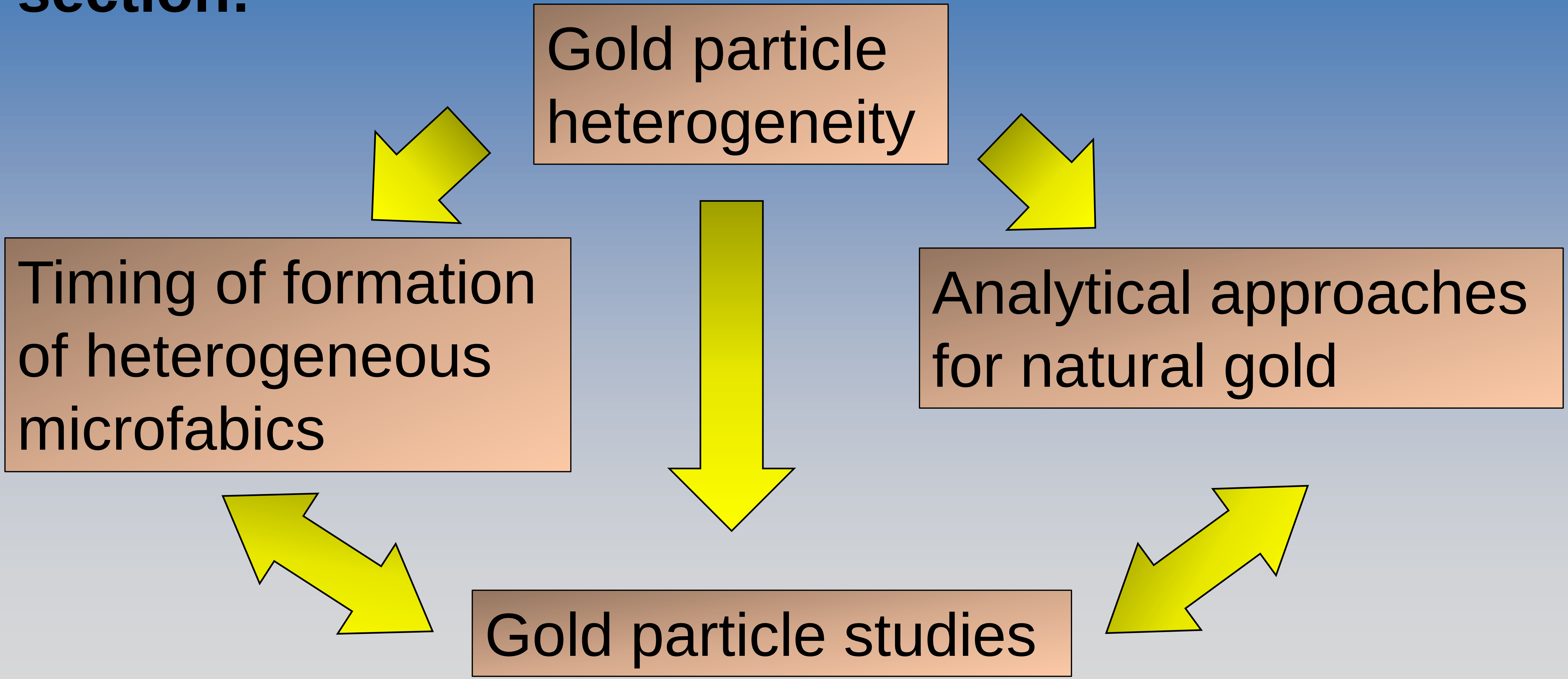
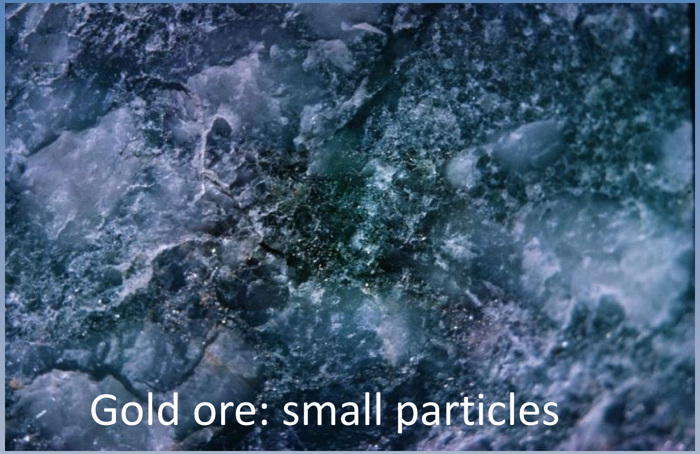
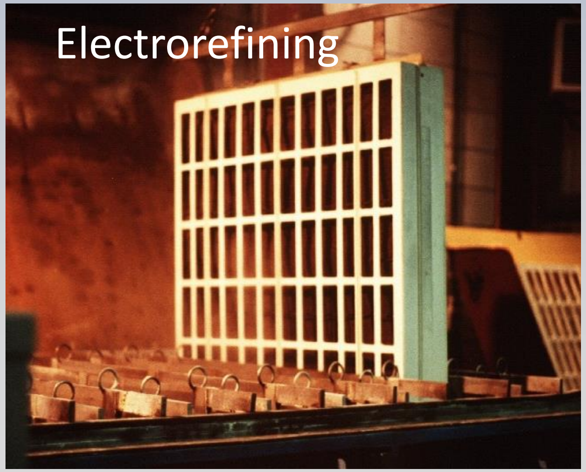
Mineralogical Characteristics of Natural Gold

Aims of this section:

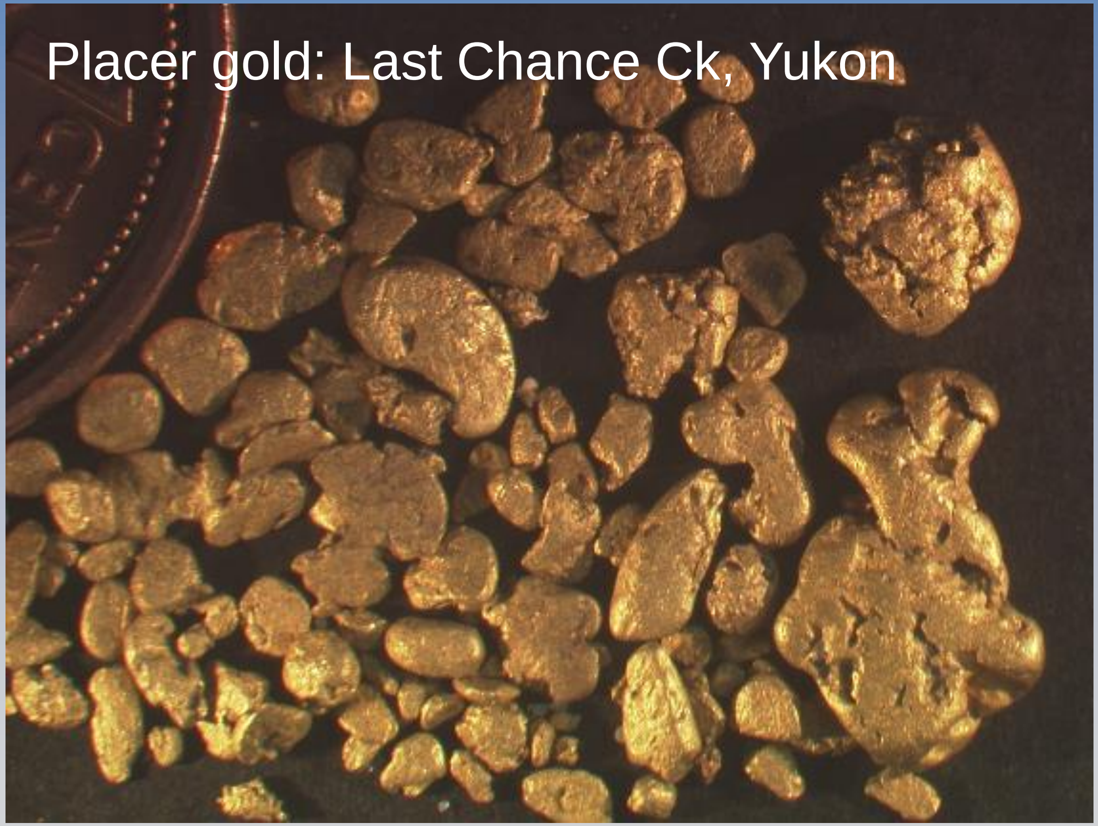


Why do we need to know about the mineralogy of natural gold?



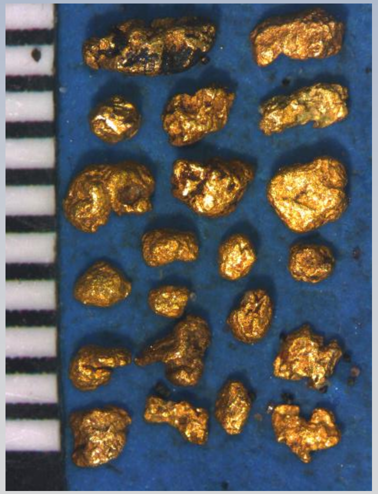


Natural gold: can we assume that these samples are also homogenous?

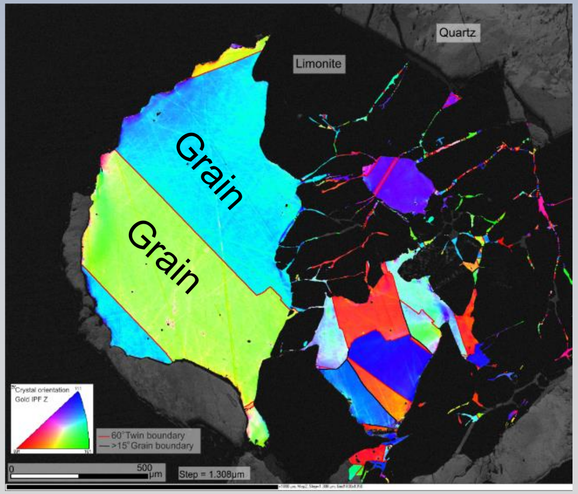


Many studies of natural gold have not questioned whether this is the case

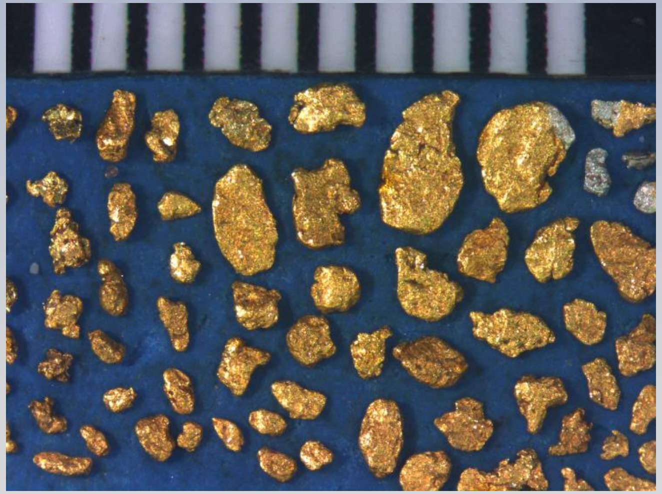
Terminology



Particles



Grains



Sample Population

Some Fundamental information- Ag/Au ratios

1. We know that gold from different localities may exhibit different silver contents.
2. We have insights as to WHY the Au/Ag ratio should vary.

