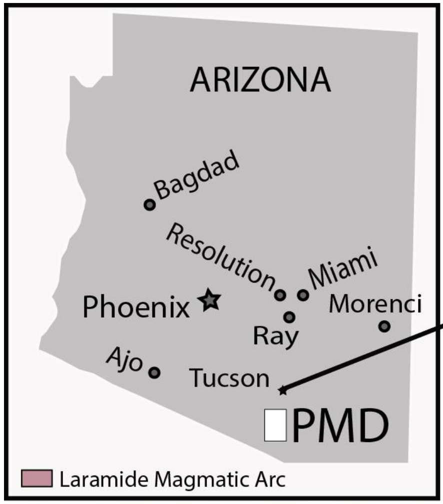
Use electron microprobe analysis to:

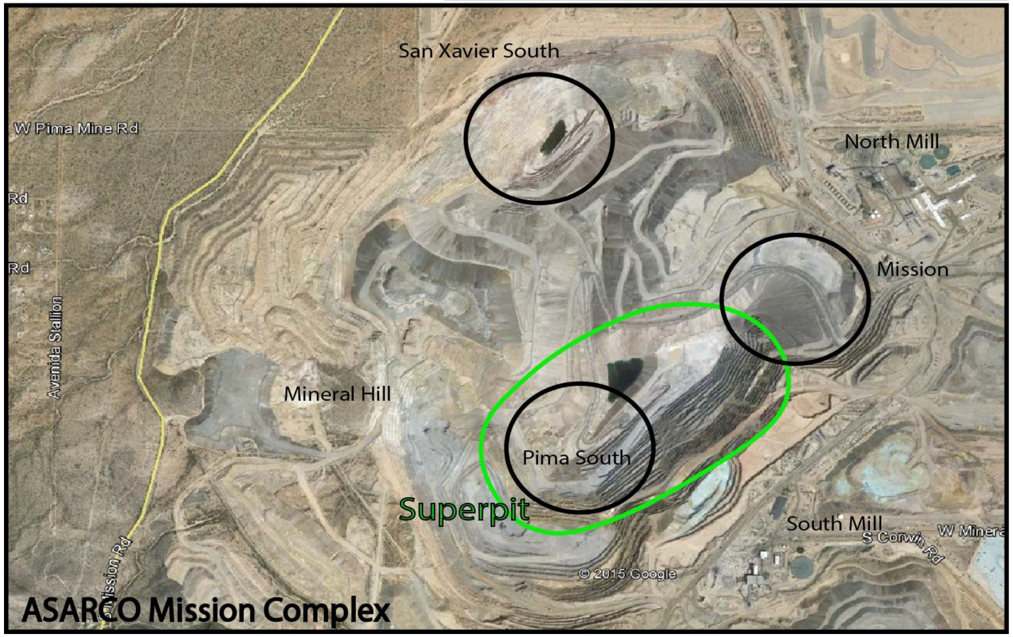
1. Identify protolith in structurally complicated areas
2. Identify the composition of MoS_2 to illuminate possible processing issues prior to production or at current operations

Location and Geologic Setting

Pima Mining District (PMD) ~ 30 km southwest of Tucson

ASARCO Mission Complex is located in the PMD on the west side of I-19





Reserves:

303.4 Mt Cu @ 0.42% TCu *

Annual production:

~ 121.8M lb. Cu *

~ 859,000 oz. Ag *

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Pima Mining District & Mission History

- 1850’s: Small Pb-Zn-Ag ± Cu deposits
- 1950: United Geophysical (Union Oil) magnetometer survey campaign
- 1954: Discovery of the Mission deposit
- 1959: Stripping at East Mission
- 1961: Production – milling sulfide ore
- 1973 to 1978: Vat leaching Cu-oxide San Xavier North & South
- 1985: Consolidation began
  - Pima (Banner Mining Company)
  - Eisenhower, Mineral Hill (Anaconda)
- 1996 to 2003: Mission Underground
  - High grade Cu-sulfide ore

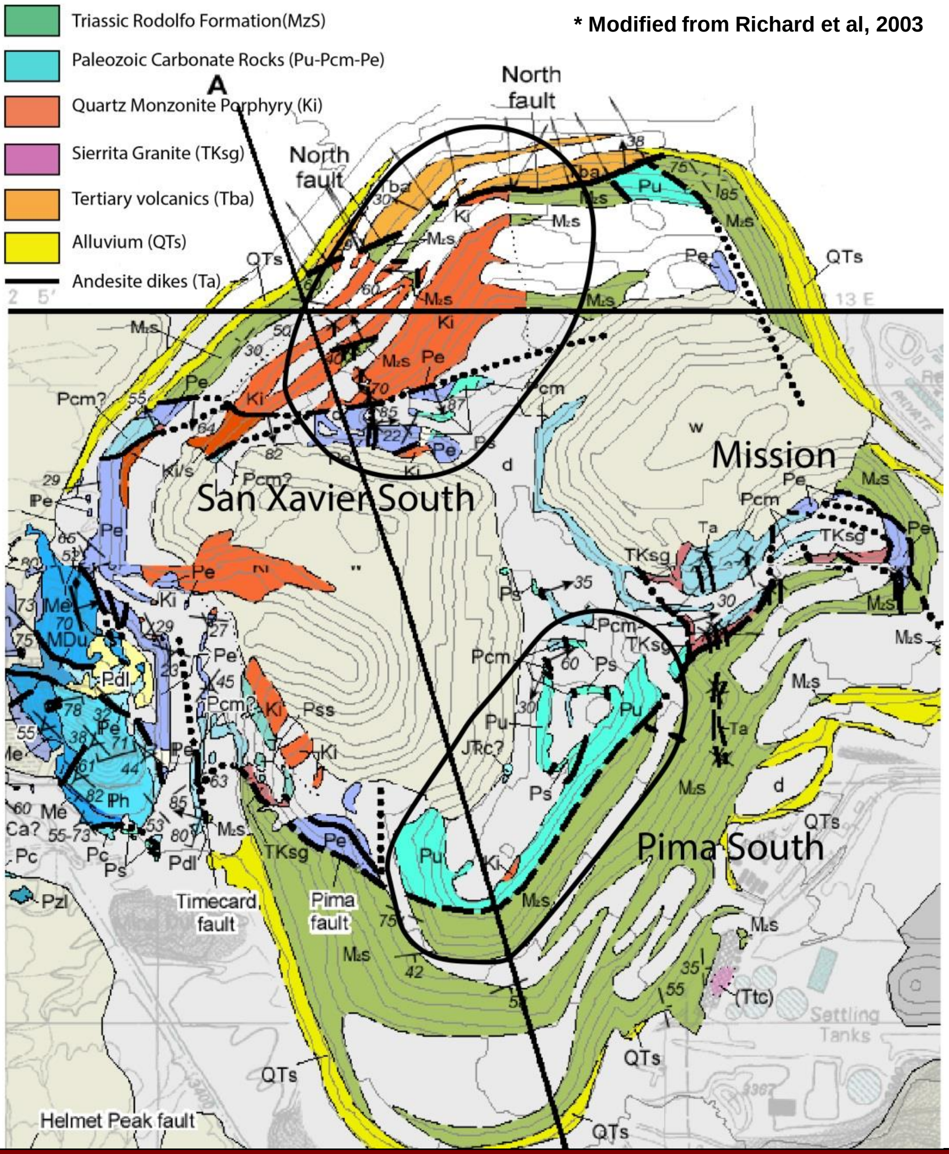
Previous Work – Regional – Pima Mining District

- Since the 1920s, many geological studies have been carried out in the Pima mining district.
  - Structure/Ore deposits of the Eastern Sierrita Mountains (Lacy, 1959; Cooper (1960)
  - Structural features - Extensional tectonics (Richard et al., 2003; Stavast et al., 2008)
  - Tectonic history and ore genesis (Titley, 1982)
  - Description of intrusive bodies related to mineralization (Mauger, 1966)
  - Calc-silicate alteration [Twin Buttes]: Gordon, 1922; Brown, 1926; Barter and Kelly, 1982; Rauschkolb, 1983
  - Pb-Zn-Ag +/- Cu satellite deposits (Whitcomb, 1948; Houser, 1949)

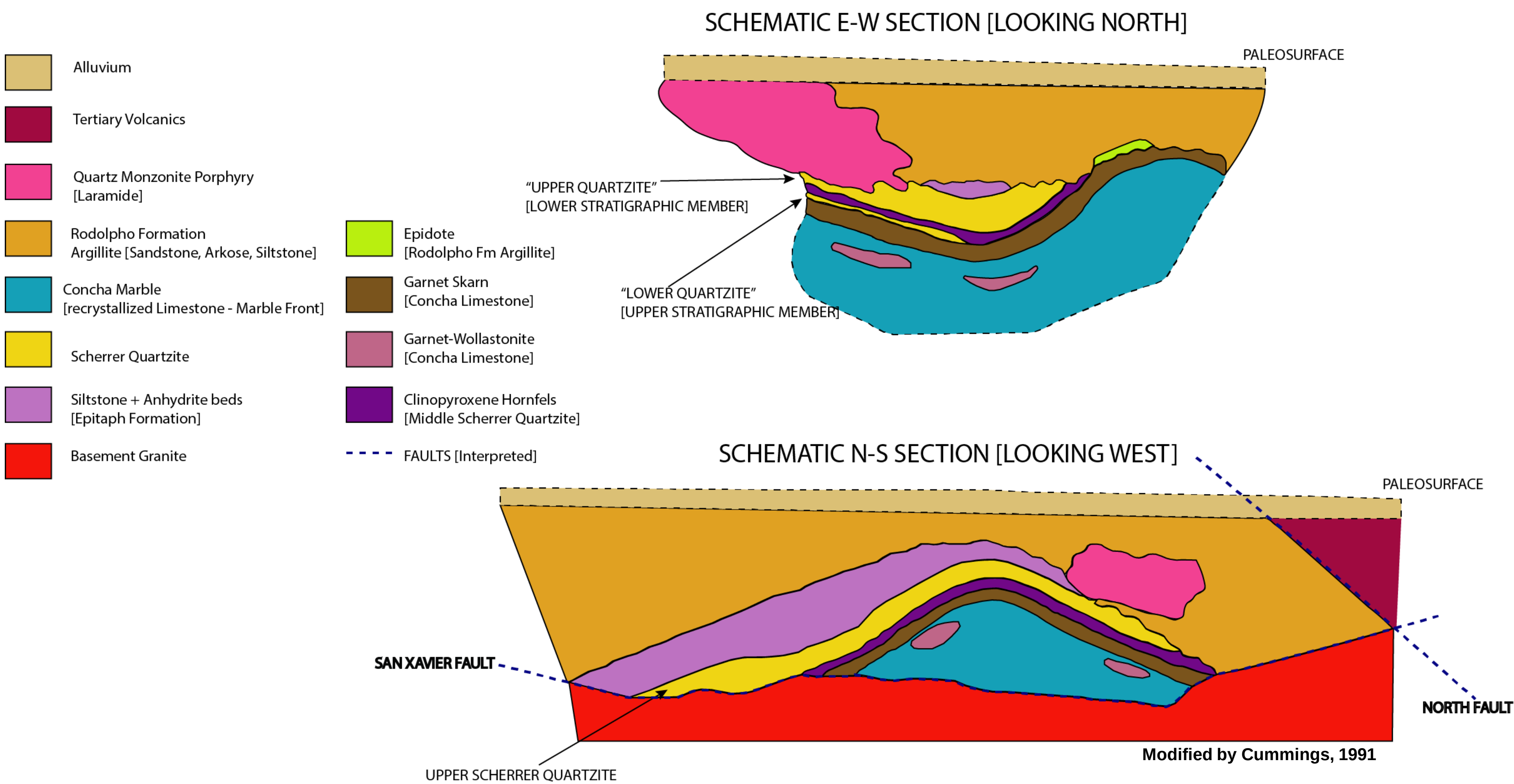
Previous Work – Mission

- ASARCO Mission Complex first described by Eckel (1930) with his study of the geology and ore deposits of Mineral Hill
  - Geology, Structure, Mineralization (Richard and Courtright, 1959)
  - Regional Studies (Cooper, 1960; 1973)
  - Description of Main Mission Ore Body (Kinnison, 1966)
  - Geology, Alteration, Mineralization (Gale, 1965)
  - Geology of the Pima Mine (Himes, 1972)
  - Updated Geology/Structure/Alteration/Mineralization (Jansen, 1982)
  - Key Alteration/Mineralization Features and Correlations between Twin Buttes-Mission-Pima (Einaudi, 1982)
  - Mineral Hill Stratigraphy Studies through Normative Mineral Composition Analysis and Neural Networks (Williamson, 1993)

