**Data Repository 2009170**

**"Decoupling of As and Cu in Hydrothermal Systems"**

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## Methods

Electron Microprobe Analysis (EMPA)

The chemical composition of arsenian pyrite was determined by electron microprobe analysis (EMPA) using a Cameca SX100 at the University of Michigan Electron Microbeam Analysis Laboratory (EMAL). Elements and X-ray lines used for the analysis are Fe ($K_\alpha$), S ($K_\alpha$), As ($L_\alpha$), Au ($L_\alpha$), Pb ($M_\alpha$), Se ($L_\alpha$), Cd ($L_\alpha$), Ag ($L_\alpha$)¸ Hg ($M_\alpha$), Zn ($K_\alpha$), Cu ($K_\alpha$), Ni ($K_\alpha$), Co ($K_\alpha$), Sb ($L_\alpha$), Te ($L_\alpha$) and Si ($K_\alpha$). Operating conditions included an accelerating voltage of 20kV and beam current of 30nA with wave-length dispersive X-ray spectrometers (WDS). In order to improve the statistics of the count rates, counting times were 30 seconds for Fe, S and Si, 60 seconds for As, Cd, Pb, Zn, Cu, Ni and Co, 120 seconds for Se, Hg, Sb and Te, 140 seconds for Ag, and 200 seconds for Au. The electron beam was ~1 μm in diameter. Standard specimens used for calibration were $FeS_2$ (for Fe and S), FeAsS (for As), $Sb_2S_3$ (for Sb), HgS (for Hg), PbS (for Pb), CdS (for Cd), ZnS (for Zn), CuS (for Cu) SbTe (for Te), $Au^0$ (for Au), $Ag^0$ (for Ag

Secondary Ion Mass Spectrometry (SIMS)

SIMS analyses were carried out with a $Cs^+$ primary beam at a current of 10-15 nA producing an analytical spot size of approximately 20 micrometers diameter and 1 to 3 micrometer depth. Secondary ions monitored include $^{32}S$, $^{56}Fe$, $^{63}Cu$, $^{65}Cu$, $^{75}As$, $^{80}Se$, $^{109}Ag$, $^{123}Sb$, $^{130}Te$ and $^{197}Au$. Molecular interferences for Au(1) were eliminated by 180V offset. Minimum detection limits (2σ) in parts per million were Cu 1, As 2, Se 0.2, Ag 6, Sb 6, Te 0.2, and Au 0.3. Elemental scans were carried out at different speeds depending on the element being analyzed, with detection limits that were usually 2 to 5 times higher than for spot analyses. The SIMS maps are shown as single-color maps; the range of contrast in the original maps was determined by the highest concentration in the sample. For scans in which the element was present in high concentrations, such as in an inclusion that contained that element as an essential constituent, variations in the much smaller concentrations of that element that substitute in the pyrite are not displayed clearly.

**Distribution of Cu, As, Au, Ag and Te indicated by SIMS and EMPA elemental mapping**

SIMS elemental maps provide information on the distribution of trace elements within the Cu and As-rich growth zones indicated by EMPA elemental maps. SIMS maps of pyrite from Pueblo Viejo show a single growth zone (outlined in white) in pyrite from Pueblo Viejo that is enriched in As and Au and depleted in Cu. It was followed by a growth zone that is enriched in Te (Fig. DR1a). Fig. DR1b shows a growth zone in which Cu is associated with Te without detectable As. Fig. DR1c shows Cu-rich growth zones that are largely devoid of As and Te. Fig. DR2a shows early, probable sectoral, zones (white arrows) containing Te, Au and Cu but not Ag and As. These were followed by a series of growth zones containing As, Cu, Au, Ag, and Te (zone I) and then As-rich pyrite with Au,Ag and Te but no Cu (zones II, III). Fig. DR2b shows early colloform As-rich pyrite with variable levels of Ag, Au and Te (white ellipsoid), including some without detectable Au and Te. Cu was deposits as Cu-As-sulfide inclusions after these growth zones form and these were followed by Cu-rich growth zones with Au and Te that alternate with As-rich growth zones with Ag (double arrow-head arrows). Fig. DR2c shows an early growth zone with Cu, As, Ag, Au and Te, followed by a broad As-rich growth zone with variable amounts of Te (two prominent growth zones) and Au and Ag (one prominent growth zone). White arrows show a Cu-rich growth zone with no other elements.