Au transported as bisulphide, Ag transported as chloride

Alloy composition : $\dfrac{Au_{alloy}}{Ag_{alloy}}$

$$\frac{Au_{alloy}}{Ag_{alloy}} = \frac{a^2_{Cl^-} \cdot a^2_{H^+}}{a^2_{H_2S} \cdot K_{16}} \cdot (Au/Ag)_{aq},$$

Gammons and Williams- Jones 1995

How do conditions at the point of gold precipitation affect Au/Ag alloy?

$$\frac{Au_{alloy}}{Ag_{alloy}} = \frac{a^2_{Cl^-} \cdot a^2_{H^+}}{a^2_{H_2S} \cdot K_{16}} \cdot (Au/Ag)_{aq},$$

Ag has been the most popular discriminant in gold particle studies because:

1. It is pretty much ubiquitous
2. It is easily measured
3. The values vary considerably

Scenario	Effect	Au_{alloy}

Working premise: Different Ag values= different conditions= different mineralizing system

What are gold particle studies trying to do?

Utilise alloy composition data to elevate potential interpretations of whether gold is present/absent

Early studies based on Ag content (and in some cases minor Cu)

Does placer gold/gold in till show compositional similarities with gold from a known source?
Populations of individual particles
(e.g. : Knight et al 1999)

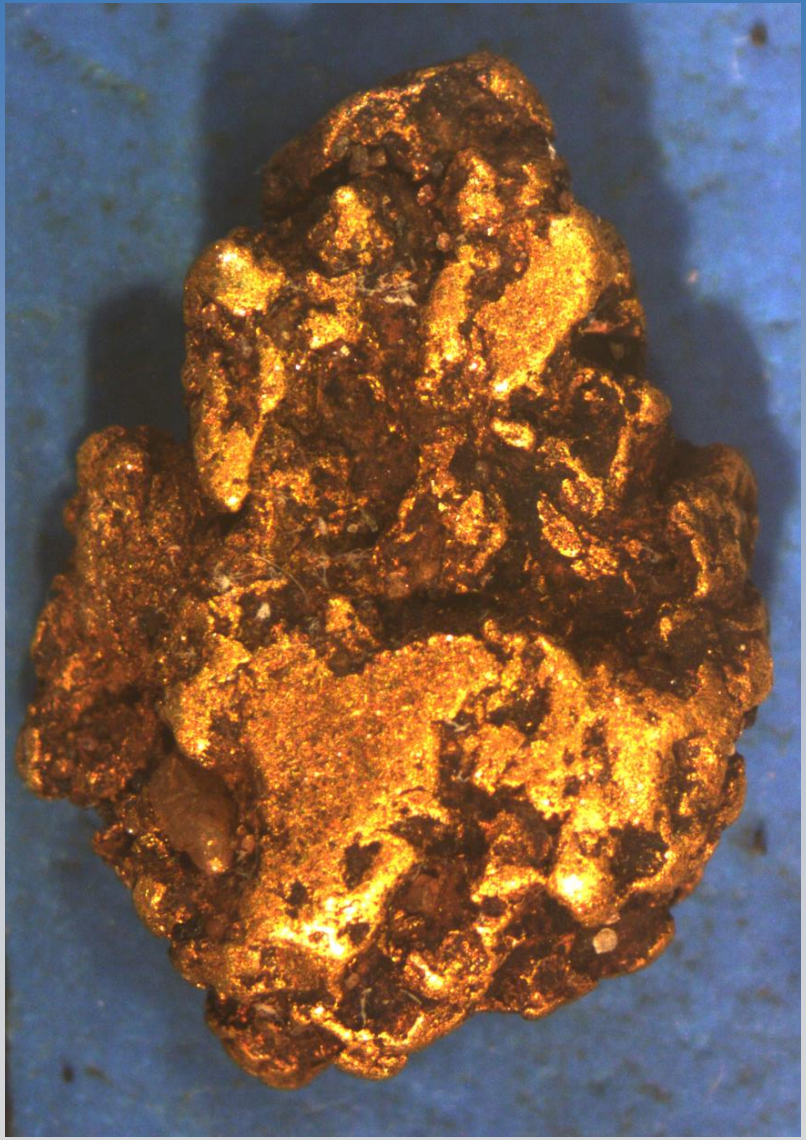
Can we infer the deposit type of placer/till gold from the compositional signature?
Bulk compositions (smelted gold)
(e.g. Morisson et al. 1990)

What methodology is appropriate to characterize a population of gold particles?

To what extent is valuable detail lost?

Depends on nature and degree of heterogeneity with gold particles AND the analytical approach employed

Examples of analytical approaches



Individual particles

Whole particle analysis

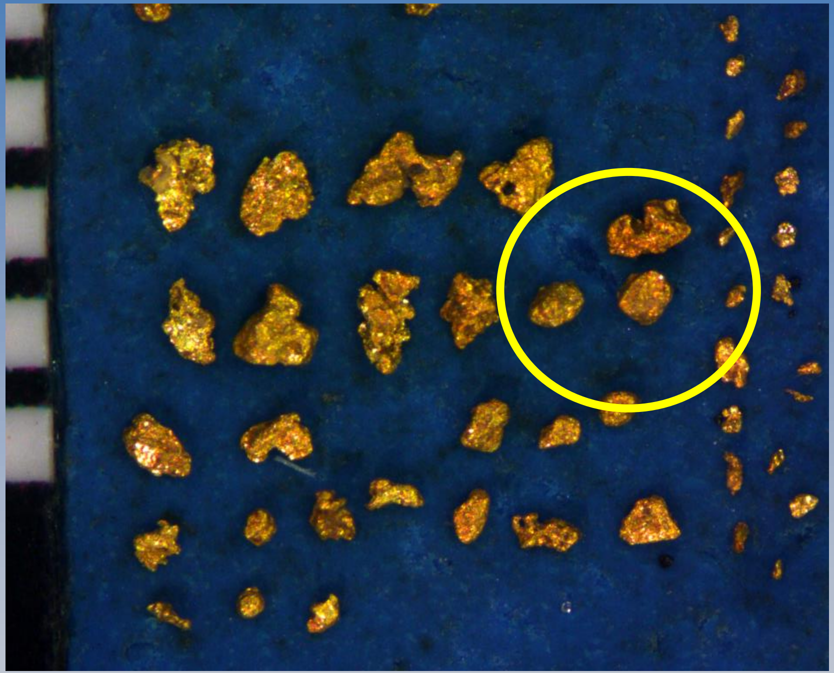
Surface analysis: XRF, or drill down by LA

Assumes intra-particle homogeneity

Section, polish: EMP or LA-ICP-MS

Can avoid major intra-particle heterogeneity

Populations of gold particles



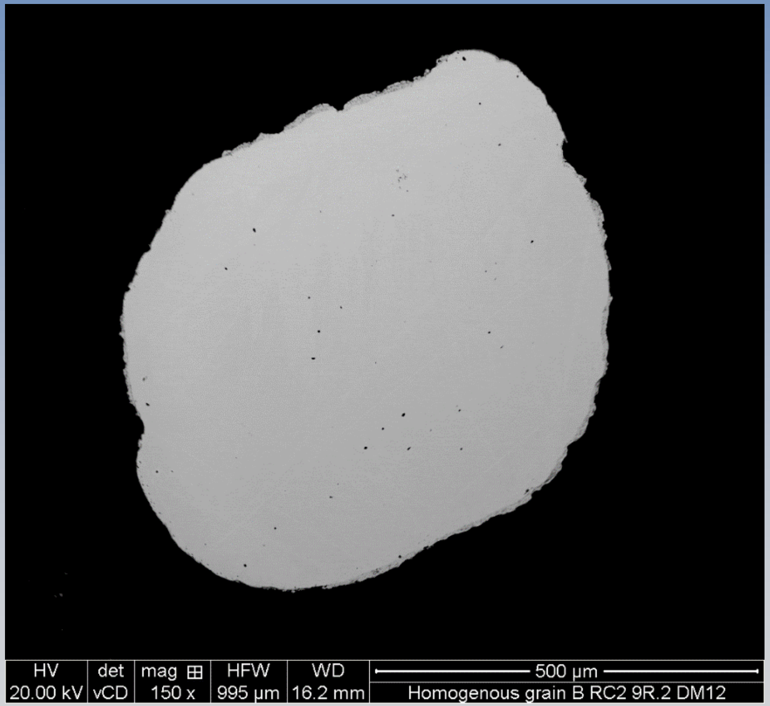
Analyse a small number (or collect a small number to start with)

Assumes inter-particle homogeneity

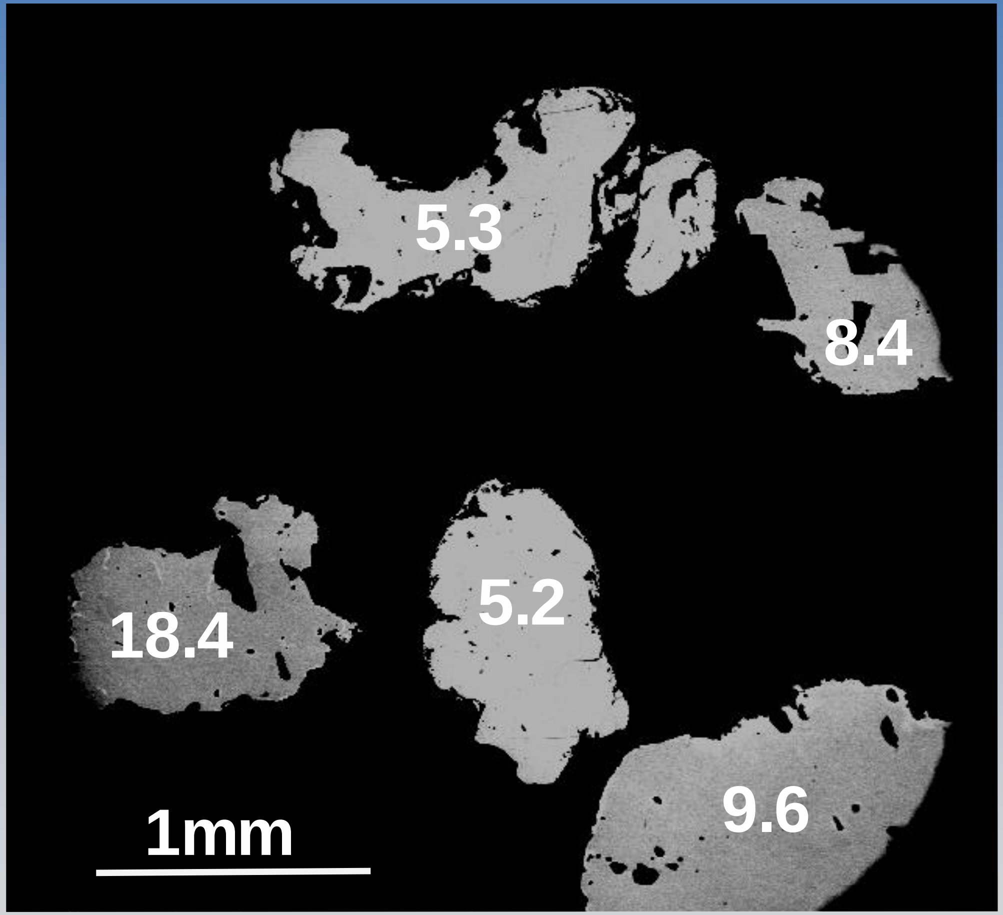
Gold particles and heterogeneity:

Major heterogeneity in gold particles- revealed in polished sections

Alloys



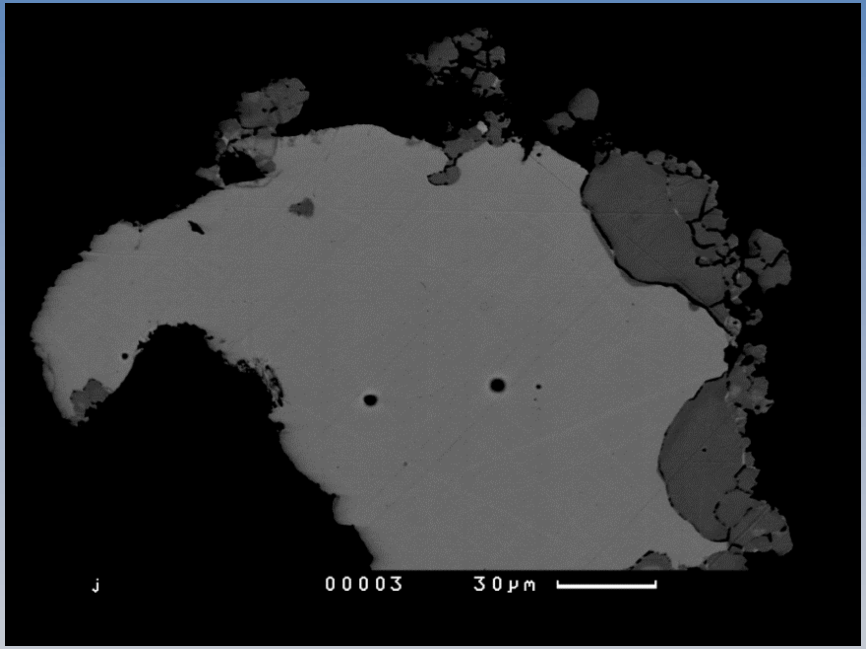
Homogenous wrt Au/Ag:
BSE SEM image



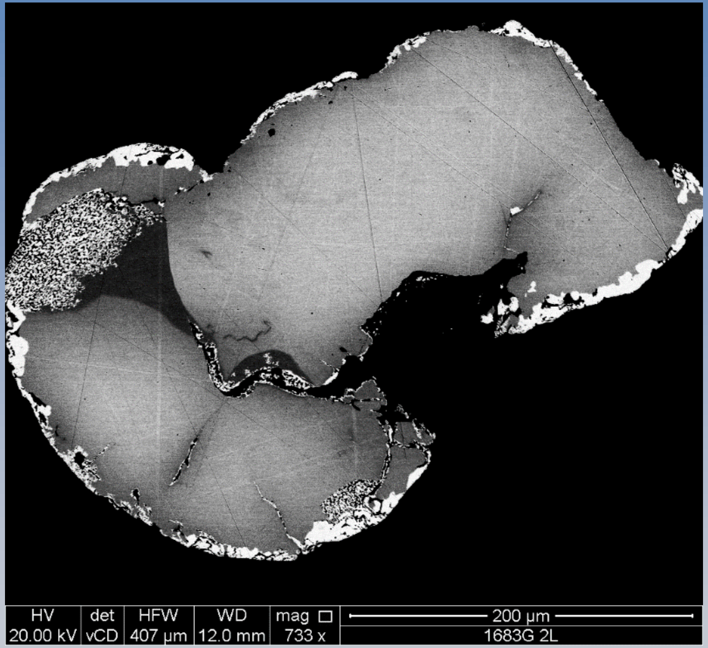
Particles from the same (placer) locality:
homogenous particles- different Ag contents

Major heterogeneity in gold particles- revealed in polished sections

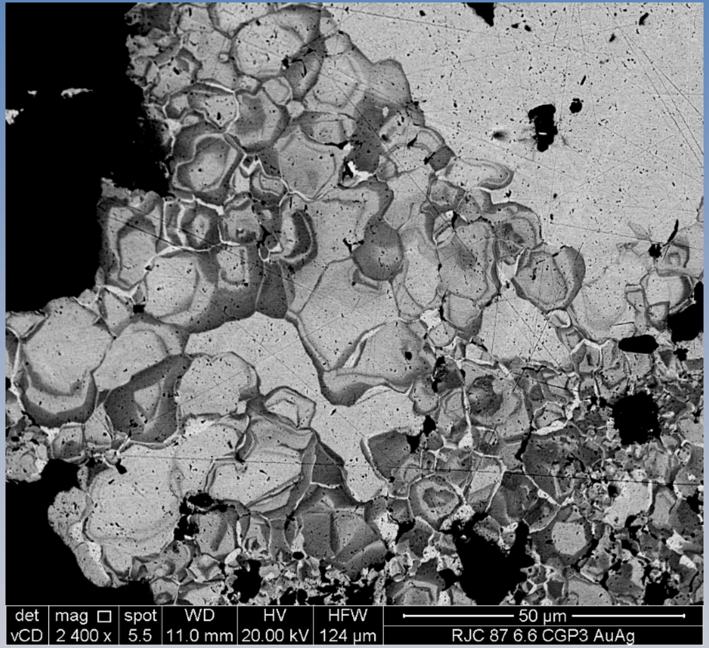
Examples of Au/Ag variation:



Two (largely) homogenous alloy compositions

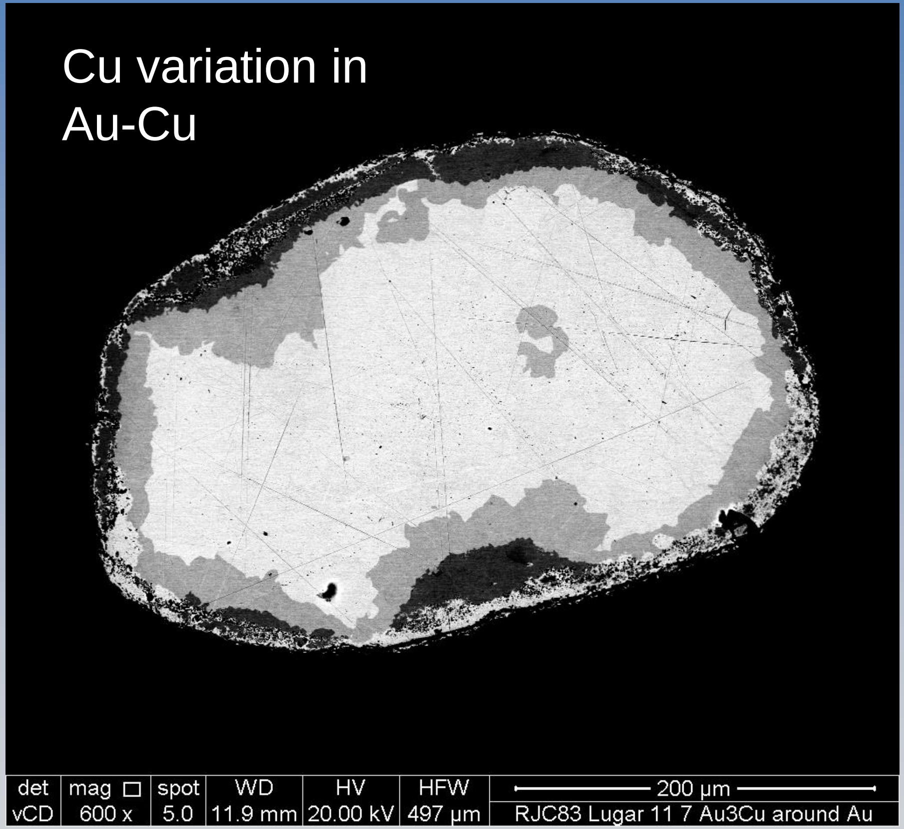


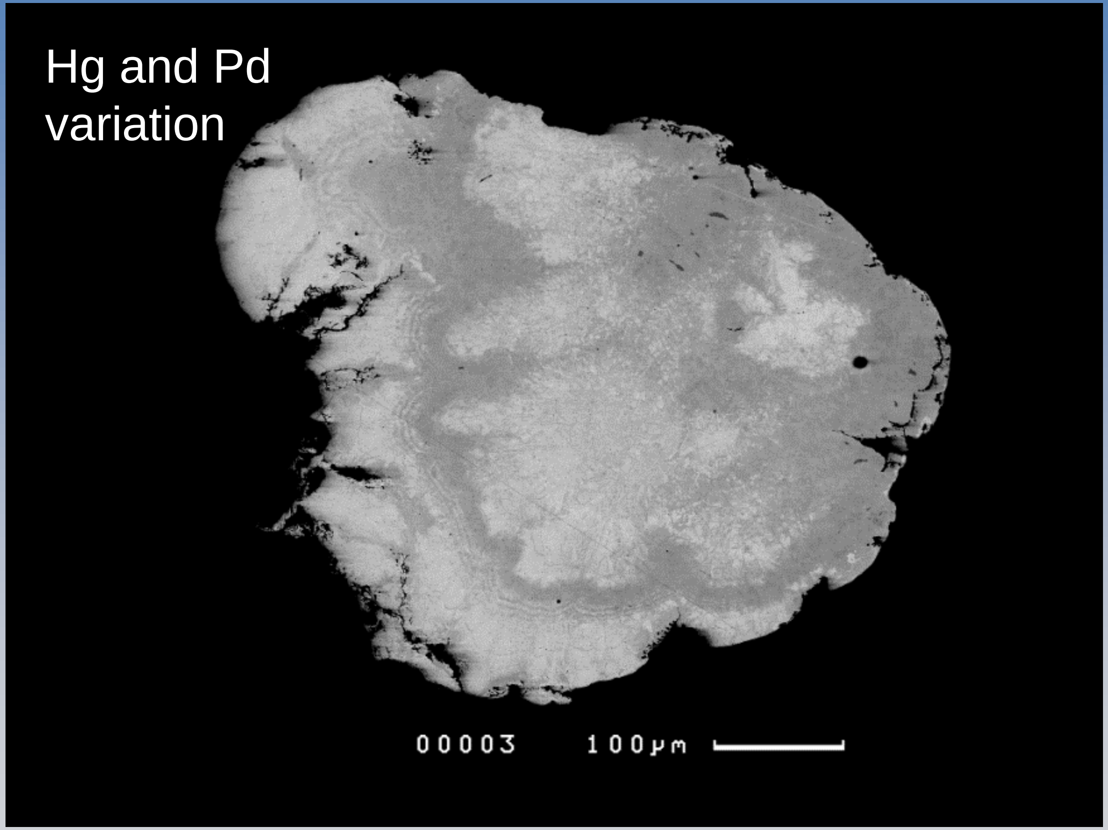
Heterogeneous alloys



Homogenous alloy + heterogeneous alloys

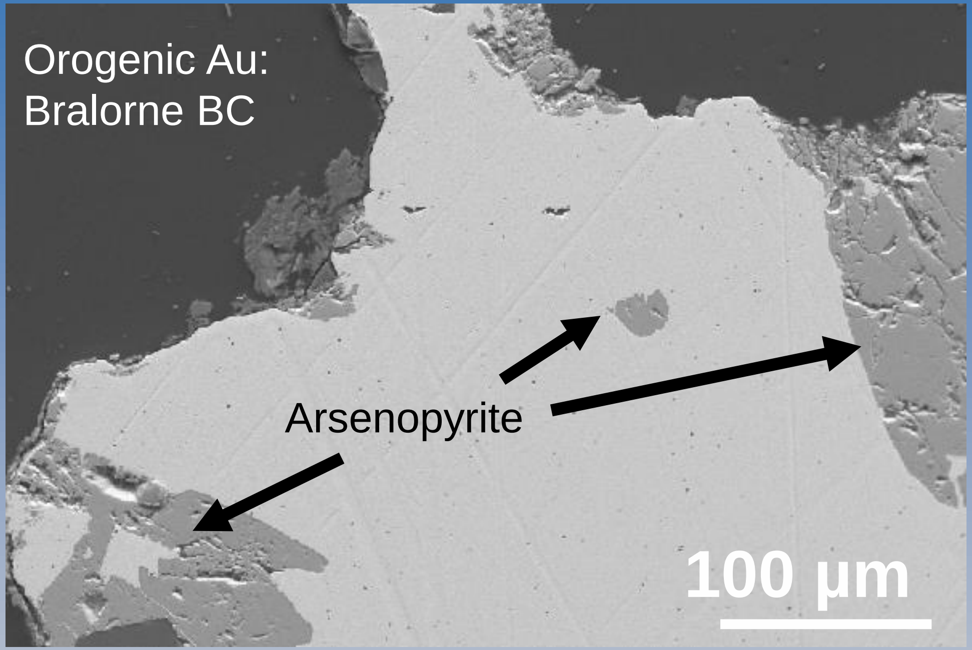
Alloy heterogeneity: Is it confined to Ag?