General Geology



General Cross-section



Methods – General Alteration Study

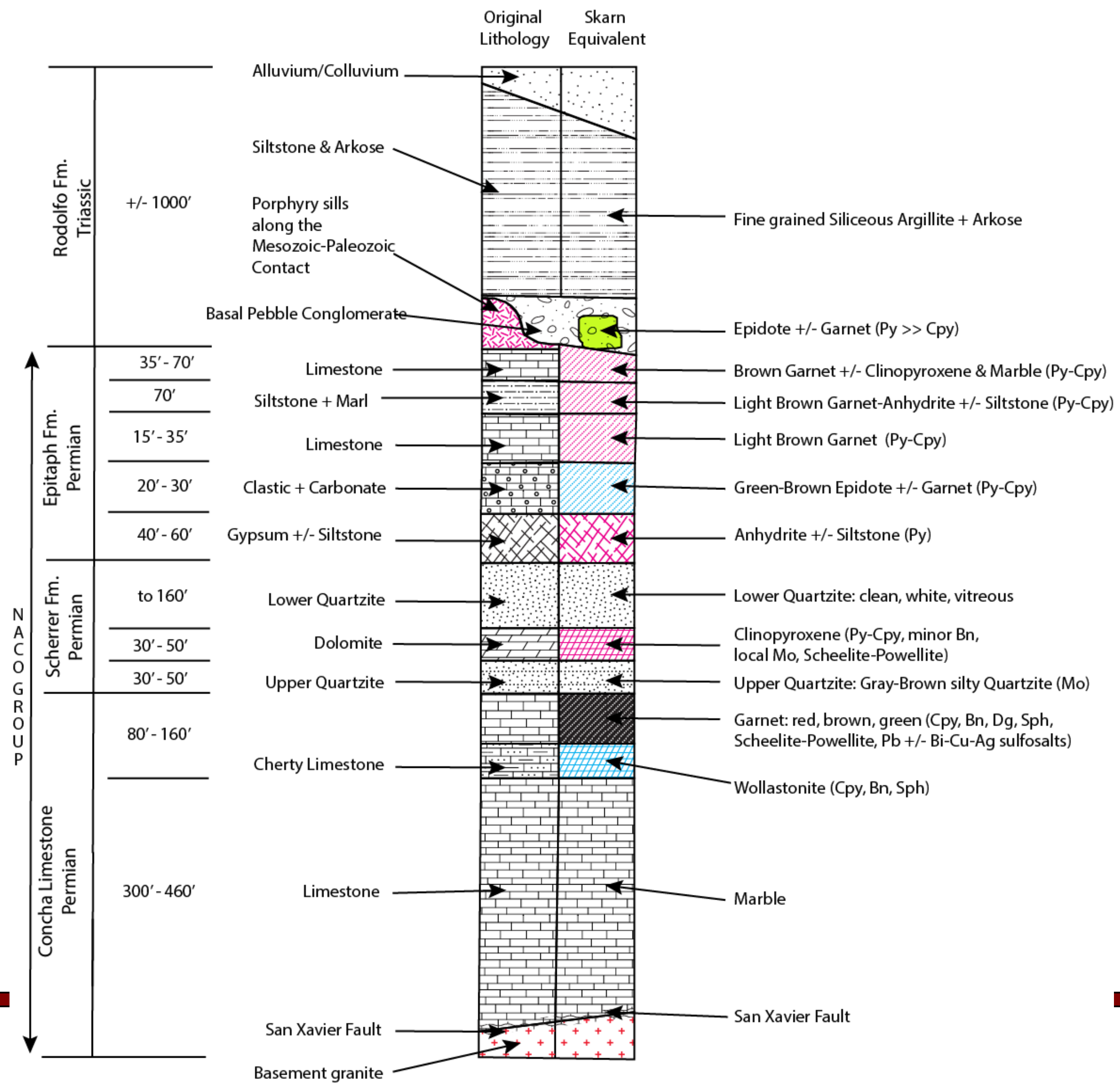
1) Re-log historic drill core and construct cross-sections that highlight alteration and associated mineralization

2) Sent representative samples of the several major alteration types from historic drill core out for thin section to perform petrography (56 samples)

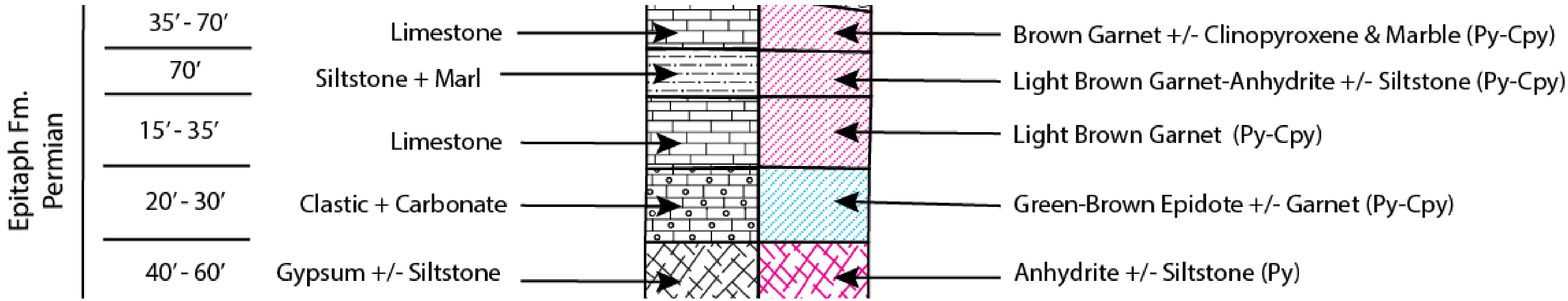
3) Electron microprobe analysis (CAMECA SX100)