SIMS and EMPA elemental maps of pyrite from Yanacocha show similar relations. Fig. DR3a-d shows that stage-1 pyrite containing Cu was followed by stage-2 pyrite containing As. Smaller amounts of Cu in stage-2 pyrite might be Cu (II) corrosion of the stage-1 pyrite that liberated Cu. Almost all Au was deposited in the earliest zone of stage-2 pyrite together with As and Ag, then its concentrations decreased below detection limits. Fig. DR4a-c shows cores of stage-1 pyrite with growth zones that are rich in As without Cu and Ag.  Later stage-2 pyrite contains both As and Cu. The As-Cu matrix contains numerous Cu-As-rich inclusions (Fig. DR4a-c). Silver is enriched in stage-2 pyrite. Gold was incorporated into both stages of pyrite, 1 and 2, at the same level of concentration.

**Figure captions to the supplementary information**

**Figure DR1.** SIMS elemental maps of vein stage pyrite in samples DDH-161-120, 161-103 and 119-49 from the Moore deposit at Pueblo Viejo.

**Figure DR2.** SIMS elemental maps of vein stage pyrite in sample DDH-206-50.7 from the Monte Negro deposit at Pueblo Viejo. Relative, temporal sequence of growth zones is indicated by time arrow above the image.

**Figure DR3.** SIMS (a-c) and EMPA (d) elemental maps of pyrite in sample CHQ-602-N3 from the Chaquicocha Sur deposit at Yanacocha.

**Figure DR4.** SIMS elemental maps of vein-stage pyrite in sample YS-734-N2 from the Yanacocha Sur deposit at Yanacocha.

**Figure DR5**. Correlations between As, Ag, Au and Te contents of pyrite from Pueblo Viejo in SIMS spot analyses.

Table DR1. Summary of the EMPA analyses of pyrite from Yanacocha and Pueblo Viejo deposits (all analyses in wt%; detection limits in ppm).

| | | **Yanacocha (N=403)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | As-zone (N=225) | | | Cu-zone (N=135) | | | "barren"-pyrite (N=43) | | |
| Element | Det. limit | Ave. | Min. | Max. | Ave | Min. | Max. | Ave. | Min. | Max. |
| S | 334 | 53.22±1.05 | 49.71 | 56.95 | 52.89±0.13 | 50.71 | 54.47 | 53.23±0.24 | 52.07 | 55.84 |
| Fe | 288 | 43.74±0.39 | 36.15 | 48.05 | 45.84±0.14 | 43.83 | 47.80 | 46.94±0.22 | 45.43 | 48.09 |
| Co | 169 | bdl | bdl | 0.41 | bdl | bdl | bdl | bdl | bdl | bdl |
| Ni | 148 | bdl | bdl | 0.40 | bdl | bdl | 0.08 | bdl | bdl | 0.05 |
| Cu | 183 | 0.06±0.01 | bdl | 0.43 | 0.31±0.06 | 0.02 | 1.51 | bdl | bdl | bdl |
| Zn | 212 | 0.04±0.01 | bdl | 0.35 | bdl | bdl | 0.10 | 0.02±0.02 | bdl | 0.36 |
| As | 164 | 1.73±0.24 | 0.02 | 5.52 | 0.07±0.02 | bdl | 0.50 | bdl | bdl | bdl |
| Se | 103 | bdl | bdl | 0.03 | bdl | bdl | 0.02 | bdl | bdl | bdl |
| Ag | 453 | bdl | bdl | 0.05 | bdl | bdl | bdl | bdl | bdl | bdl |
| Cd | 740 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Sb | 233 | bdl | bdl | 0.06 | bdl | bdl | 0.04 | bdl | bdl | 0.04 |
| Te | 203 | bdl | bdl | bdl | bdl | bdl | 0.03 | bdl | bdl | bdl |
| Au | 417 | 0.09±0.02 | bdl | 0.46 | bdl | bdl | bdl | bdl | bdl | bdl |
| Hg | 633 | bdl | bdl | bdl | bdl | bdl | 0.07 | bdl | bdl | bdl |
| Pb | 654 | 0.49±0.13 | bdl | 4.14 | bdl | bdl | 0.25 | bdl | bdl | 0.15 |
| Total | | 99.42±0.13 | 96.20 | 102.22 | 99.18±0.18 | 96.02 | 100.83 | 100.25±0.19 | 97.30 | 101.53 |