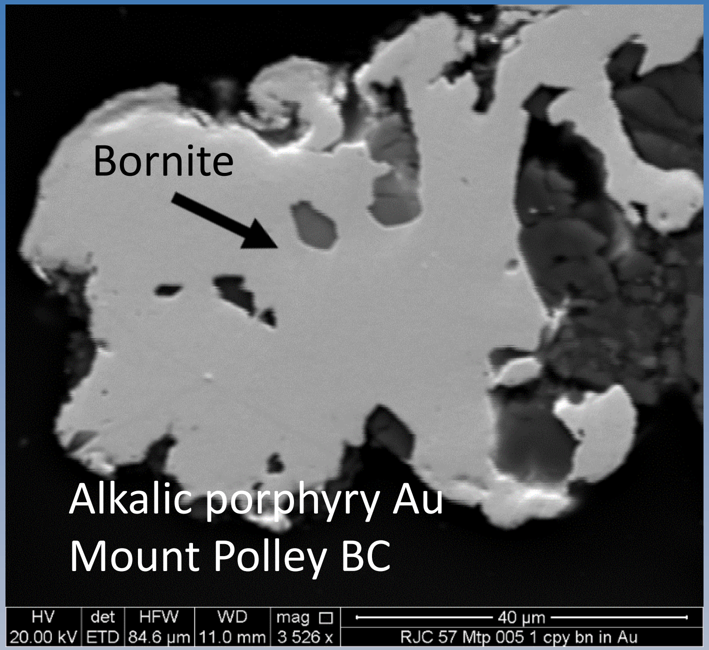


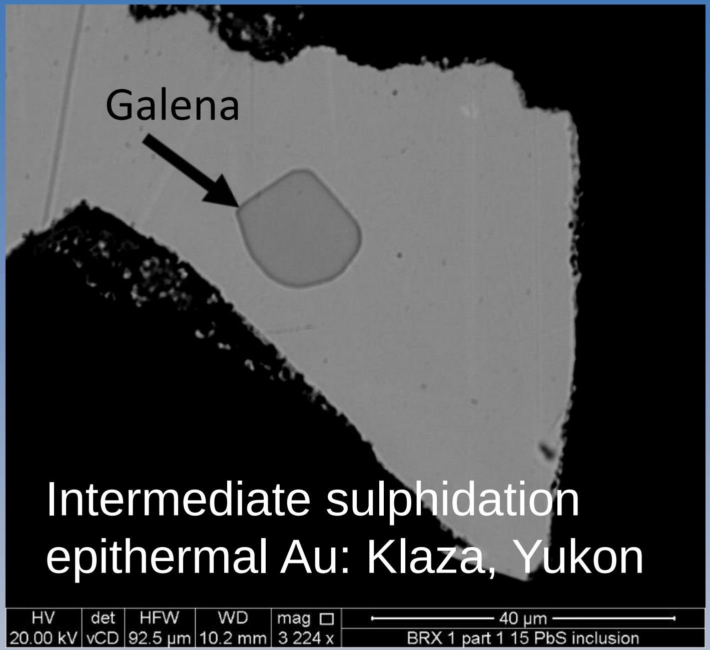


These features are nowhere near as common- but when present they may be very useful.

Alloy heterogeneity: inclusions

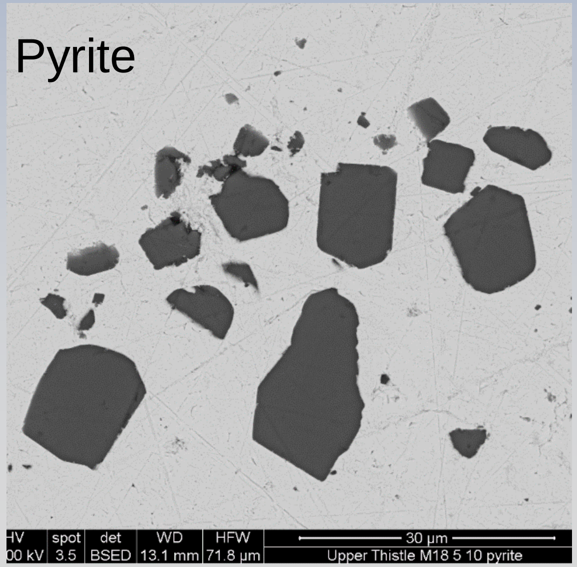


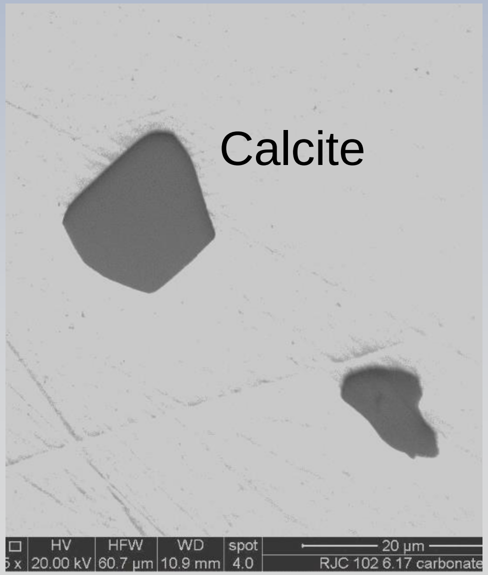


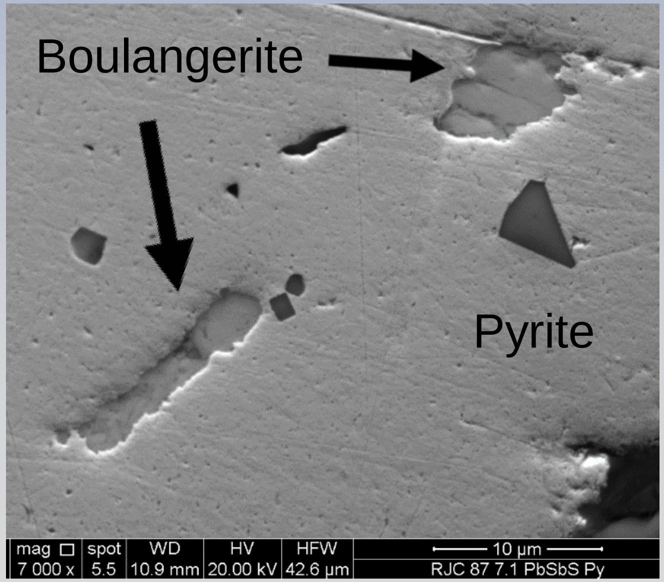


Primary features: related to mineralogy coeval with Au alloy

Inclusions inherited by detrital particles





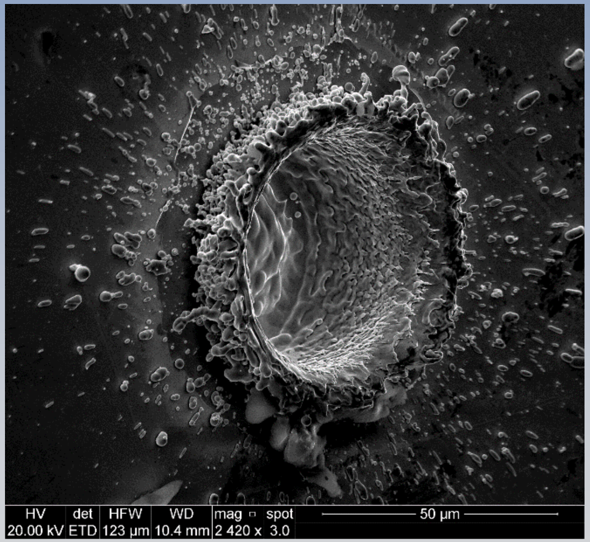


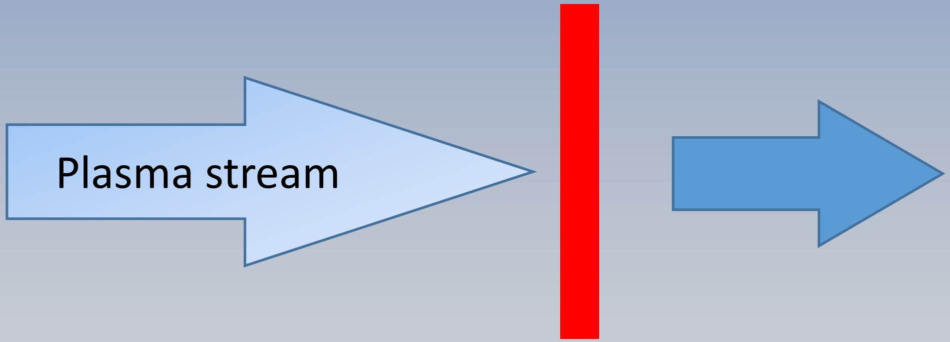
Trace element heterogeneity

Trace element analysis of gold : LA-ICP-MS approaches

LA systems provide far lower LOD for elements than EMP

1. Quadrupole MS systems



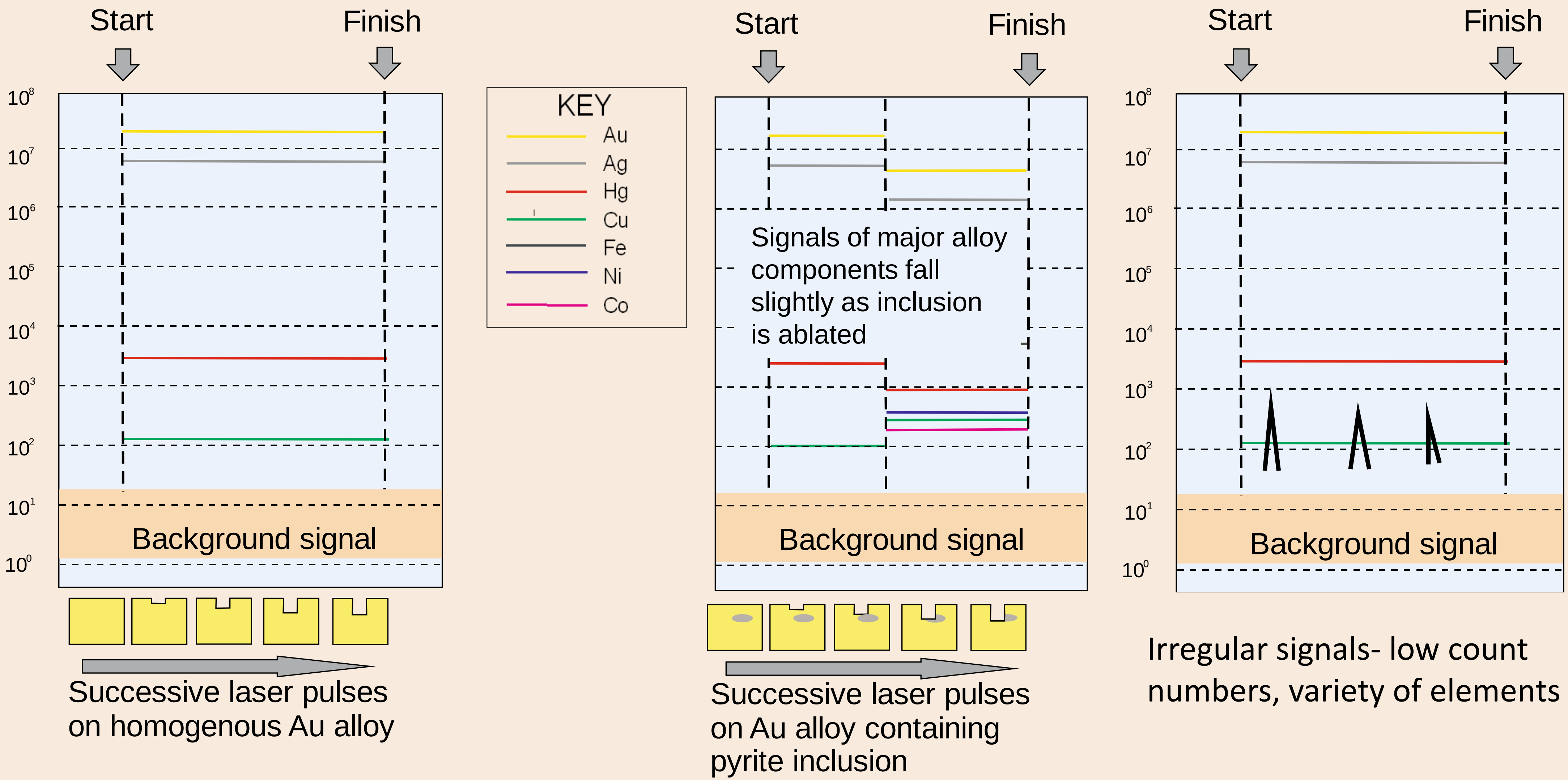


Sequential analysis of particle mass

LA quadrupole MS promoted as a method to provide more discriminants because of the low LOD values. Pioneered in studies of gold bullion for gold smuggling studies (Watling et a. 1994)