   - Multi-element analysis of calc-silicate gangue alteration minerals

Stratigraphy



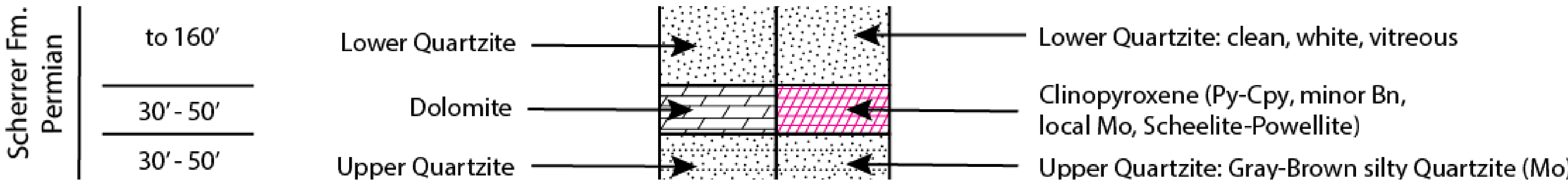
Epitaph Formation

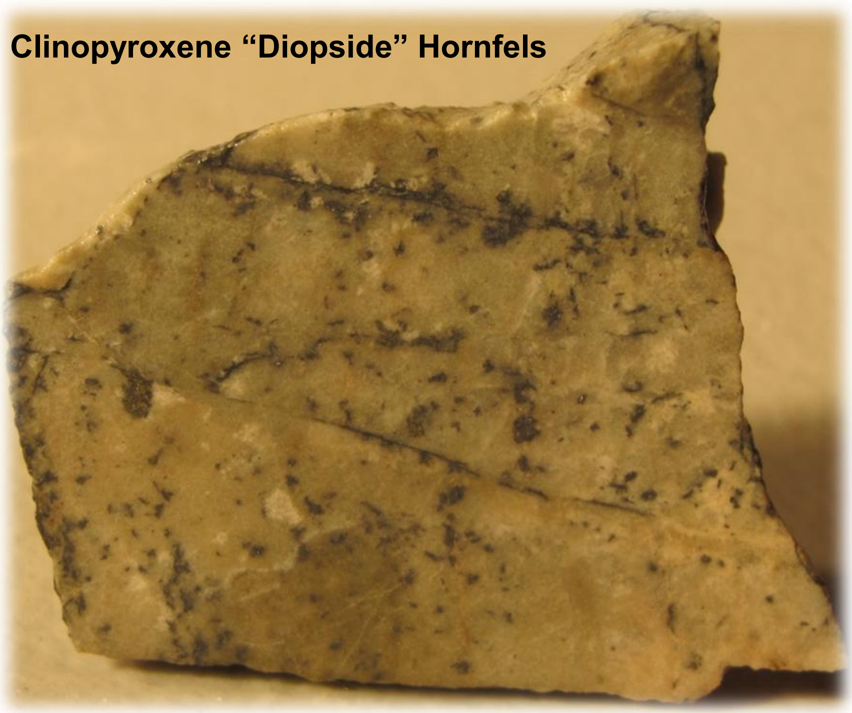


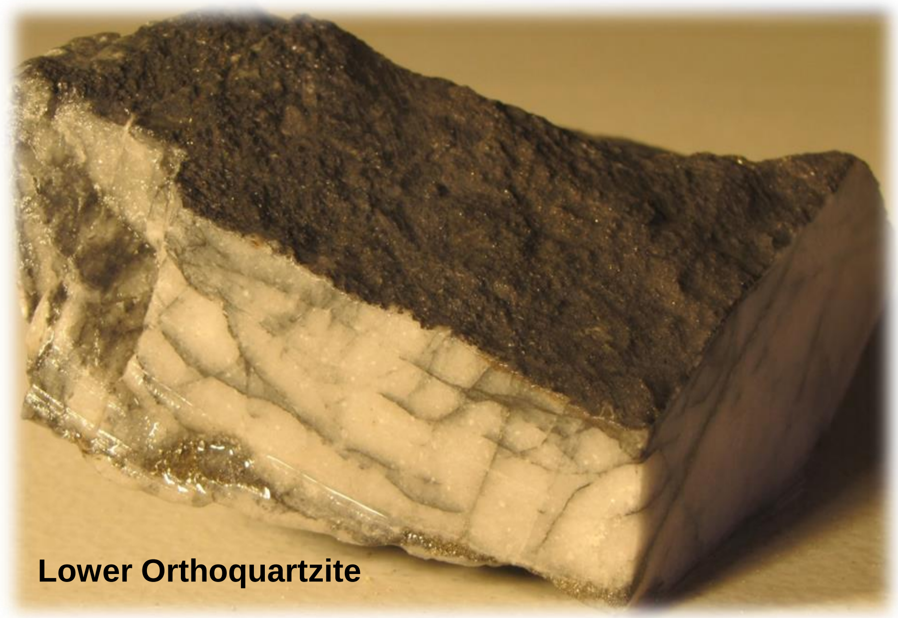

Garnet-Anhydrite-Quartz Skarn


Diopside-Actinolite-Serpentine Hornfels

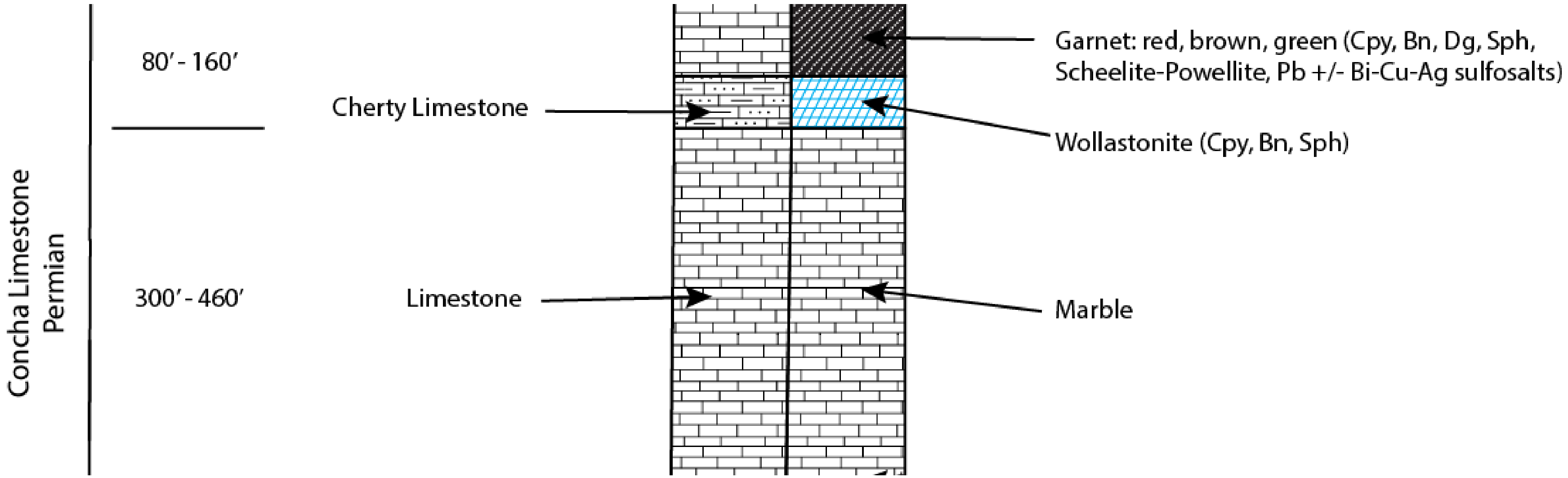
Scherrer Formation

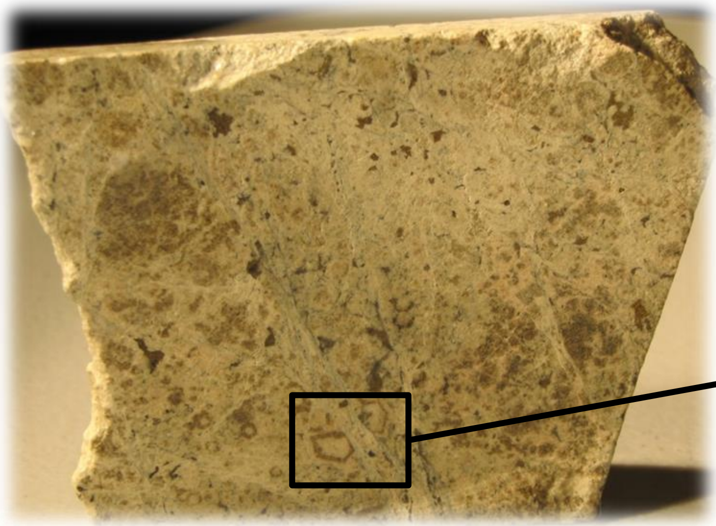


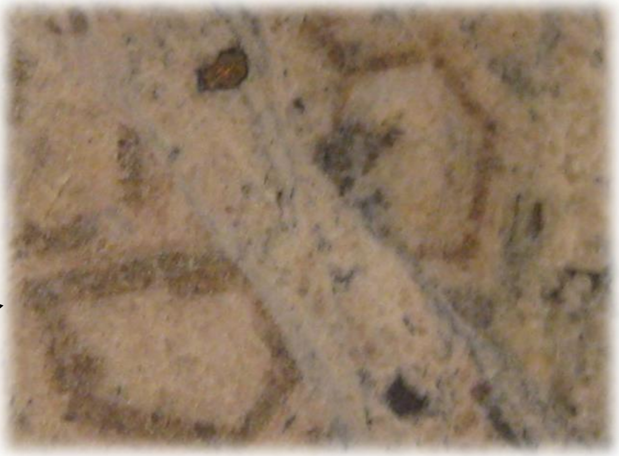

Clinopyroxene "Diopside" Hornfels


Lower Orthoquartzite

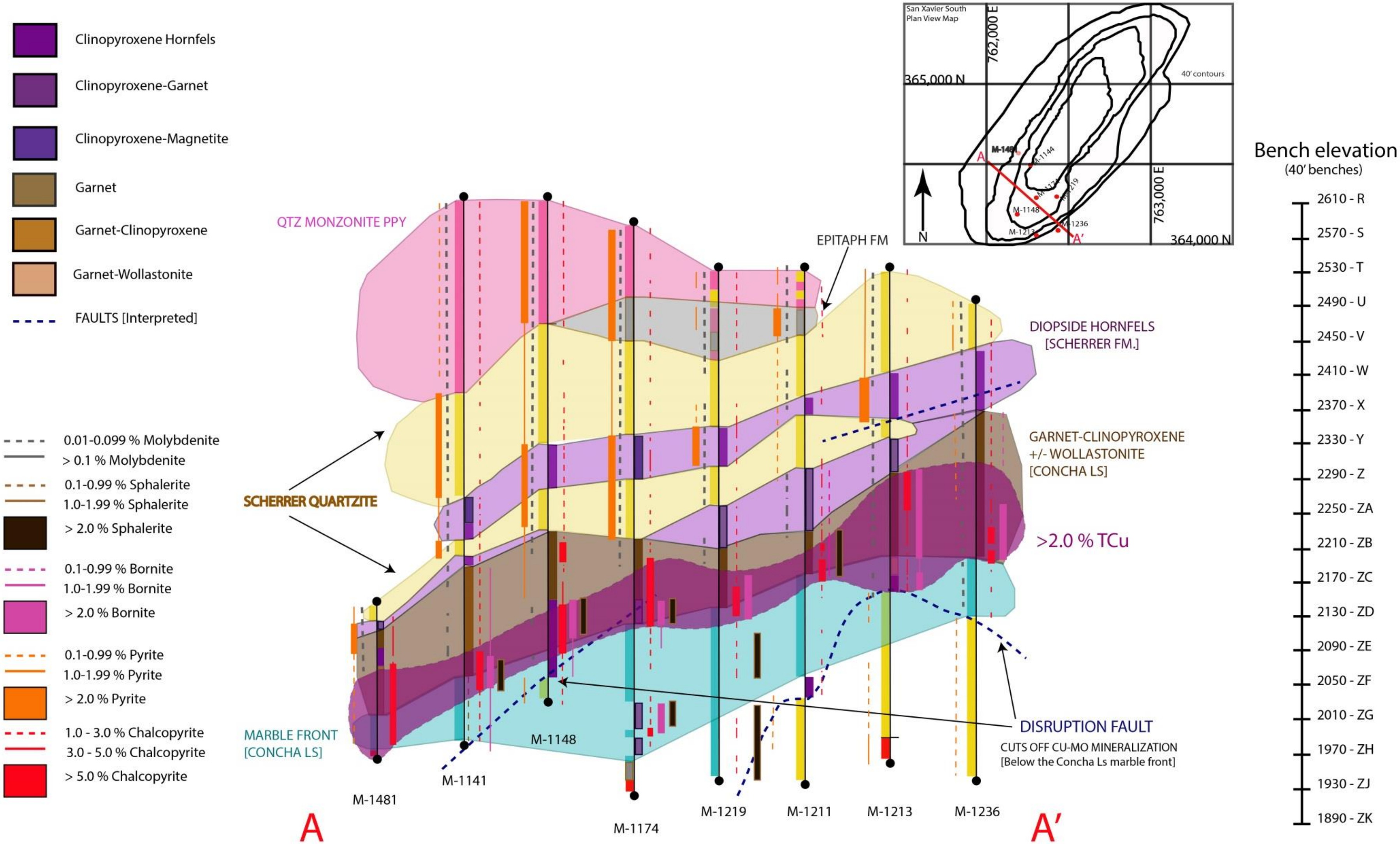
Concha Limestone







Alteration and Sulfide Mineralization – San Xavier South



San Xavier South Ore Body Alteration-Mineralization Zonation

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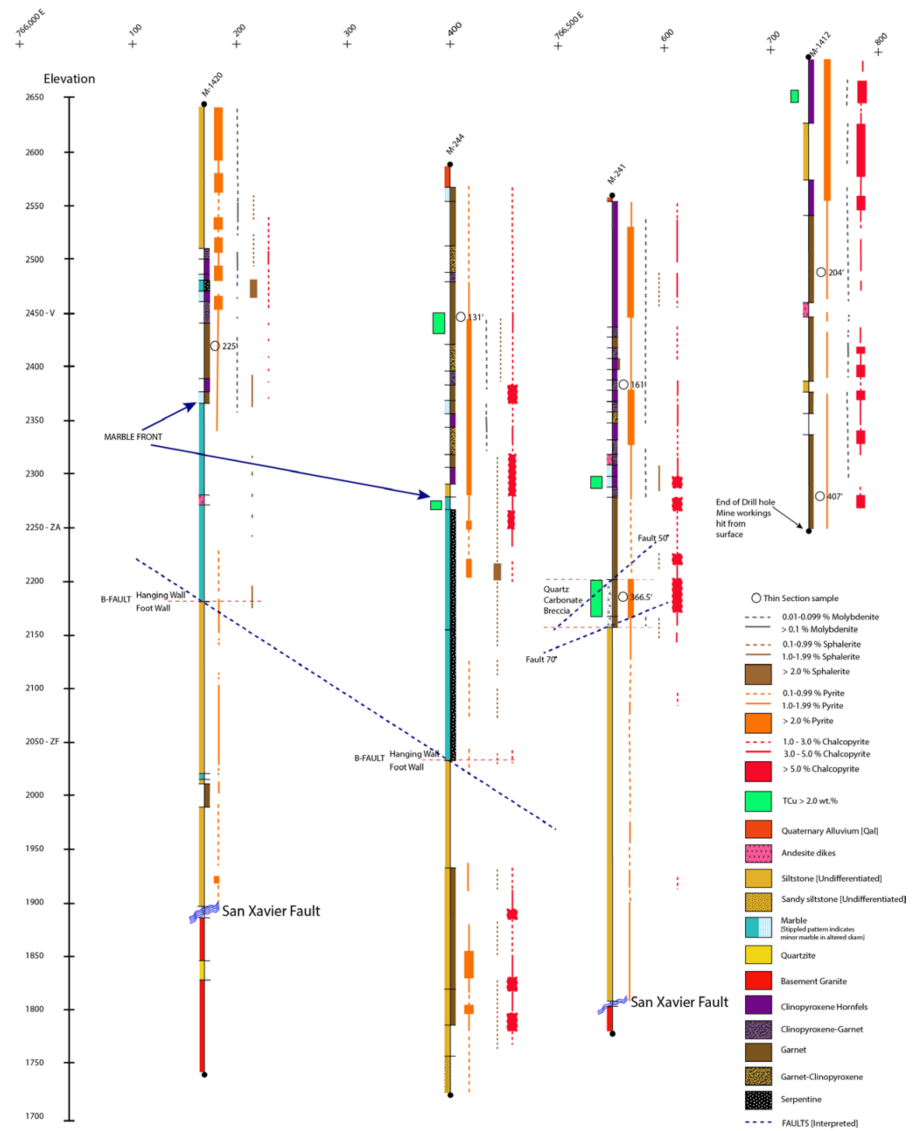
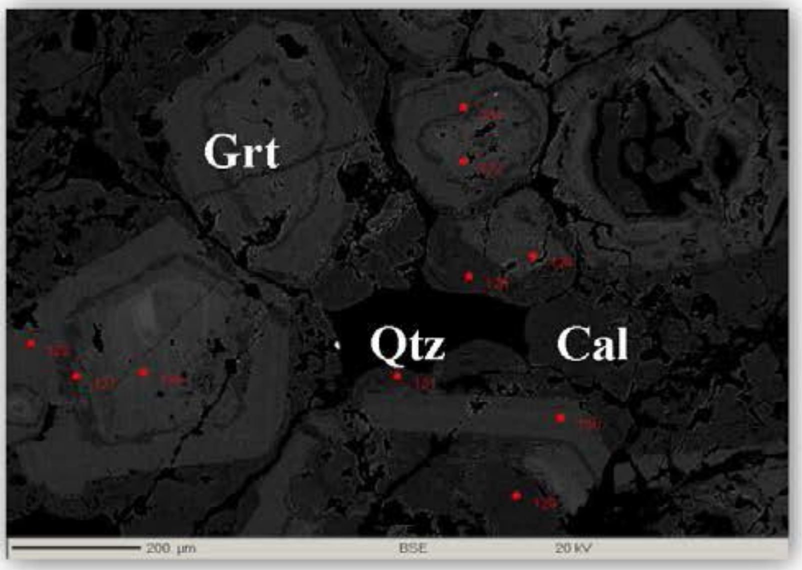
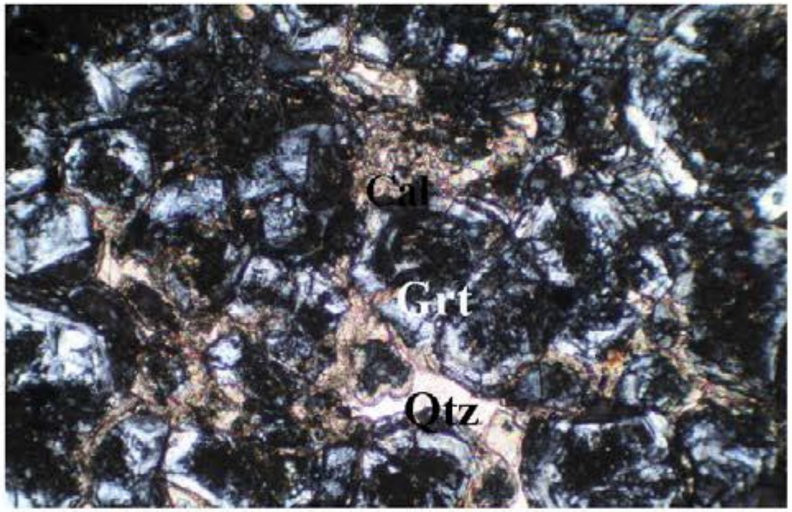
Alteration and Sulfide Mineralization – East Mission