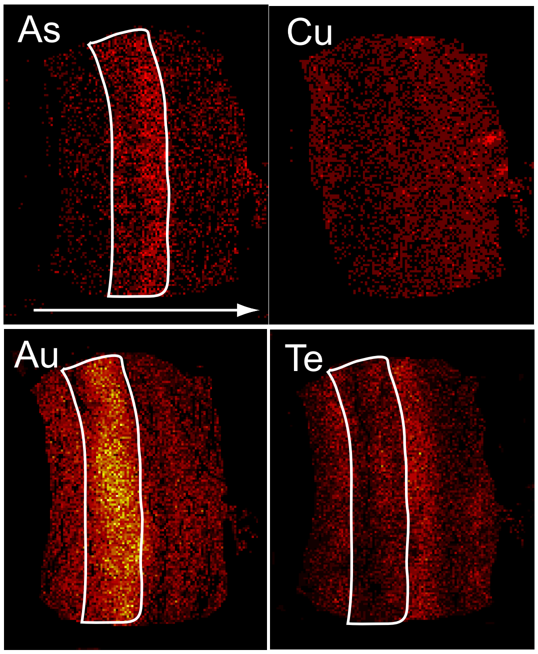
| | | **Pueblo Viejo (N=1225)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | As-zone (N=535) | | | Cu-zone (N=556) | | | "barren" pyrite (N=134) | | |
| Element | Det. limit. | Ave. | Min. | Max. | Ave. | Min. | Max. | Ave. | Min. | Max. |
| S | 334 | 52.95±0.78 | 50.06 | 55.82 | 53.32±0.42 | 50.62 | 55.61 | 53.33±0.46 | 53.50 | 54.01 |
| Fe | 288 | 45.30±1.05 | 41.42 | 48.03 | 45.46±0.93 | 42.54 | 47.93 | 46.68±0.51 | 46.11 | 47.26 |
| Co | 169 | bdl | bdl | 0.06 | 0.02±0.03 | bdl | 0.16 | bdl | bdl | 0.06 |
| Ni | 148 | bdl | bdl | 0.02 | bdl | bdl | 0.06 | bdl | bdl | bdl |
| Cu | 183 | 0.11±0.13 | bdl | 0.73 | 0.80±0.80 | 0.02 | 3.27 | bdl | bdl | bdl |
| Zn | 212 | 0.02±0.04 | bdl | 0.59 | bdl | bdl | 0.33 | bdl | bdl | 0.02 |
| As | 164 | 0.69±0.73 | 0.02 | 3.59 | 0.02±0.05 | bdl | 0.44 | bdl | bdl | bdl |
| Se | 103 | 0.01±0.01 | bdl | 0.13 | bdl | bdl | 0.10 | bdl | bdl | 0.04 |
| Ag | 453 | 0.06±0.08 | bdl | 0.64 | bdl | bdl | 1.41* | bdl | bdl | 0.05 |
| Cd | 740 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Sb | 233 | 0.08±0.14 | bdl | 1.05* | bdl | bdl | 0.39 | bdl | bdl | 0.04 |
| Te | 203 | 0.04±0.04 | bdl | 0.25 | bdl | bdl | 0.74* | bdl | bdl | bdl |
| Au | 417 | bdl | bdl | 0.11 | bdl | bdl | 0.16* | bdl | bdl | bdl |
| Hg | 633 | bdl | bdl | 0.06 | bdl | bdl | bdl | bdl | bdl | bdl |
| Pb | 654 | 0.49±0.74 | bdl | 4.39* | bdl | bdl | 0.89* | bdl | bdl | bdl |
| Total | | 99.72±1.02 | 96.11 | 102.11 | 99.70±0.81 | 96.21 | 102.26 | 100.06±013 | 96.50 | 100.89 |

Ave. – represents average concentration and standard deviation; bdl – below detection limit; *analyses contaminated by inclusions of other minerals.