Sequential element sampling does not generate data on covariance

Trace element heterogeneity: alloys

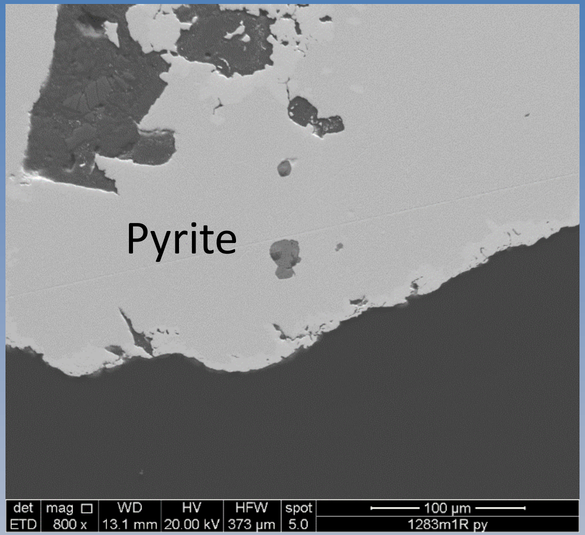


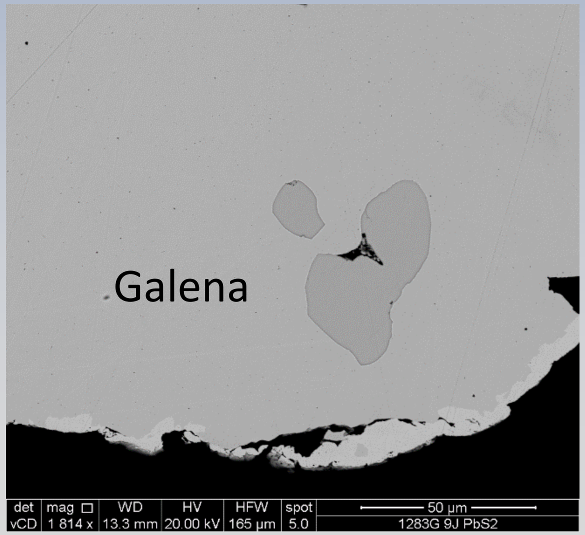
Irregular signals- low count numbers, variety of elements

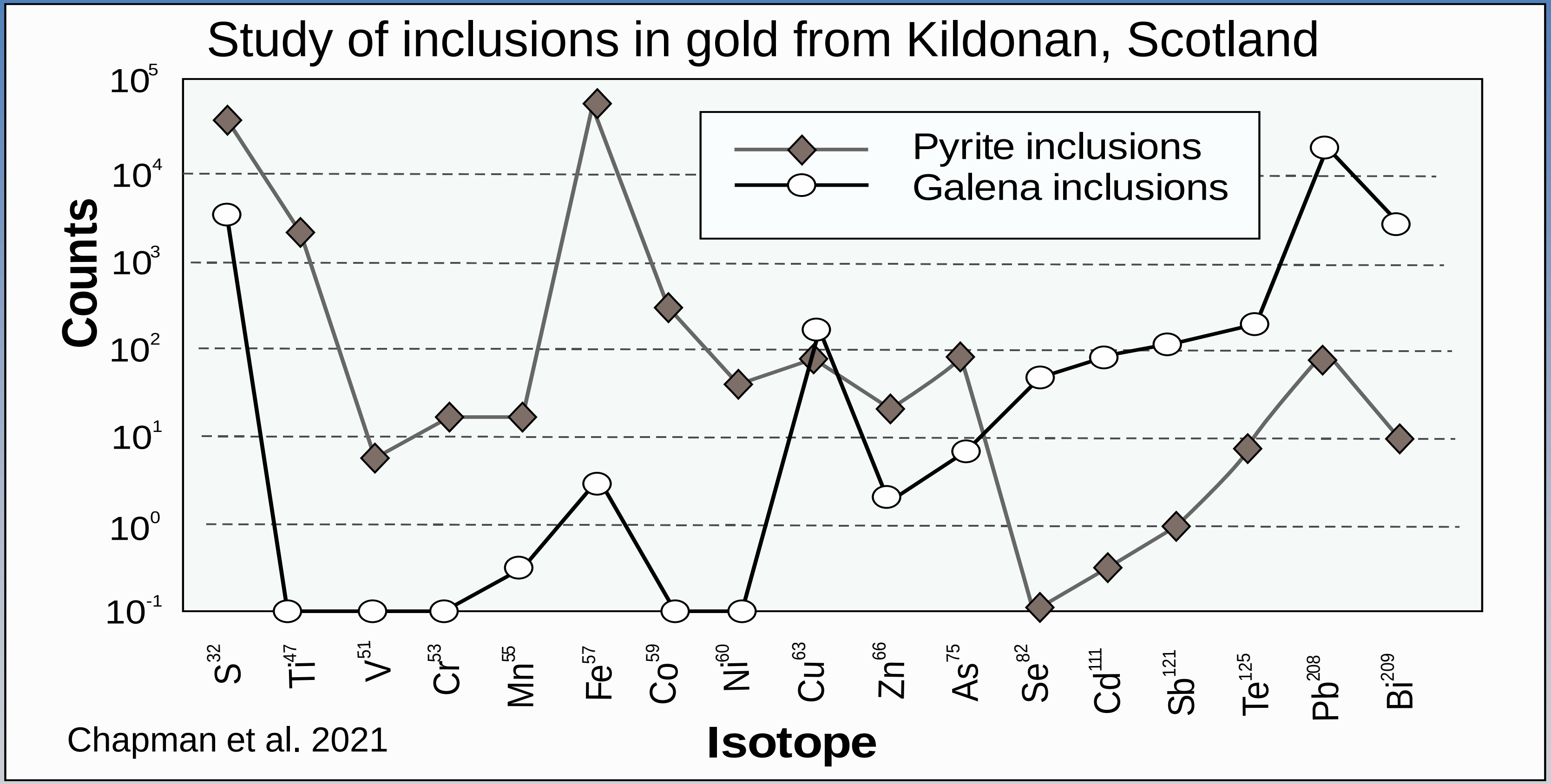
Quadrupole MS systems

Trace element heterogeneity: inclusions

New research direction





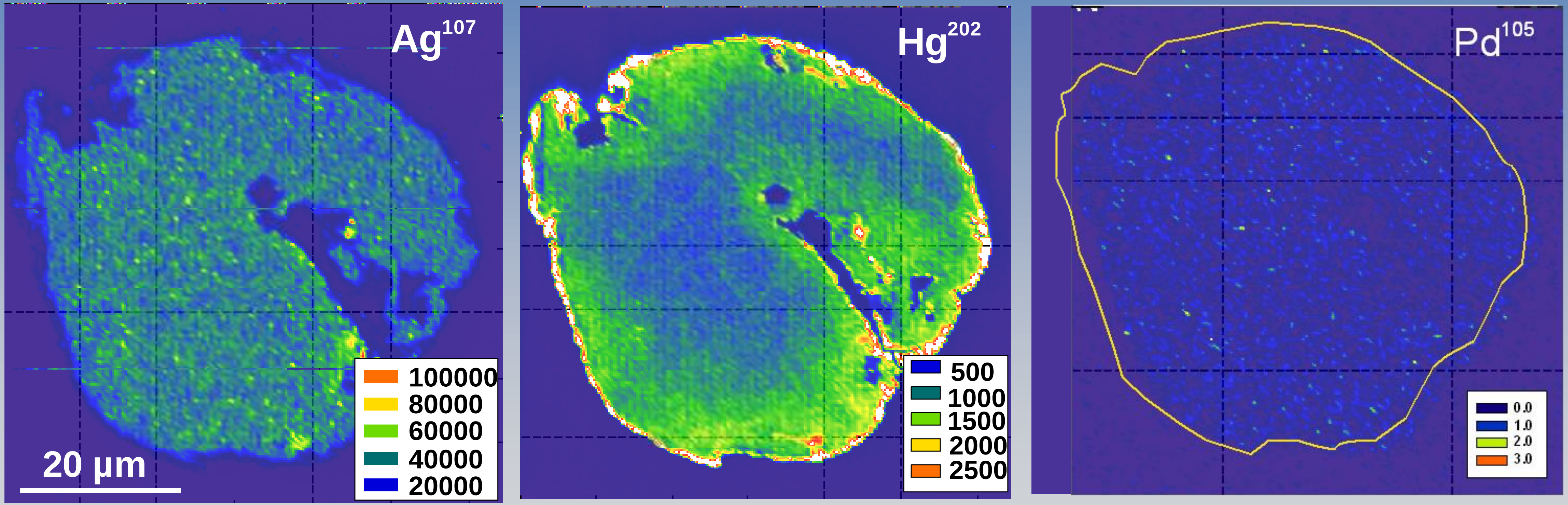


Total trace element signature is not only within the alloy.