- Alteration varies considerably between drill holes
- Stratigraphic sequence is interrupted by the B Fault
- Correlation between drill holes extremely complicated, however,
- Garnet zonation in individual units shows a interesting chemical evolution of the system

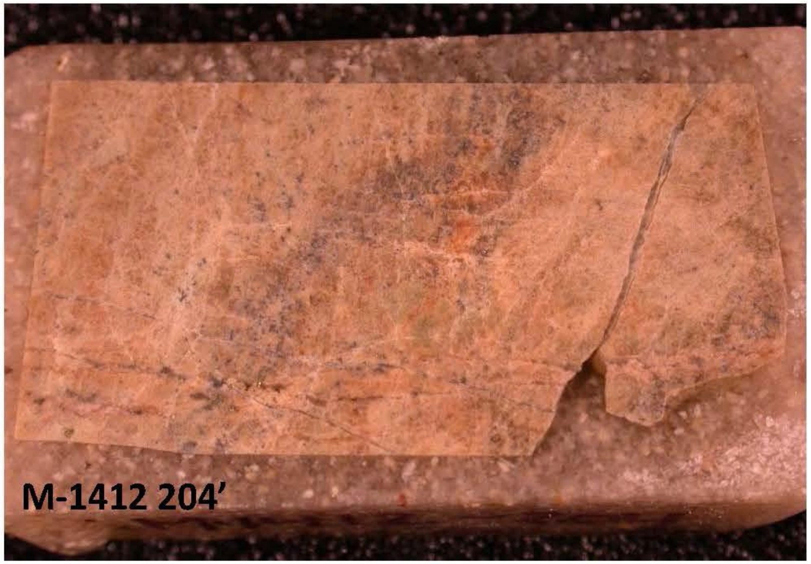


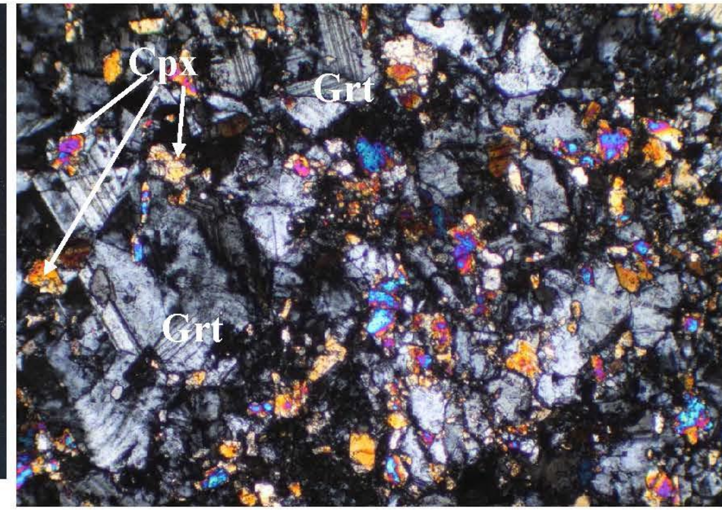
Garnet Composition – Zonation – East Mission





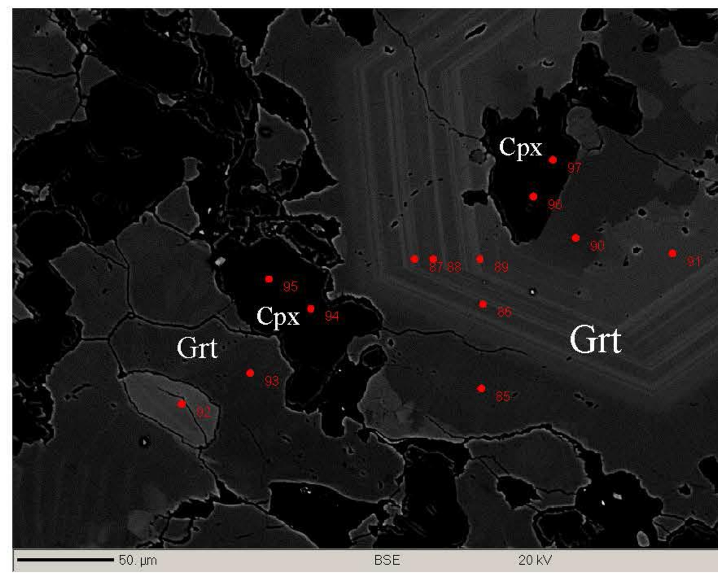
Garnet Composition – Zonation – East Mission





Zoned Garnet associated with Pyroxene in Chalcopyrite (oxide wt.%)

#	Mineral	Formula
85	Garnet	$Ca_{2.95}Fe^{2+}_{0.02}Mg^{2+}_{0.03}Al_{1.23}Fe^{3+}_{0.70}Ti^{4+}_{0.07}(Si_3O_4)_3$
86	Garnet	$Ca_{2.97}Mg^{2+}_{0.03}Al_{0.97}Fe^{3+}_{0.95}Ti^{4+}_{0.08}(Si_3O_4)_3$
87	Garnet	$Ca_{2.98}Mg^{2+}_{0.02}Fe^{3+}_{1.24}Al_{0.70}Ti^{4+}_{0.06}(Si_3O_4)_3$
88	Garnet	$Ca_{2.98}Mg^{2+}_{0.03}Fe^{3+}_{1.01}Al_{0.93}Ti^{4+}_{0.07}(Si_3O_4)_3$
89	Garnet	$Ca_{2.98}Mg^{2+}_{0.03}Fe^{3+}_{1.37}Al_{0.58}Ti^{4+}_{0.05}(Si_3O_4)_3$
90	Garnet	$Ca_{2.96}Fe^{2+}_{0.02}Mg^{2+}_{0.02}Al_{1.24}Fe^{3+}_{0.56}Ti^{4+}_{0.16}V^{3+}_{0.01}(Si_3O_4)_3$
91	Garnet	$Ca_{2.98}Mg^{2+}_{0.02}Fe^{3+}_{1.06}Al_{0.90}Ti^{4+}_{0.07}(Si_3O_4)_3$
92	Garnet	$Ca_{2.99}Fe^{3+}_{1.28}Al_{0.70}Ti^{4+}_{0.03}(Si_3O_4)_3$
93	Garnet	$Ca_{2.96}Mg^{2+}_{0.02}Al_{1.32}Fe^{3+}_{0.70}Ti^{4+}_{0.03}(Si_3O_4)_3$
94	Px	$Ca_{1.01}Mg^{2+}_{0.83}Fe^{2+}_{0.08}Mn^{2+}_{0.04}Fe^{3+}_{0.03}Si_2O_6$
95	Px	$Ca_{1.01}Mg^{2+}_{0.82}Fe^{2+}_{0.09}Mn^{2+}_{0.04}Fe^{3+}_{0.03}Si_2O_6$
96	Px	$Ca_{1.01}Mg^{2+}_{0.8}Fe^{2+}_{0.13}Mn^{2+}_{0.04}Fe^{3+}_{0.03}Si_2O_6$
97	Px	$Ca_{1.01}Mg^{2+}_{0.9}Fe^{2+}_{0.1}Si_2O_6$