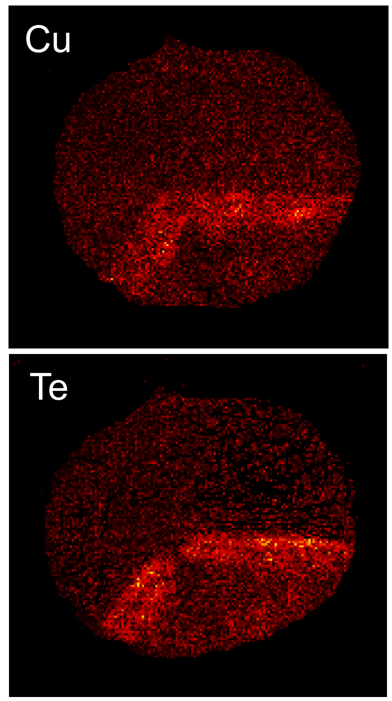
# Pueblo Viejo

Figure DR1

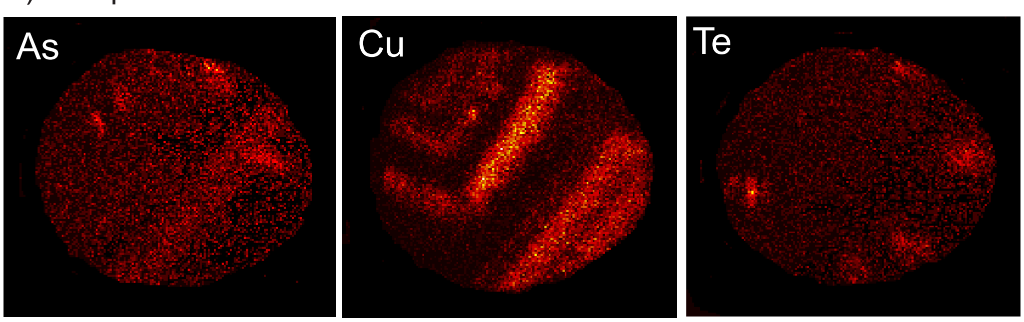
a) Sample DDH-161-120