Trace element heterogeneity: alloys

LA-ICP-(ToF) MS

Elements measured simultaneously. Permits generation of trace element maps



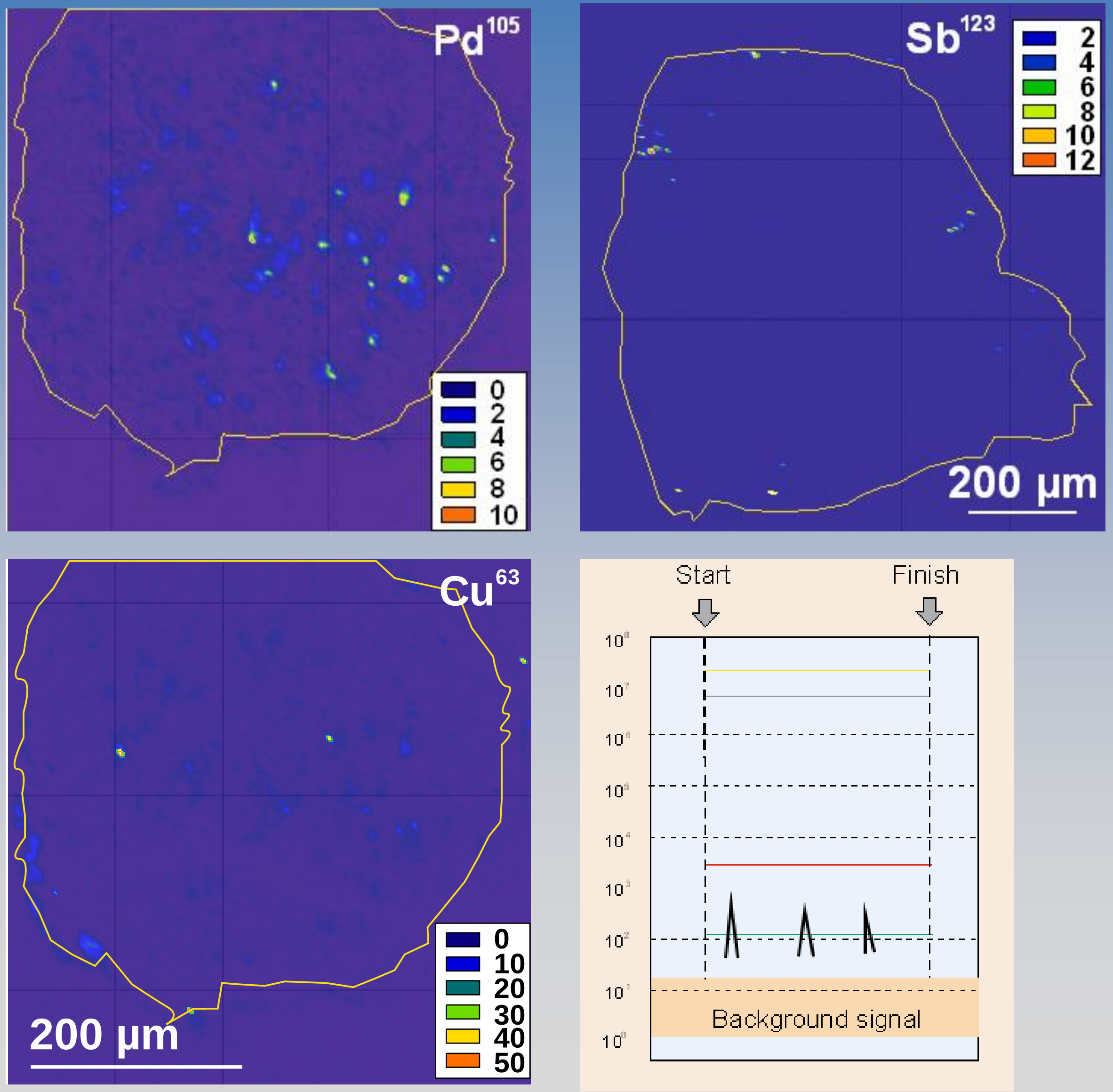
Particles may be homogenous wrt Ag (left) but heterogeneous wrt other minor alloying metals (right).

Trace elements: Pd intensities are far lower than the Hg intensities (left): but homogeneously distributed

Trace element heterogeneity: alloys

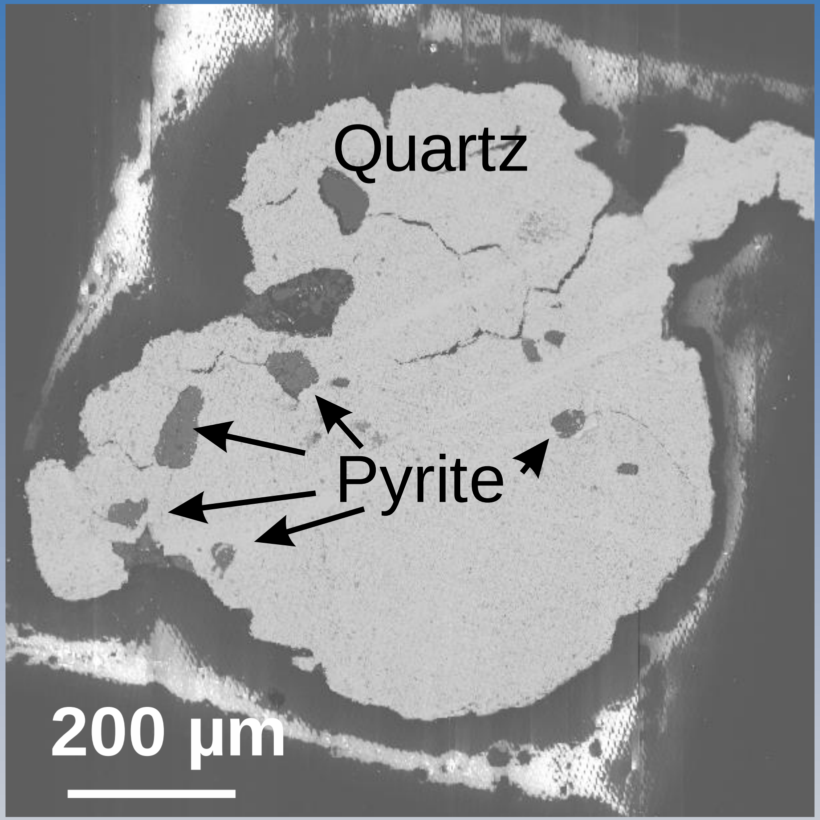
Elemental 'Clusters' : Highly localized But LOW concentrations of specific Elements.

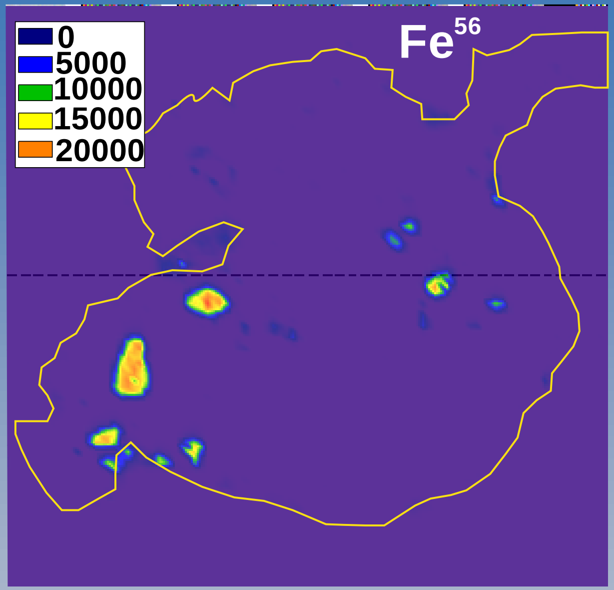
The cluster comprise single elements at intensities far <u>lower</u> than components of inclusions and are spatially divorced from inclusions. Their presence explains the irregular low responses reported using the quadrupole system

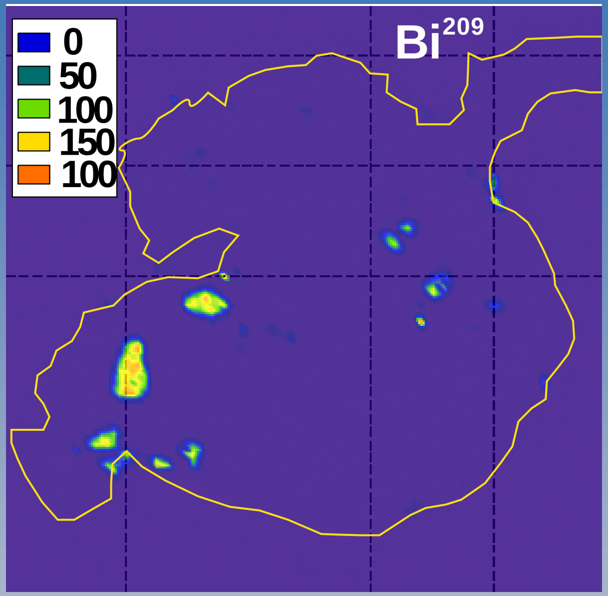


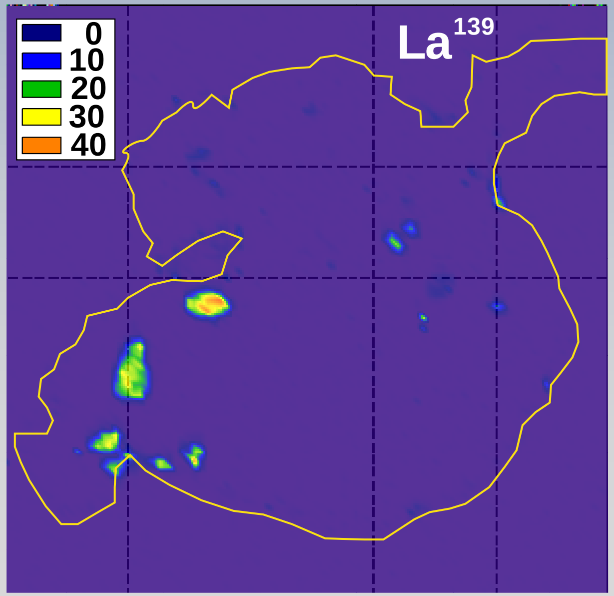
LA-ICP-(ToF) MS

Trace element heterogeneity: inclusions









High intensities of Fe correspond to pyrite inclusions observed in SE image (left). Bi and La are present at trace levels within pyrite, but are absent in the alloy.

Inclusions in placer particle:
Similkameen R.

LA-ICP-(ToF) MS

Recap

We observe heterogeneity within and between gold particles.

Alloy variation – usually with respect to Ag but also in some cases wrt Cu, Pd or Hg

Heterogeneous microfabrics may take various forms

Inclusions of other minerals indicate the hypogene mineralogy

Alloys homogenous with respect to Au and Ag may be highly heterogeneous wrt other elements

Trace element signatures of inclusions may be completely different from that of the host alloy.

Key question : WHEN do these textures form?

Microfabrics in gold particles: timing of formation

Initial precipitation of gold alloy

Modifications to initial alloy occurring as a consequence of an evolving hydrothermal system