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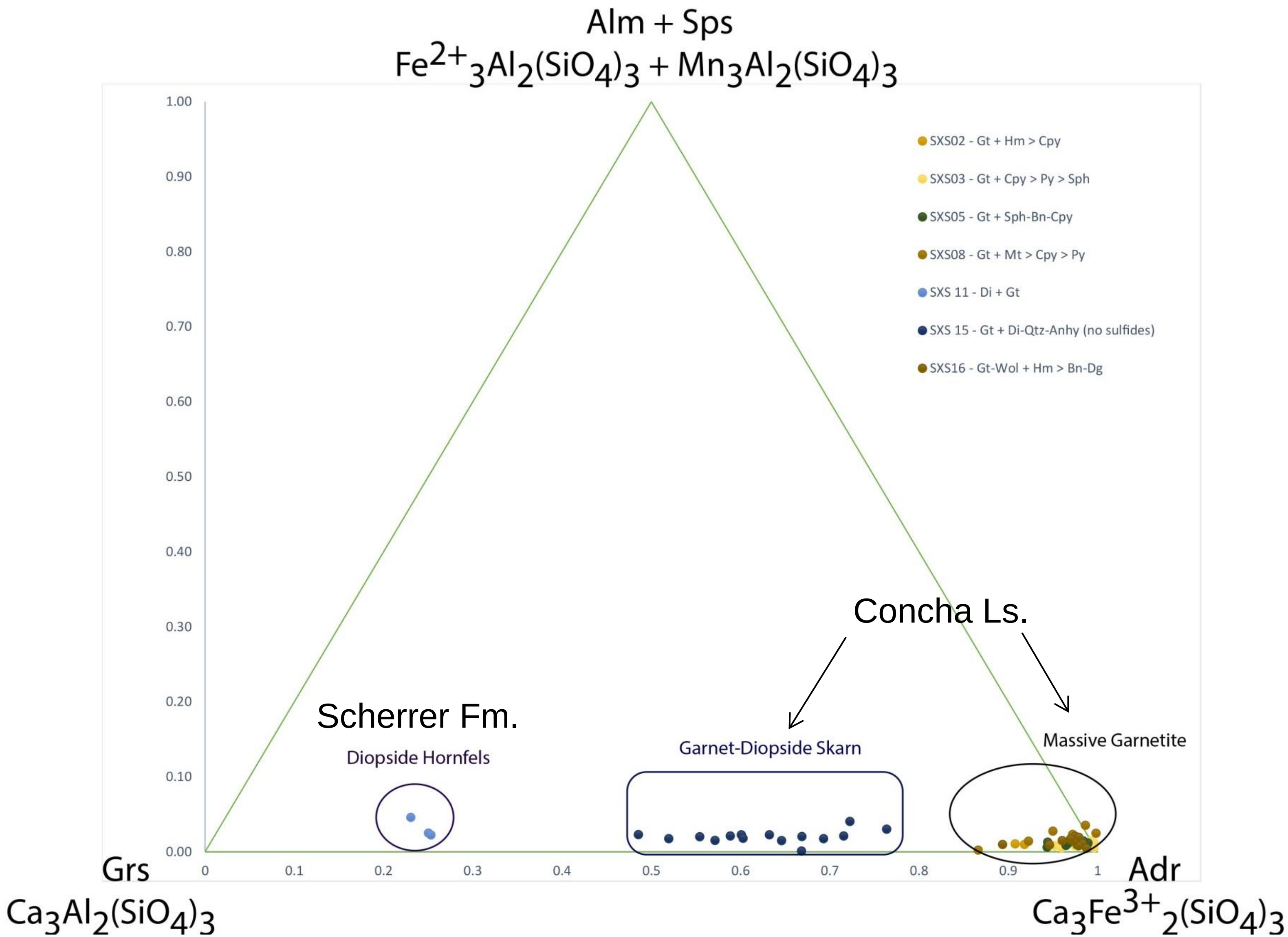
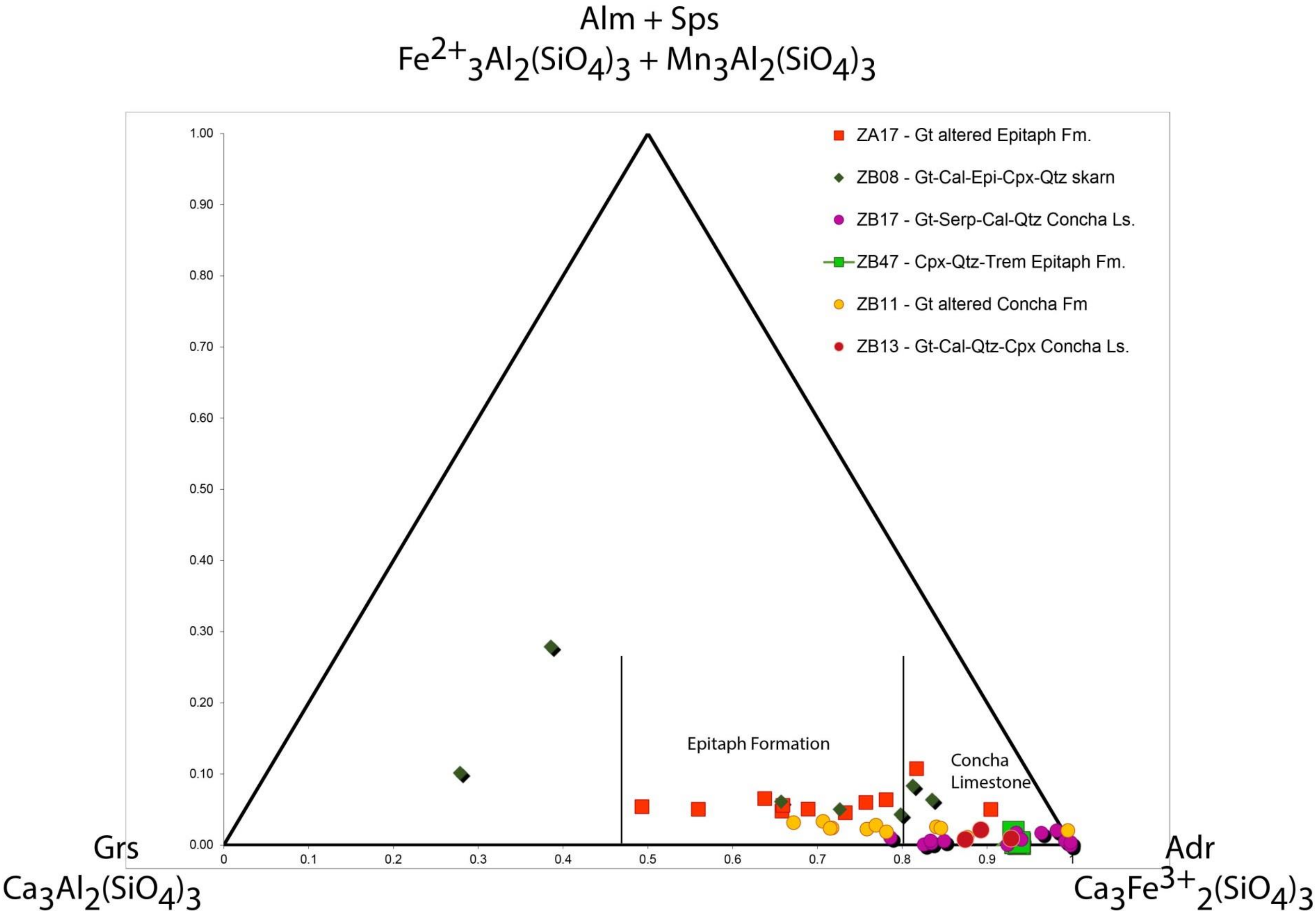
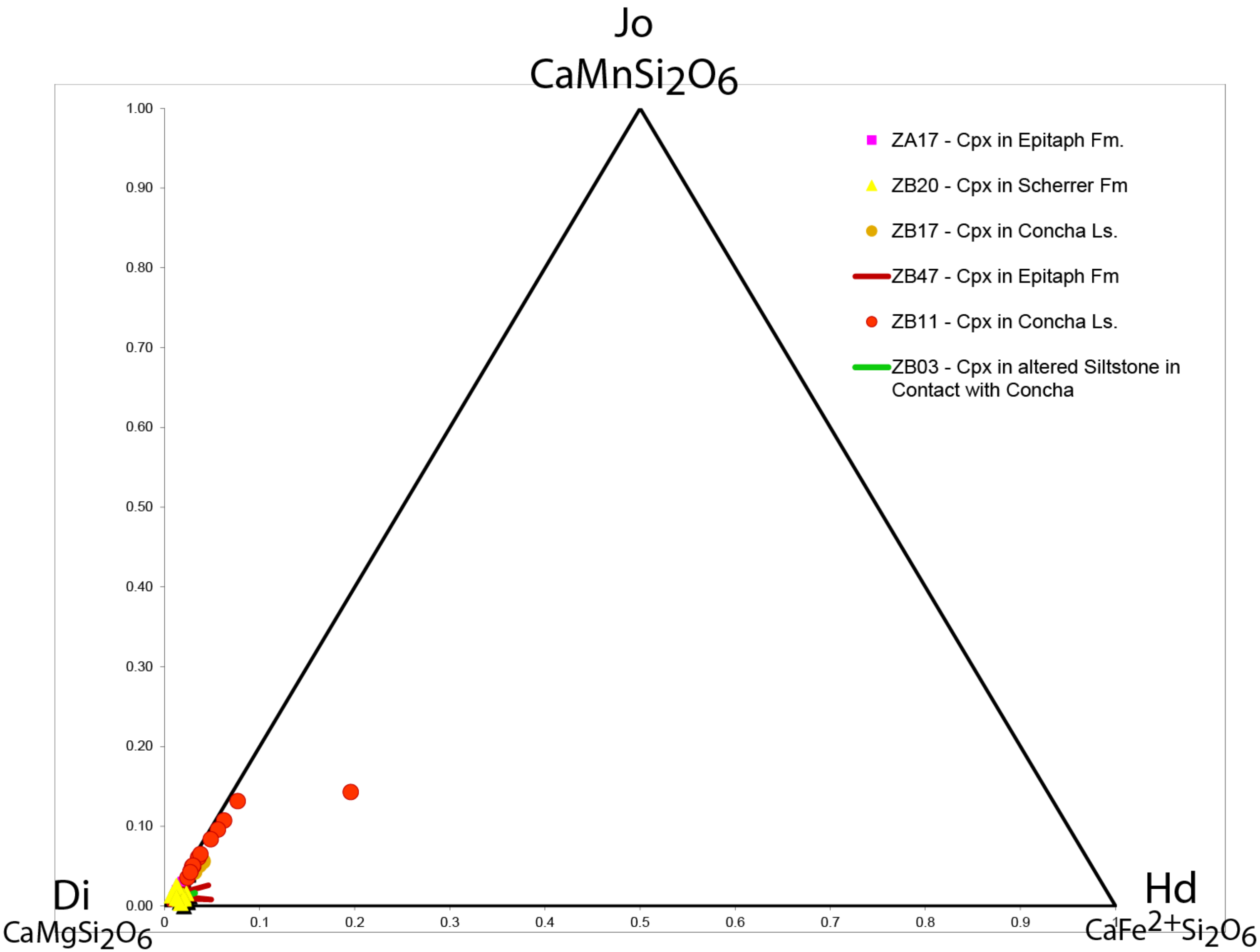
Garnet Compositions – San Xavier South



Garnet Compositions – Pima South



Clinopyroxene Compositions



Zonation

- Zoning and mineral composition differ between skarns hosted by relatively pure and impure carbonate lithologies
- The Permian Concha Limestone represents an example of a nearly pure carbonate host, whereas the older Permian Epitaph Formation, an interbedded silty carbonate-rich sediment, represents the impure carbonate
- Compositions of garnet and pyroxene from mixed Permian-hosted skarn, based on microprobe analyses, indicate:
  - 1) considerable ranges in composition between lithologies,
  - 2) differences in composition between ore types,
  - 3) irregular zoning due to oscillations in crystal chemistry between Fe-rich cores to Al-rich rims on zoned garnets from both the Mission and Pima South orebodies,
  - 4) regular zonation patterns from Fe-rich garnets in areas where higher grade Cu occurs to more aluminous garnets in non-sulfide bearing calc-silicate altered units

Zonation

- Mission and Pima South orebodies:
  - Clinopyroxene compositions in the middle member of the Scherrer Formation are generally pure diopside and show little to no compositional zoning in individual grains
- Thus, the diopside hornfels of the Mission and Pima South ore bodies, commonly likely originated by isochemical metamorphism rather than metasomatism
- In contrast - San Xavier South:
  - Clinopyroxene are compositionally zoned
  - The pure diopside cores represent an earlier alteration event influenced by isochemical metamorphic processes, whereas the rims contain a higher Fe^{2+} content--a more common composition of clinopyroxene formed by metasomatic processes, which is largely governed by protolith chemistry

Methods – Geometallurgy Study

How the secondary objective was met?

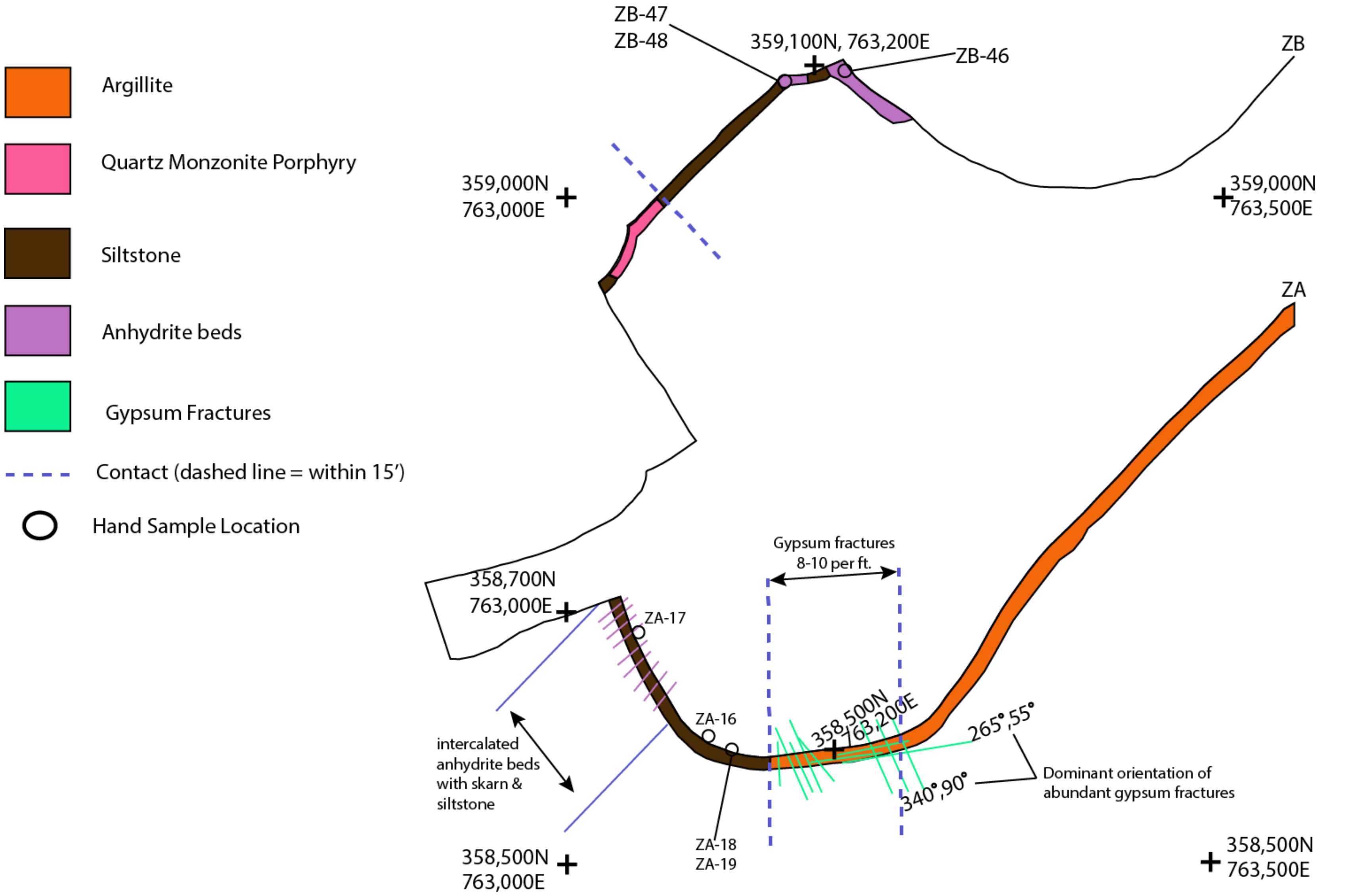
1) Alteration and mineralization bench mapping where high grade Mo mineralization occurs to record key paragenetic relationships

2) 25 key samples from 74 hand samples sent for thin section and subsequent petrography