b) Sample DDH-161-103

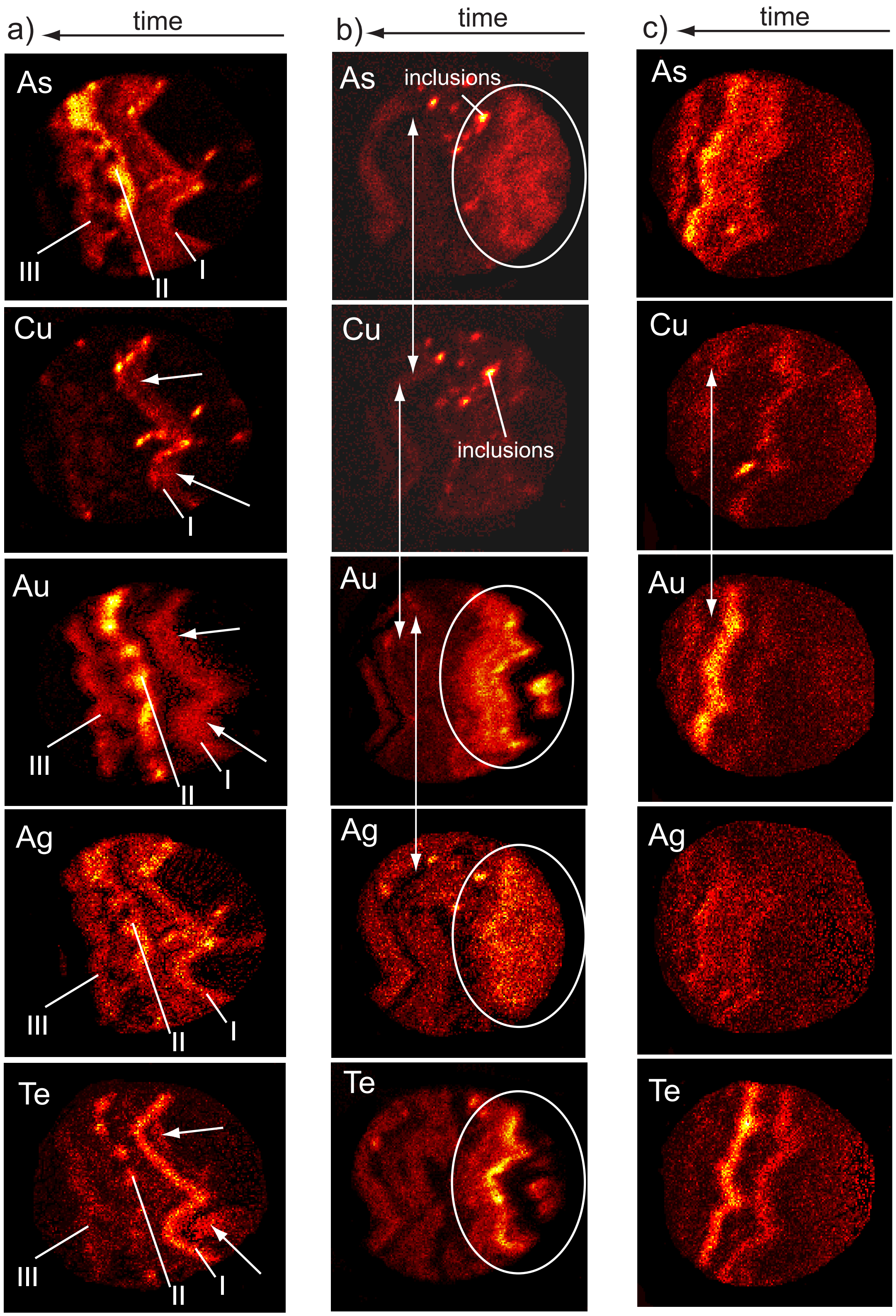



c) Sample DDH-119-49



# Pueblo Viejo

Figure DR2. Sample DDH-206-50.7