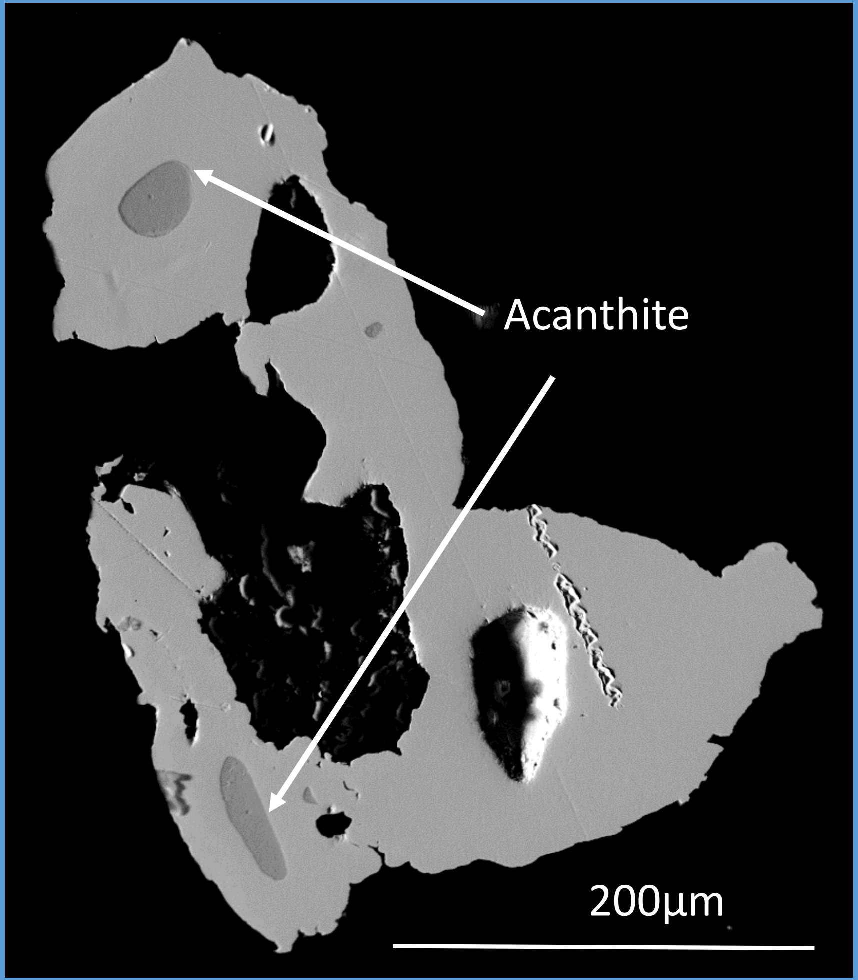
Mineralizing system

Changes during residence in the Hypogene environment-subsequent orogen

Modifications to gold particles in the Surficial environment

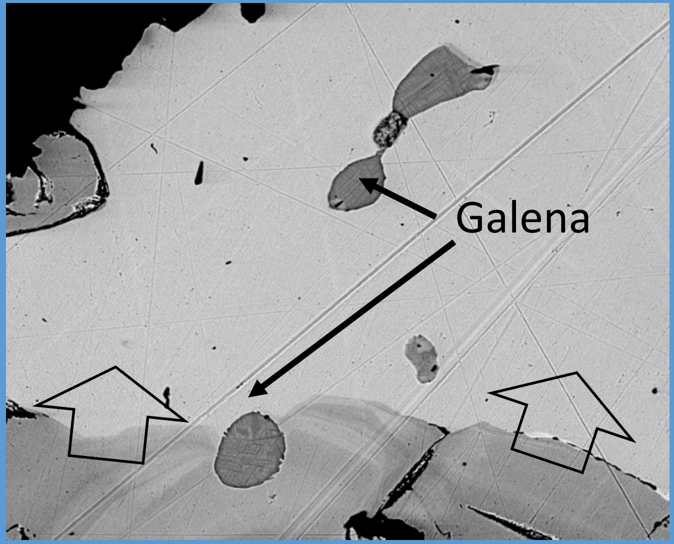
Features formed in the Mineralizing environment

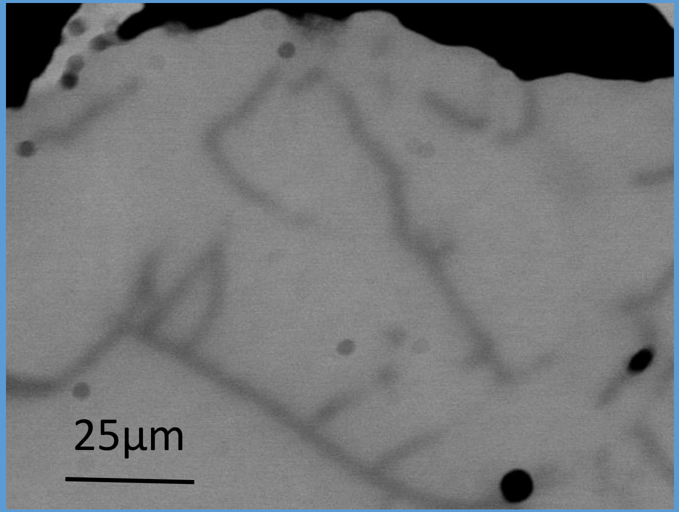
Primary mineralizing environment



Homogenous alloy and inclusions

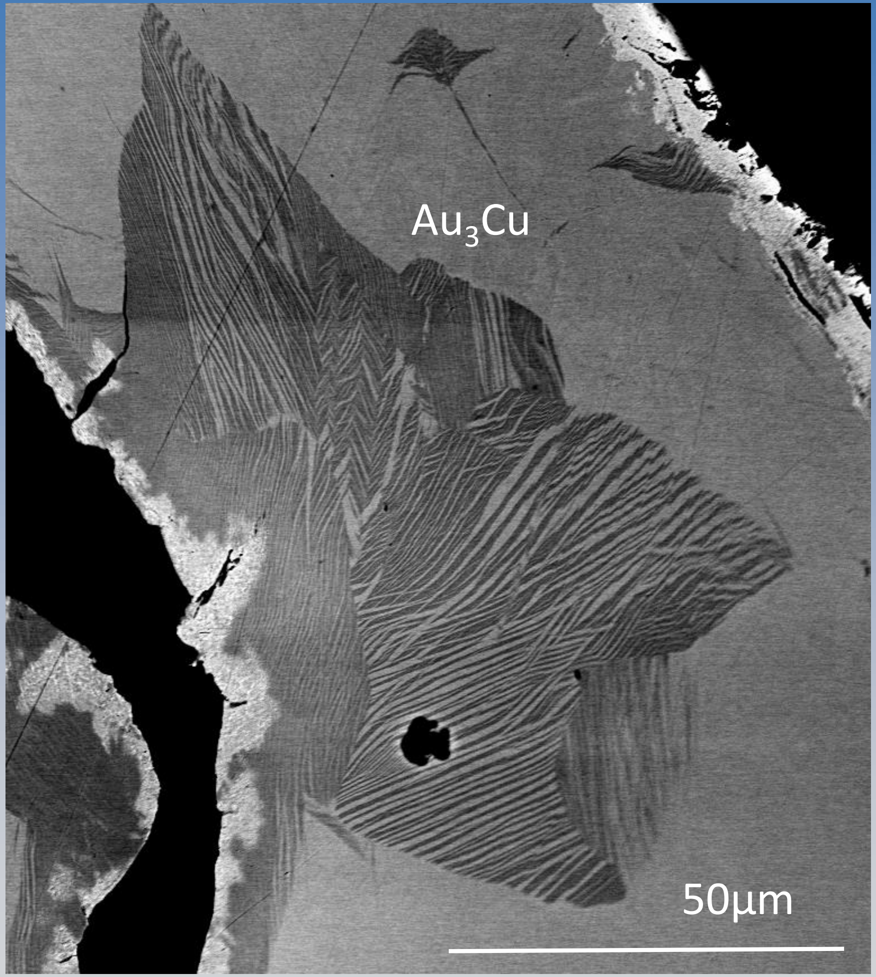
Evolving mineralizing environment



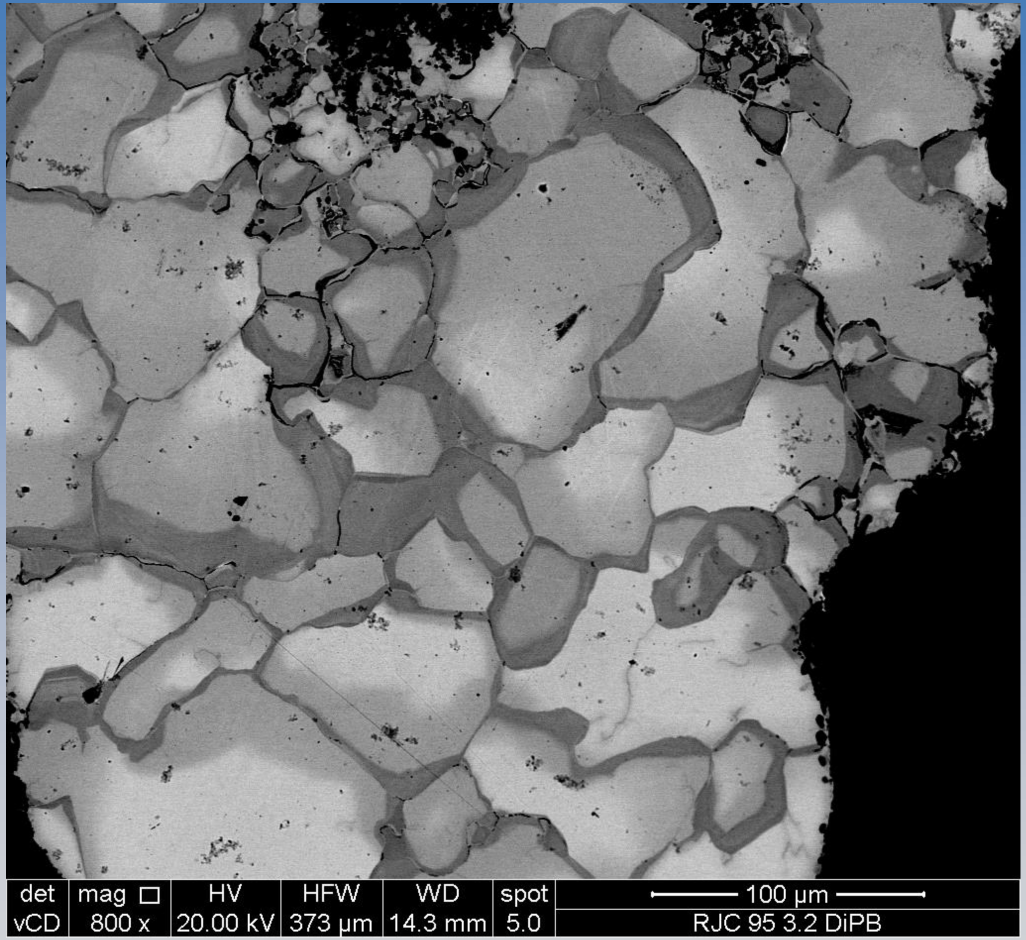


Ag-rich alloy is compatible with lower T and decreased Au/Ag (aq). Ag-rich gold in equilibrium with evolved fluids- these may replace pre existing alloy (top) or penetrate along grain boundaries (below). Late alloy is almost always relatively Ag-rich- (see exception in a few slides time)

Modification of original alloy: subsequent residence

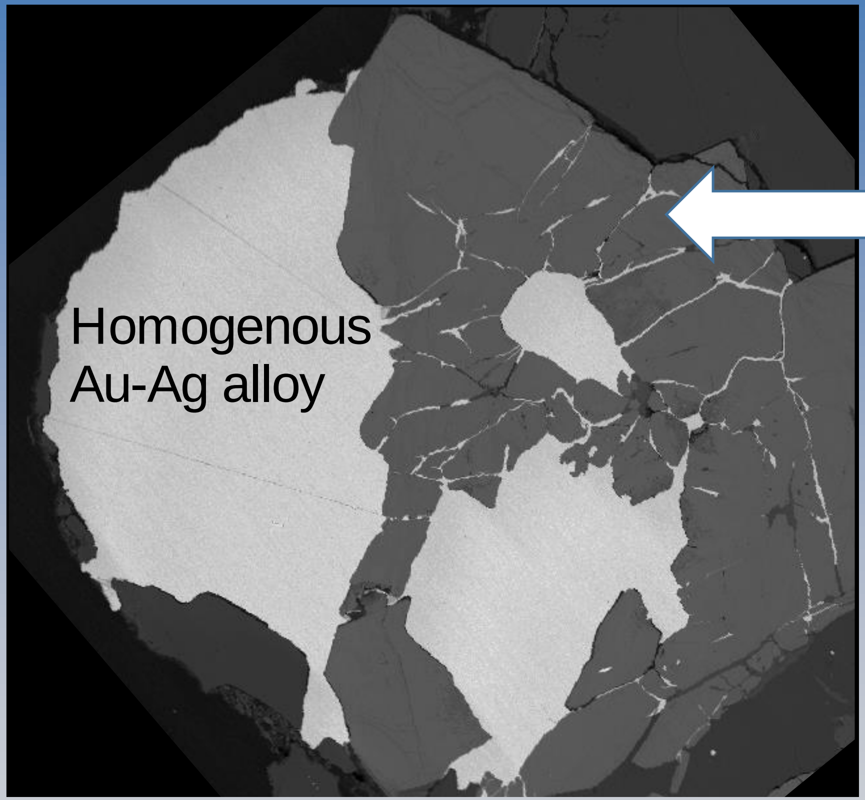


Exsolution of Au-Cu intermetallics from Cu-rich alloys.