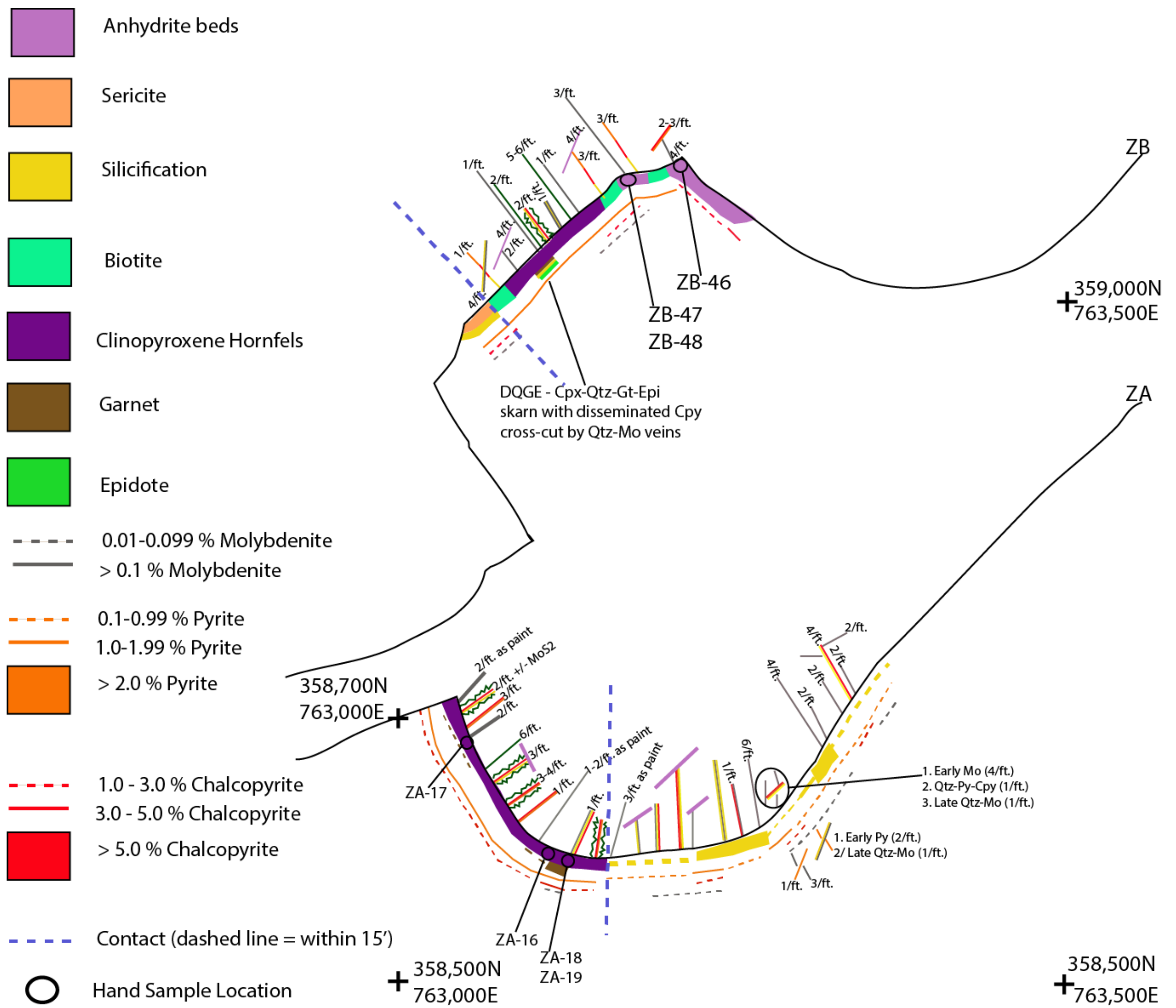
3) Electron microprobe analysis (CAMECA SX100)

   - Multi-element analysis of calc-silicate gangue alteration minerals
   - Mo-W minerals to determine concentrations of Re-Mo-W

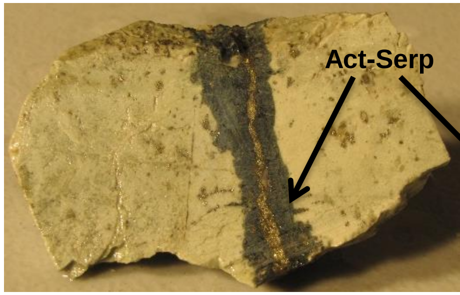
Lithology & Structure

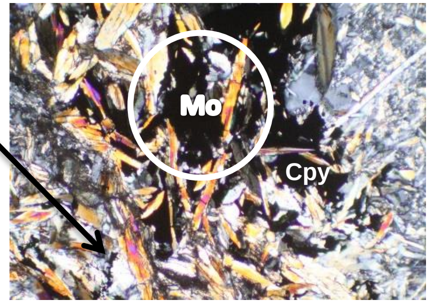


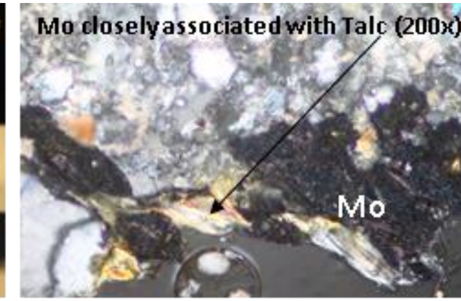
Alteration, Mineralization & Vein Assemblages – Pima South

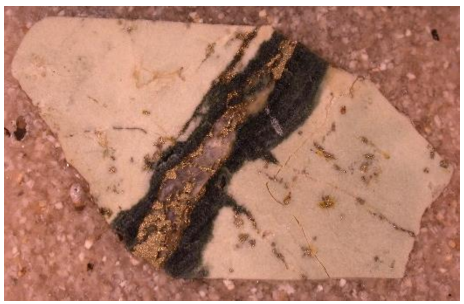


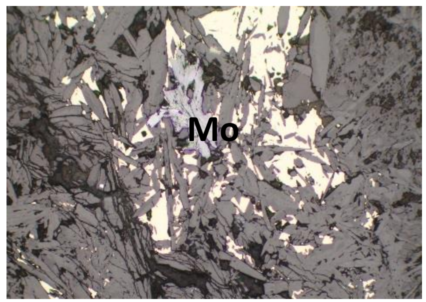
Cu & MoS_2 associations in Scherrer & Epitaph skarn

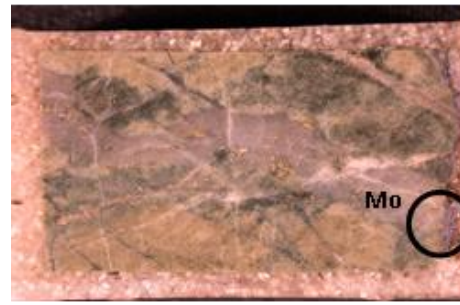


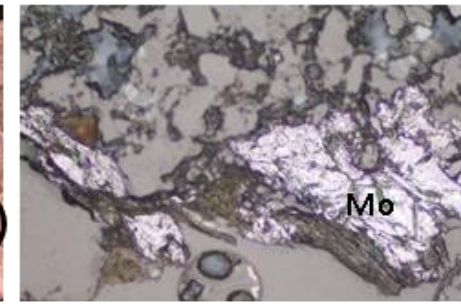


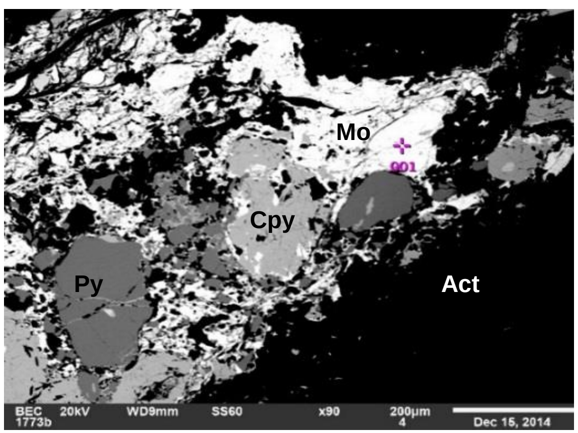




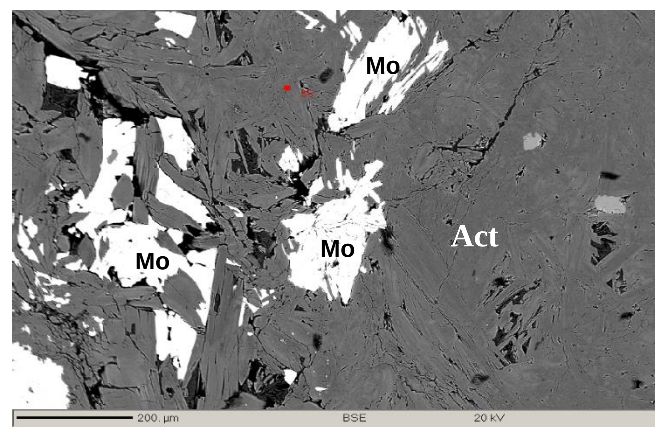






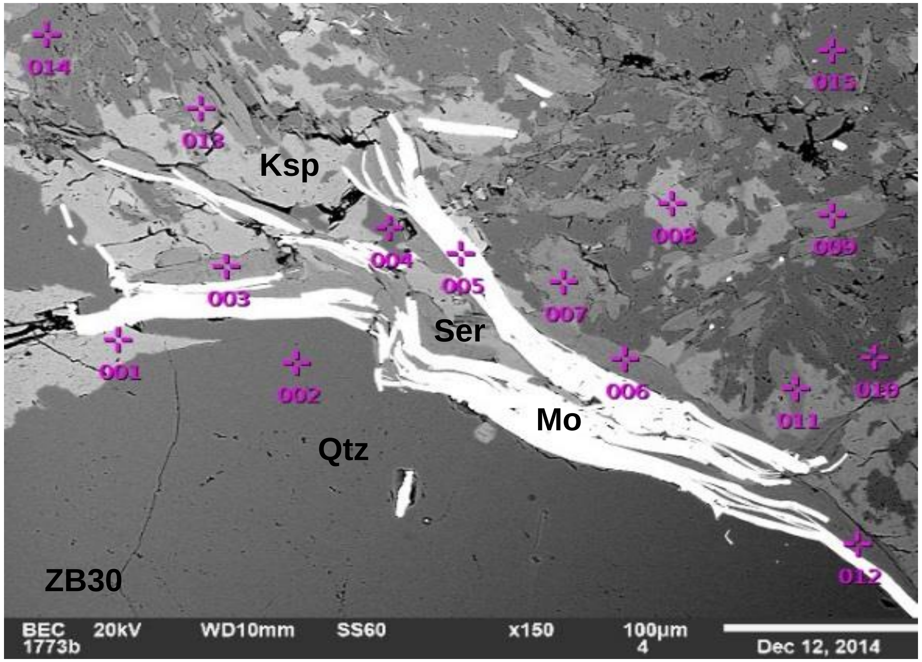


Actinolite (Act), Pyrite (Py), Chalcopyrite (Cpy), Molybdenite (Mo)

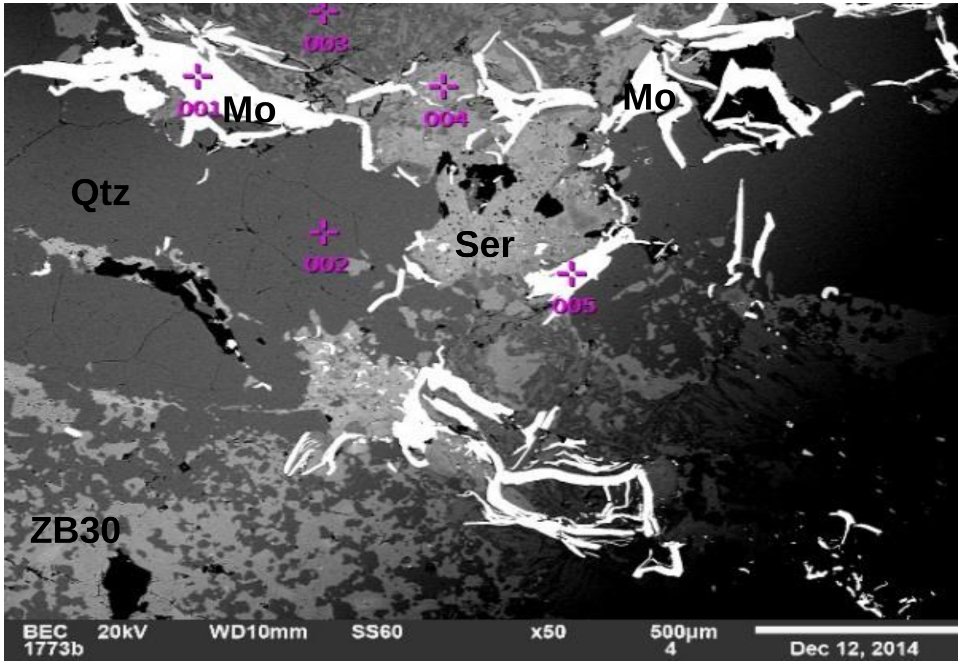


Actinolite (Act), Molybdenite (Mo)