# Yanacocha

Figure DR3. Sample CHQ-602-N3

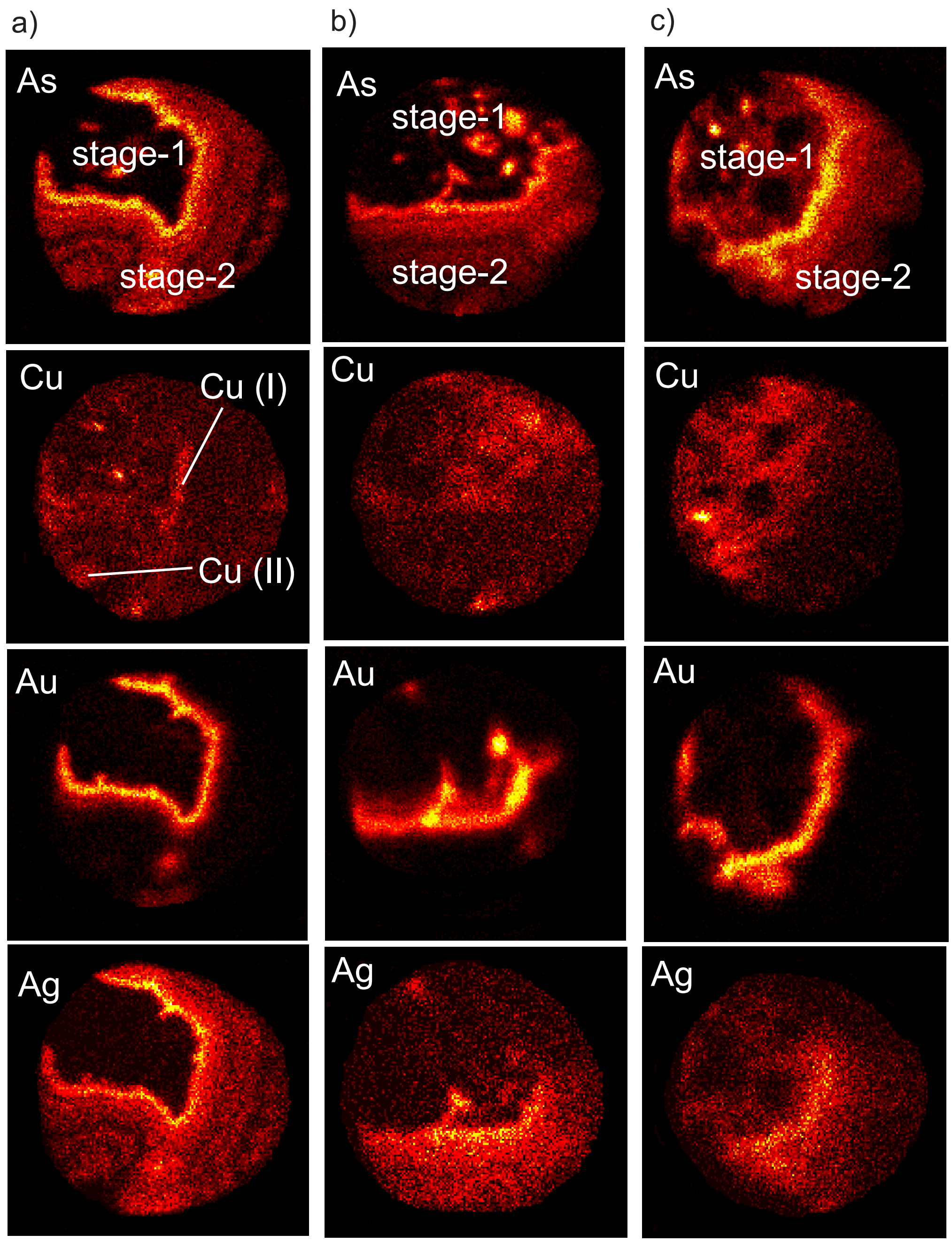
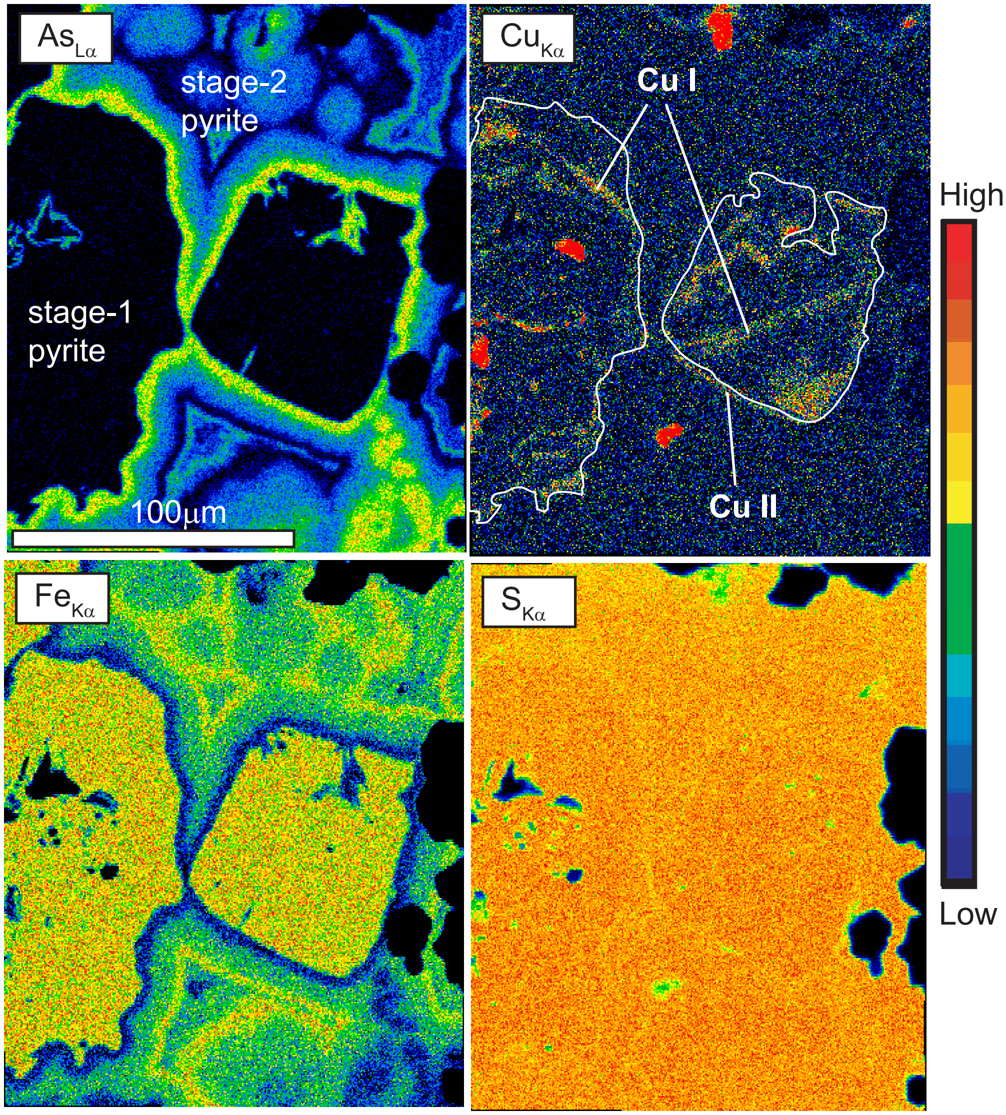


Figure DR3d



As Lα
stage-2 pyrite
stage-1 pyrite
100μm
Cu Kα
Cu I
Cu II
Fe Kα
S Kα
High
Low

# Yanacocha

Figure DR4. Sample YS-734-N2

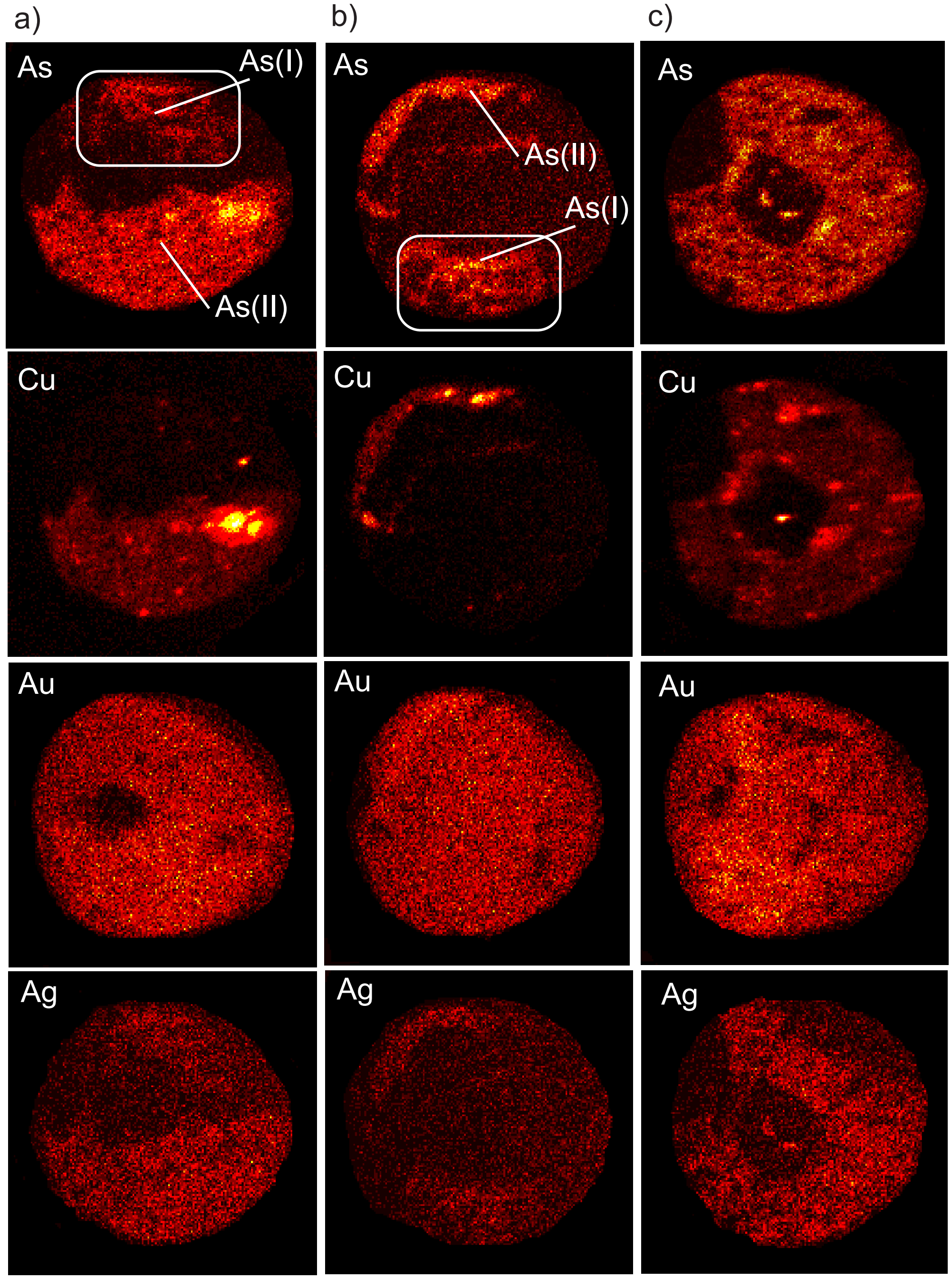