MoS$_2$ associations in Qtz Monzonite Porphyry

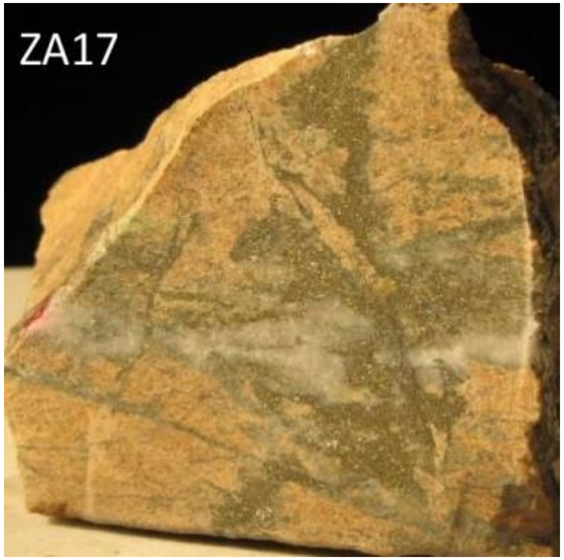


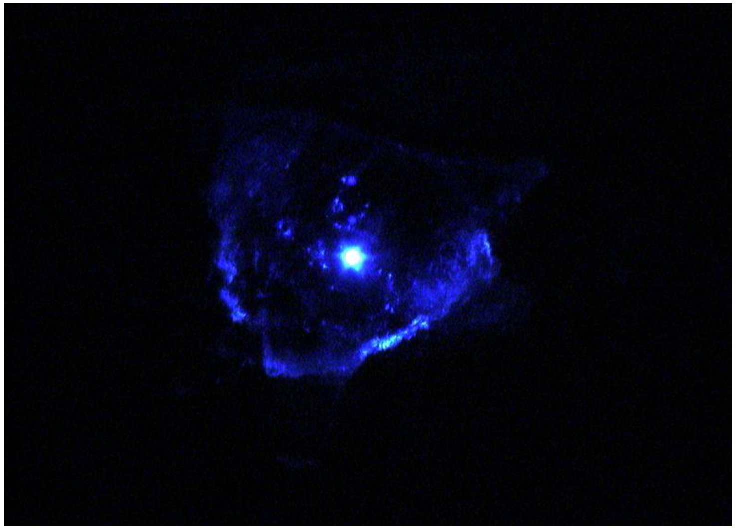
Molybdenite grains closely associated with sericite (Ser), orthoclase (Ksp) and quartz (Qtz)



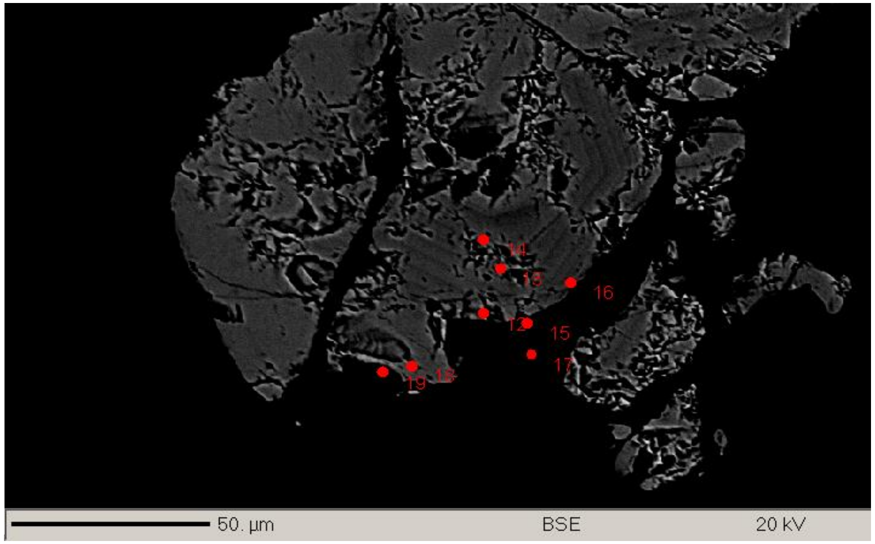
Molybdenite grains closely associated with sericite (Ser), and quartz (Qtz)

Mo mineralization as $Ca(W\text{-}Mo)O_4$



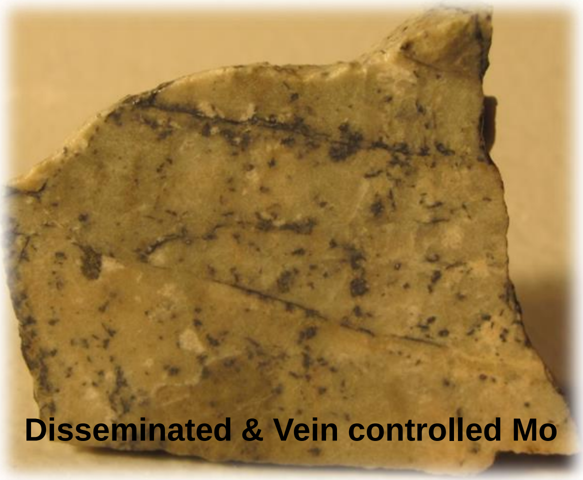


Point#	Ca	O	W	Mo	Total
12	14.243	23.085	59.366	3.116	100
13	13.888	22.579	63.909	0.000	100
14	13.604	22.321	63.307	0.000	99
15	13.889	22.546	60.980	1.468	99
16	13.979	22.582	60.255	1.865	99
17	13.871	22.621	61.675	1.249	99
18	13.806	22.655	62.678	0.846	100
19	13.815	22.346	60.223	1.464	98

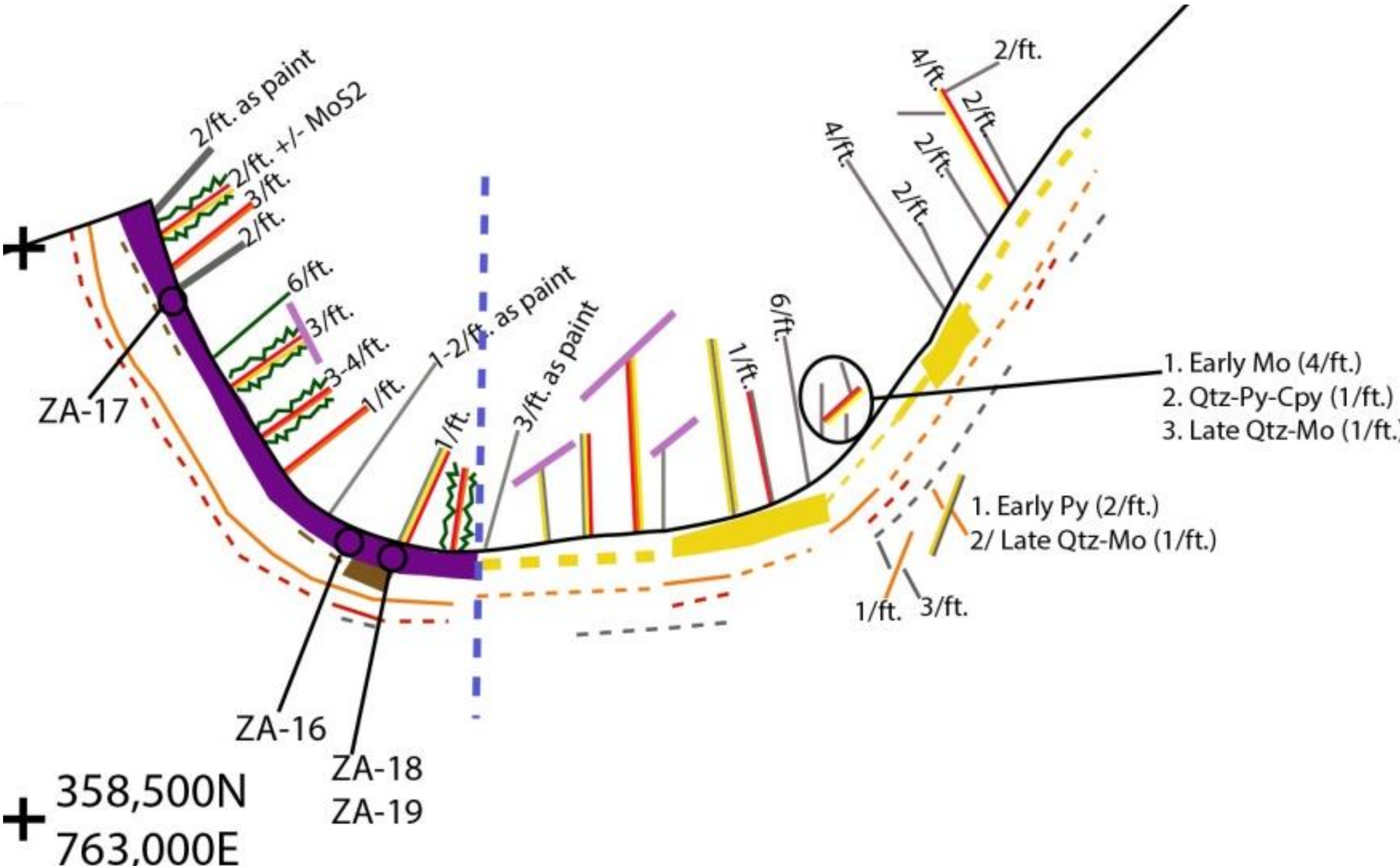


Mo Mineralization

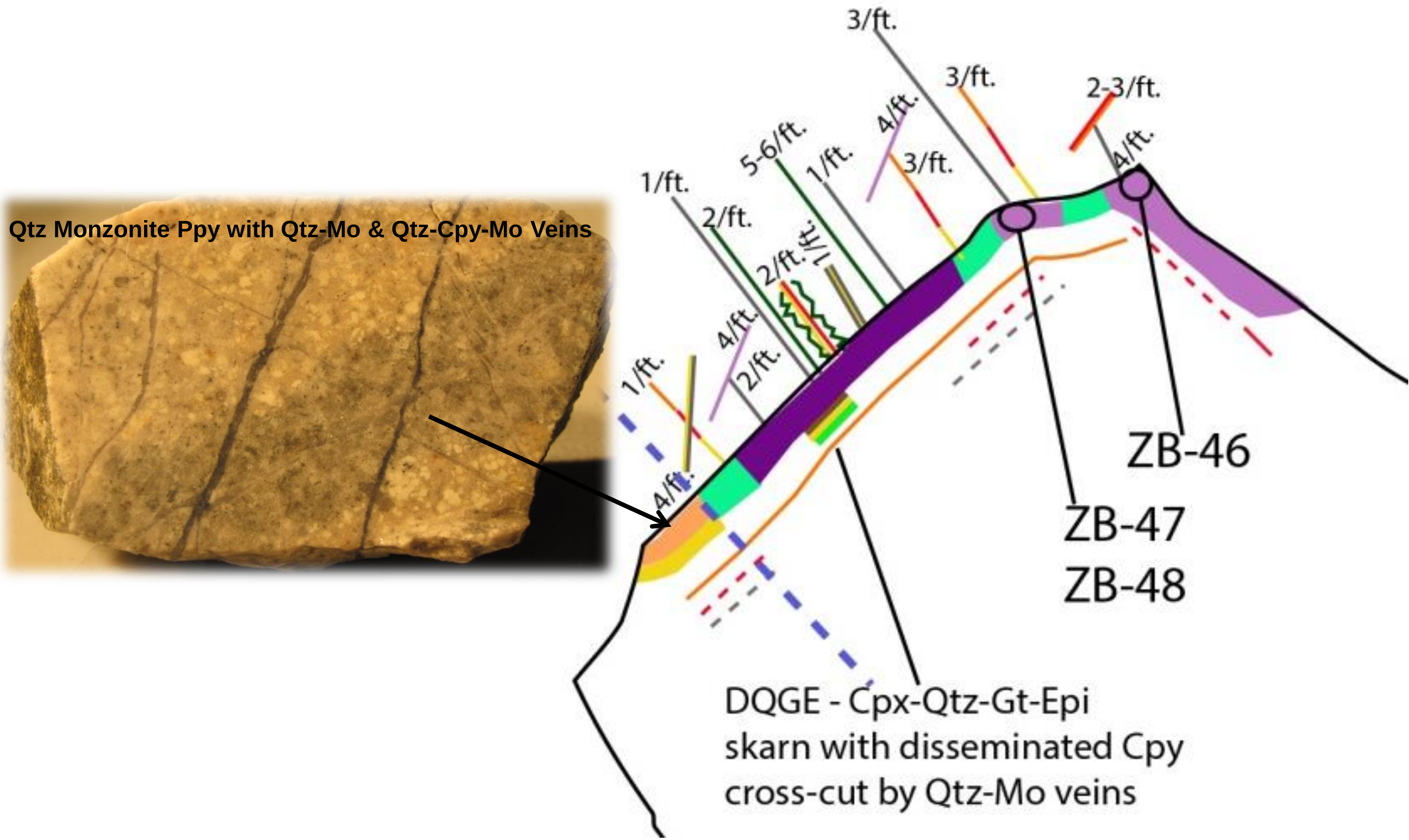
- High grade Mo mineralization generally occurs in three modes:
  - 1) disseminated masses in clinopyroxene-tremolite (± calcite, anhydrite) hornfels,
  - 2) trace amounts in garnet ± clinopyroxene skarn locally closely associated with scheelite, and
  - 3) as fracture-controlled mineralization