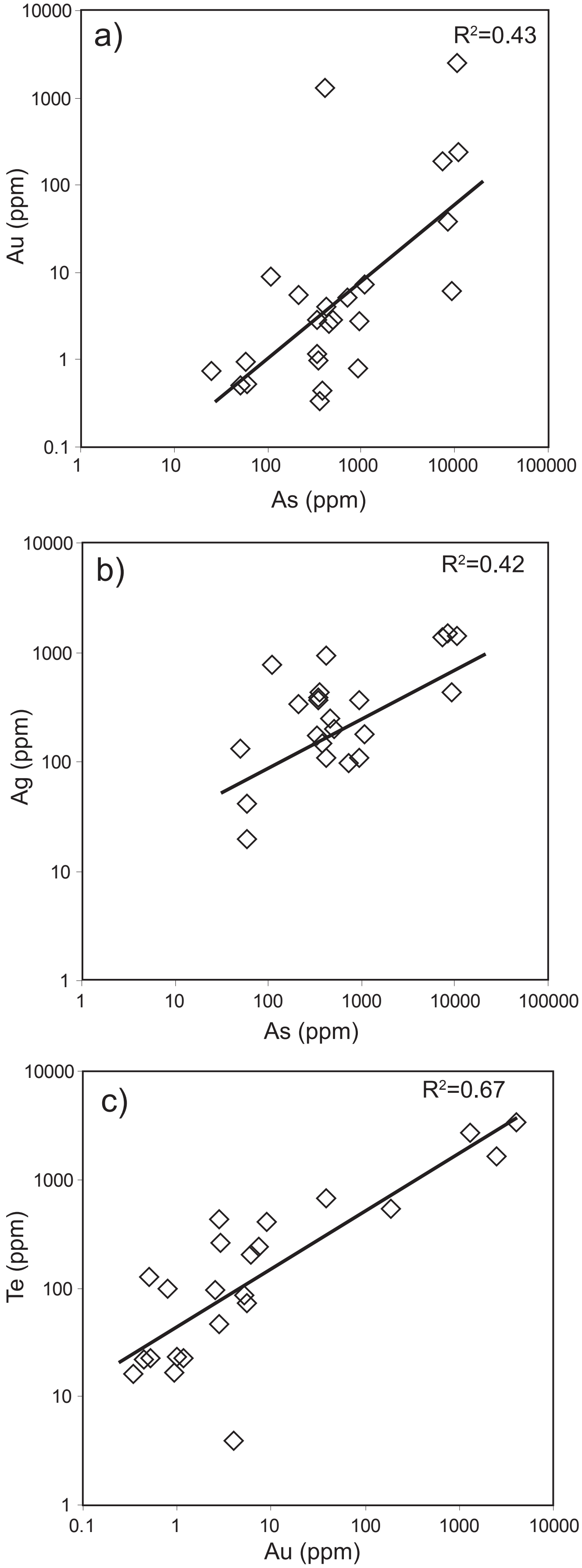


Figure DR5



a)
R²=0.43
Au (ppm)
As (ppm)
0.1
1
10
100
1000
10000
100000
b)
R²=0.42
Ag (ppm)
As (ppm)
c)
R²=0.67
Te (ppm)
Au (ppm)