Vein Assemblages & Paragenesis – Pima South



Vein Assemblages & Paragenesis – Pima South



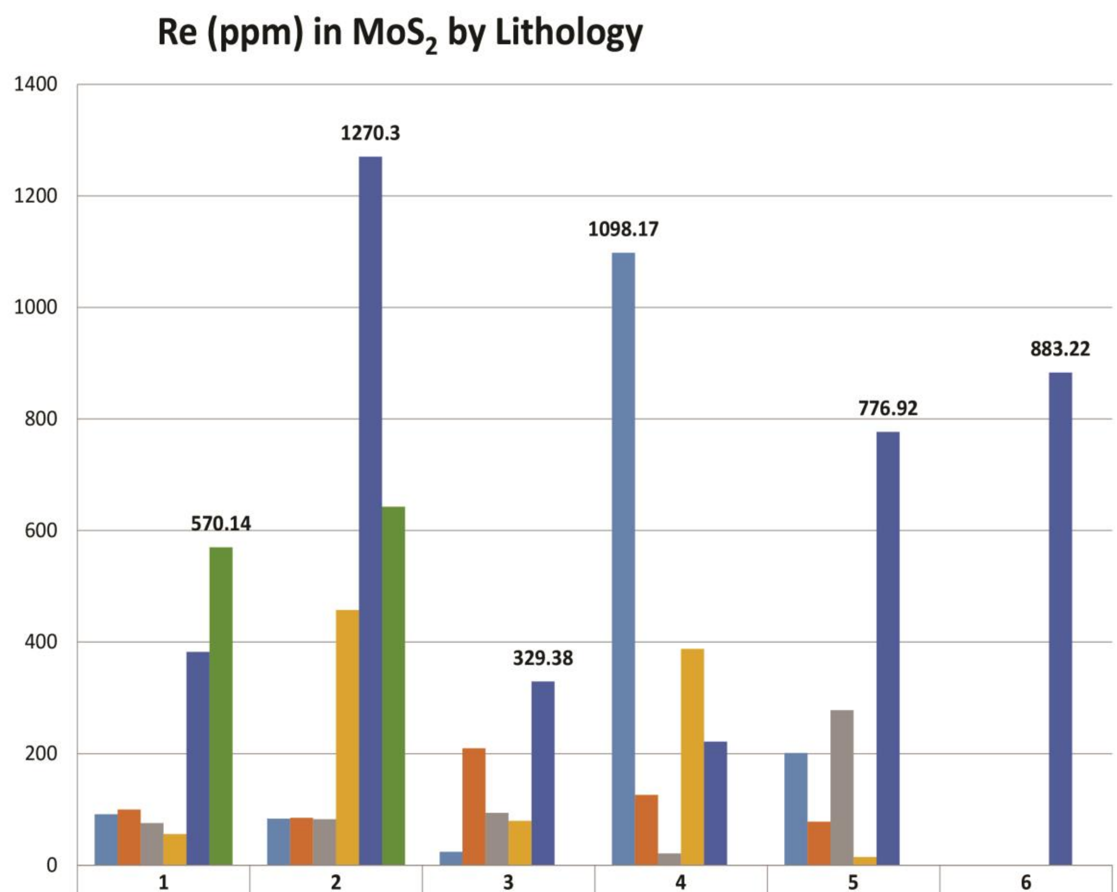
Paragenetic Implications

Several veining generations and different associated alteration may be the cause of differing concentrations of Mo

EXAMPLES:

- QMP from San Xavier South have several generations of Cu-Mo sulfide mineralization:
  1) Early Chalcopyrite
  2) Quartz-Chalcopyrite
  3) Quartz veins
  4) Quartz-Molybdenite-Chalcopyrite veins
  5) Molybdenite “paint” micro-fractures
- Mineralized siltstones, argillite, and skarn exhibit different generations of Mo mineralization
  - Epi-Cpy-Mo +/- Py (Concha Limestone)
  - Molybdenite “paint” fracture coating (Argillite, SXS QMP, Epitaph Fm.)
  - Disseminated molybdenite (Quartzite & Diopside Hornfels – Scherrer Fm.)

MoS_2 composition reveal additional Re resource



	1	2	3	4	5	6
Diopside altered Epitaph Fm.	91.28	83.32	24.23	1098.17	201.37	
Actinolite altered Epitaph Fm.	99.88	85.12	209.68	126.07	77.98	
Biotite altered QMP - Pima South	75.6	82.62	93.77	21.33	278.16	
Biotite altered QMP - San Xavier South	55.67	457.84	79.76	387.73	14.91	
Biotite altered Rodolpho Fm.	382.51	1270.3	329.38	221.74	776.92	883.22
Scherrer Fm Quartzite	570.14	642.79				

Regional Context: 12 “Common” characteristics

- The Basin and Range province has a higher proportion of carbonate strata, which vary considerably between districts
- While there are always differences between deposits, many of these districts have several common genetic characteristics:

1. The host rocks are dominantly Paleozoic; ranging from the Cambrian to the Permian

   Exception: Ludwig/Casting Copper – Yerington (Jurassic-Triassic)

   ASARCO Mission – Pima (Triassic Rodolfo Fm.)

12 “Common” Characteristics (cont.)

2. Polylithic stratigraphic column of limestone, dolostone, siltstones, quartzites/sandstones, and shales

3. Associated plutonic rocks are dominantly granitic, ranging from granodiorite to quartz monzonite

4. Mineralization is largely associated with quartz monzonite porphyry that was emplaced during the Laramide

Exceptions:

A. Yerington (Jurassic)
B. Bisbee (Jurassic)
C. Carr Fork (Eocene)

12 “Common” Characteristics (cont.)

- 5. Majority of skarns are mineralized by Laramide quartz monzonite porphyry
- 6. Although there are variations in individual deposits, calc-silicate alteration is lithologically controlled
- 7. Within each deposit, the “main stage” or mineralizing event is associated with:
  - A) Dominantly andraditic garnets
  - B) Garnets most likely formed from the fluids that introduced Cu into the system

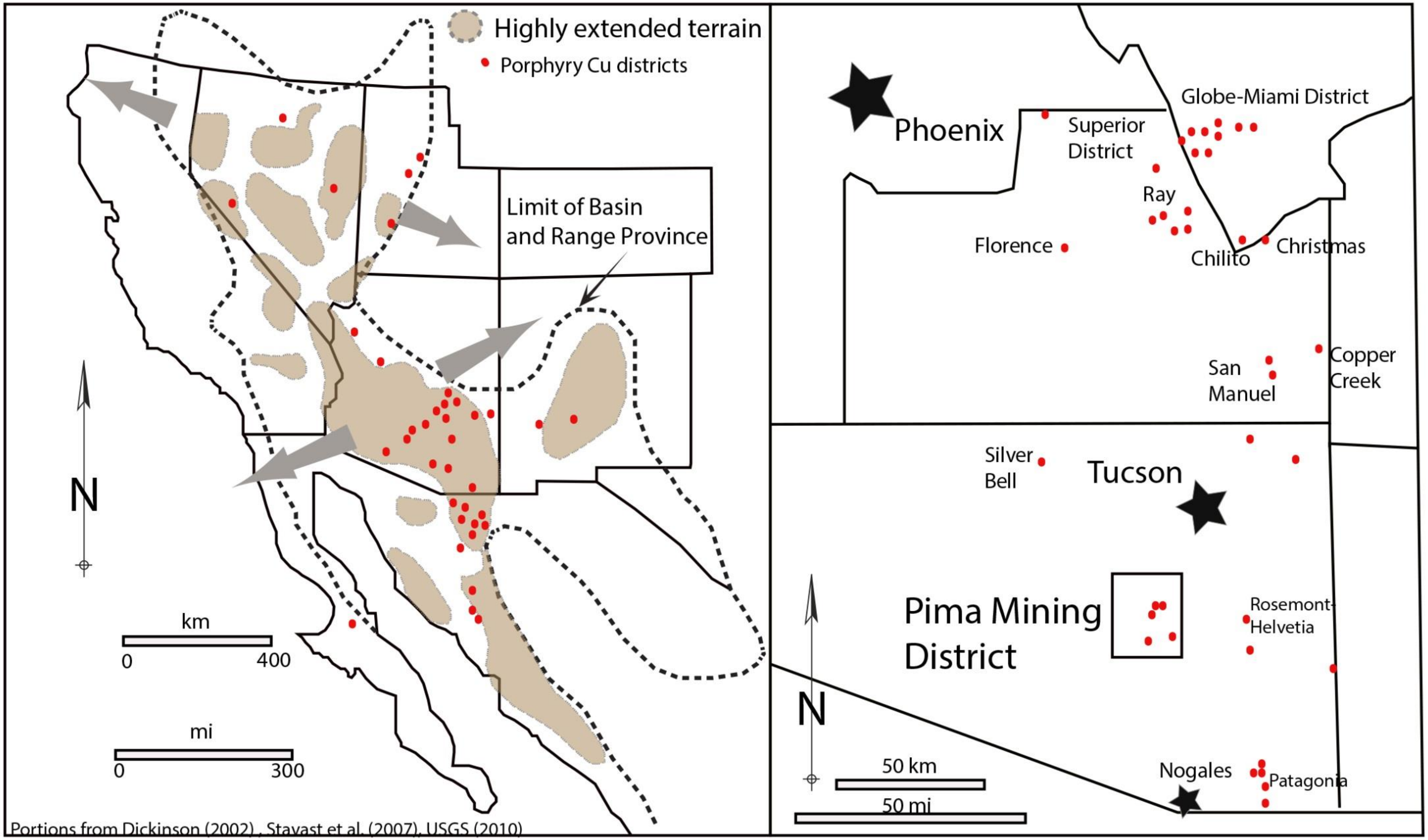
12 “Common” Characteristics (cont.)

- 8. Silty, sandy and/or shale-rich metasedimentary rocks with only minor Ca (± Fe, Mg) CO_3 are altered to a silica-rich hornfels dominated by:
  - Diopside
  - Quartz
  - K-feldspar ±
  - Garnet (typically more grossularitic in composition)
- 9. The majority of these deposits exhibit crosscutting, overprinting, and other textural relationships that suggest more than one stage of mineralization
  - Examples: Yerington, Twin Buttes, Silver Bell
- 10. Associated base & precious metals: Mo, Zn, Ag, Pb

12 “Common” Characteristics (cont.)

- 11. Deposits mineralized by quartz diorite tend to be higher in bornite than those associated with QMP or other granitic type intrusives
  - Example: Oracle Ridge Mine, Pima County, AZ
- 12. Lastly, variation between skarn deposits lies in the following aspects:
  - A) Accessory minerals associated with garnet-dominant alteration
  - B) Presence or absence of dolomitic sedimentary units in the stratigraphic sequence

Skark Exploration Potential in the Basin and Range



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In Conclusion: What did we learn?

- The practical application of alteration and sulfide zonation of a deposit highlight favorable areas for further exploration or expansion
- Zonation studies also identify areas where production challenges exist and assist in processing optimization
- Garnet composition may help to identify the protolith in structurally complicated areas
- Garnet compositions range from Adr_{50} to Adr_{100}
- Clinopyroxene is Di_{100}

In Conclusion: What did we learn?

- Several samples contain appreciable Re. While this does not represent total concentration of Re in Mo for the deposit, this new data is promising
- Scheelite-powellite is closely associated with molybdenite in altered calc-silicate hornfels and the massive garnetite near the marble front (Concha Ls.)
- Knowing MoS_2 composition with the goal of troubleshooting processing issues prior to production at greenfield projects and seek to optimize Mo recovery at current operations worldwide

Acknowledgements

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