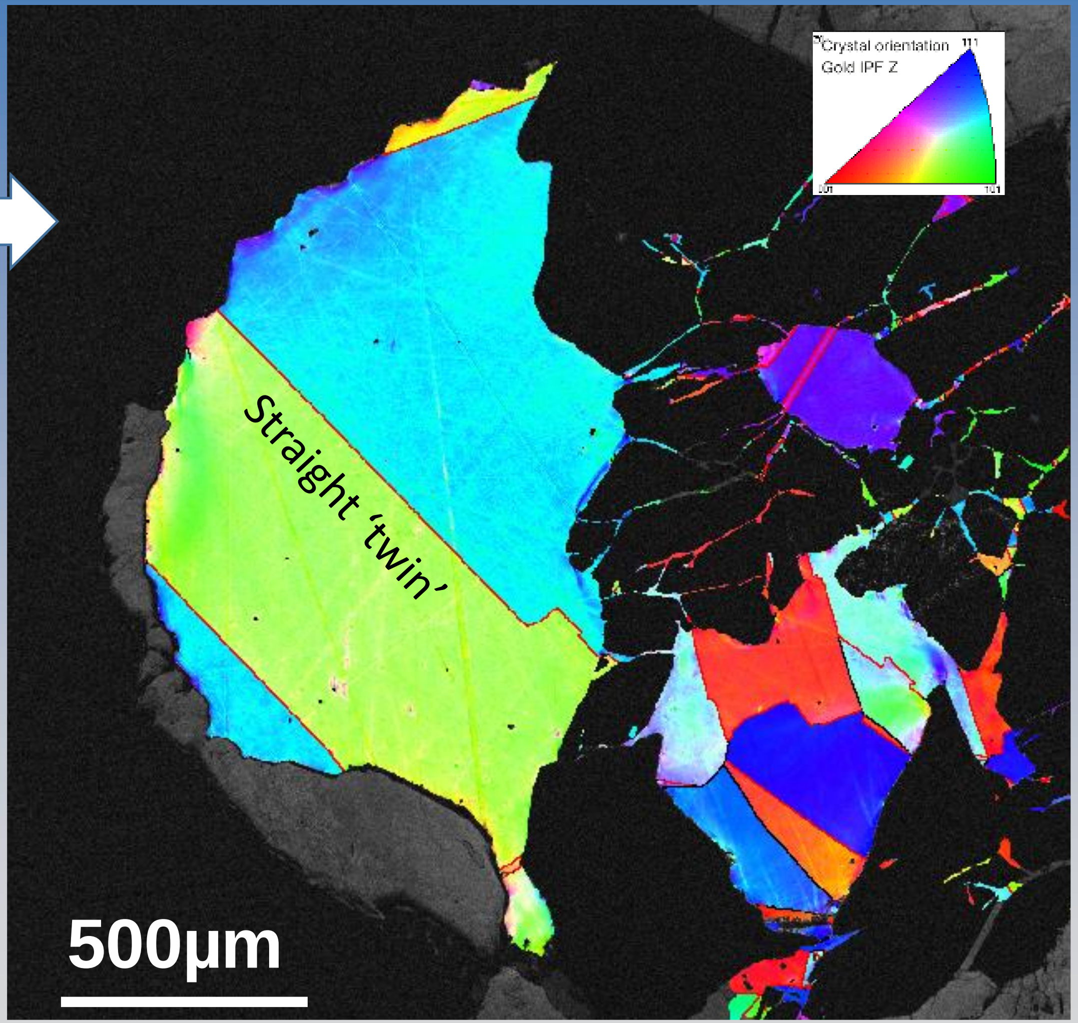


Texturally this is more similar to the Ag-rich tracks than the bulk replacement. There is a key feature to consider….

Crystallography of native gold



Same particle

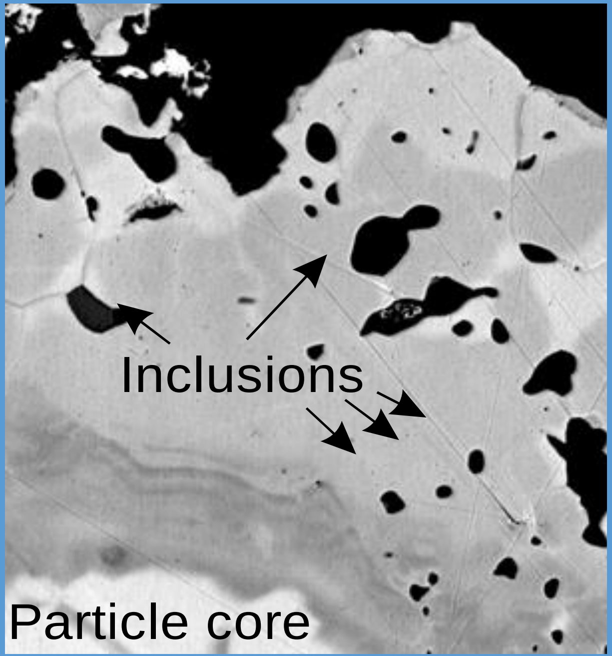


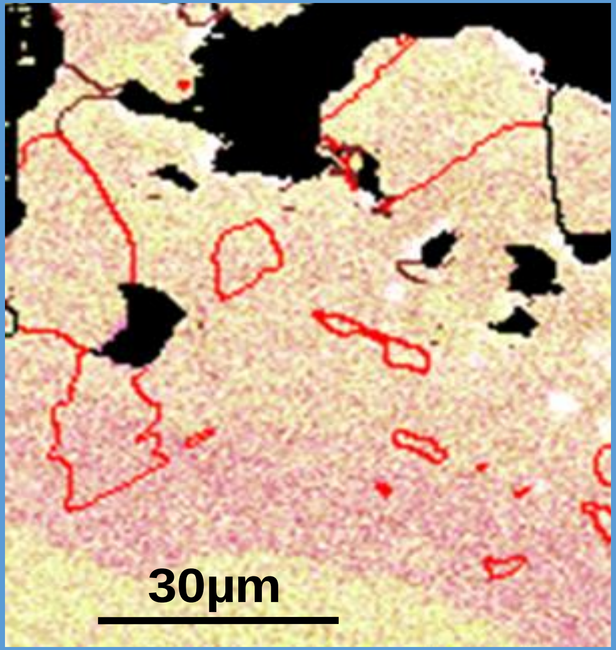
EBSD analyses reveal crystal domains (grains) denoted by colour-coded crystal orientation .

A 'particle' may contain several 'grains'

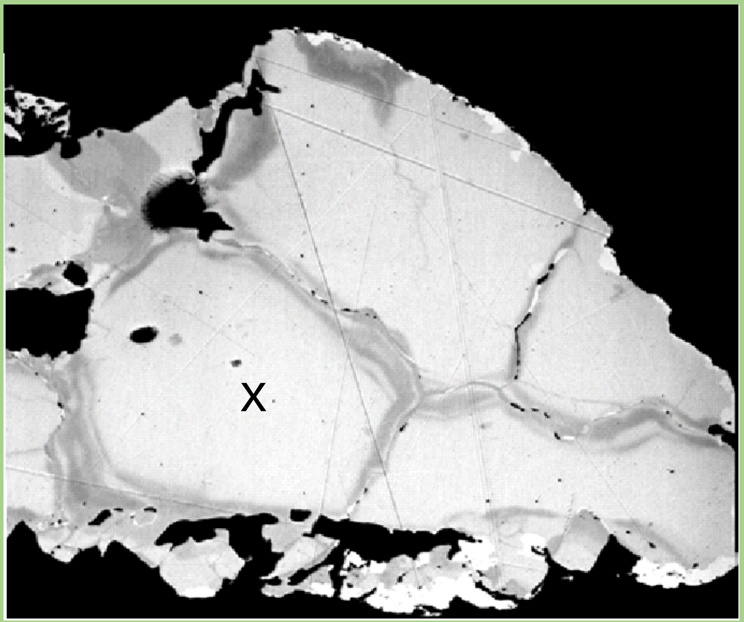
We use relationships between grain boundaries and composition to tell us how microfabrics form

Integration of composition and crystallography

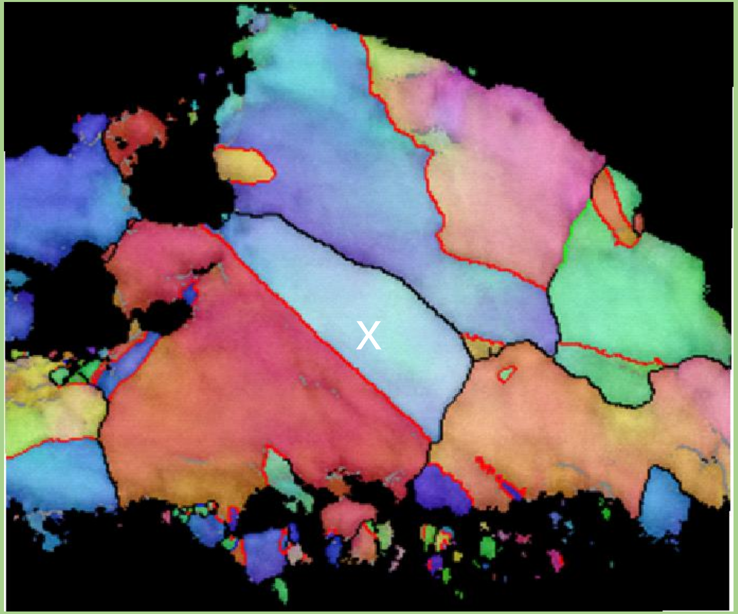




Ag-rich alloy (grey and red) replaces particle core- independent of grain boundaries. Texture associated with 'soaking' long contact at relatively elevated T -
PRIMARY MINERALIZATION



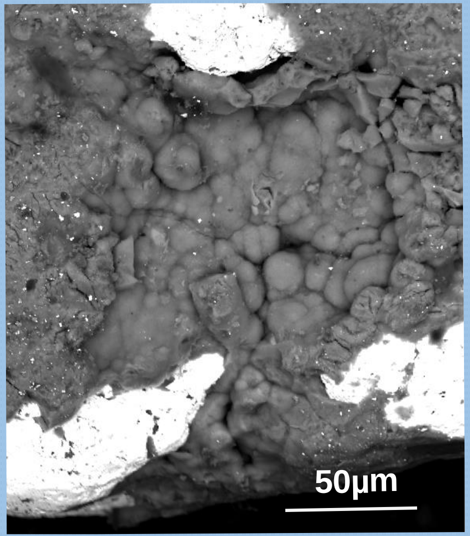
Grain boundaries control ingress of fluid, which permits grain boundary migration and formation of new alloy in equilibrium with the fluid.
Twin boundaries (X) do not permit fluid ingress
EITHER PRIMARY MINERALIZATION OR SUBSEQUENT RESIDENCE

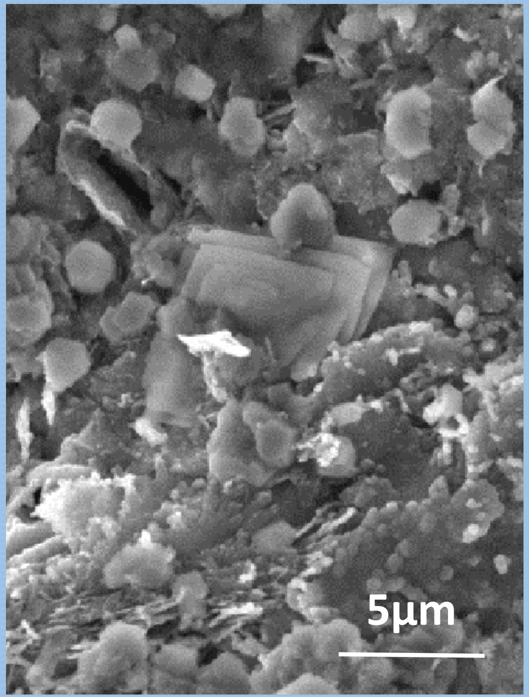


Modification of original particle: surficial environment

Surface coatings

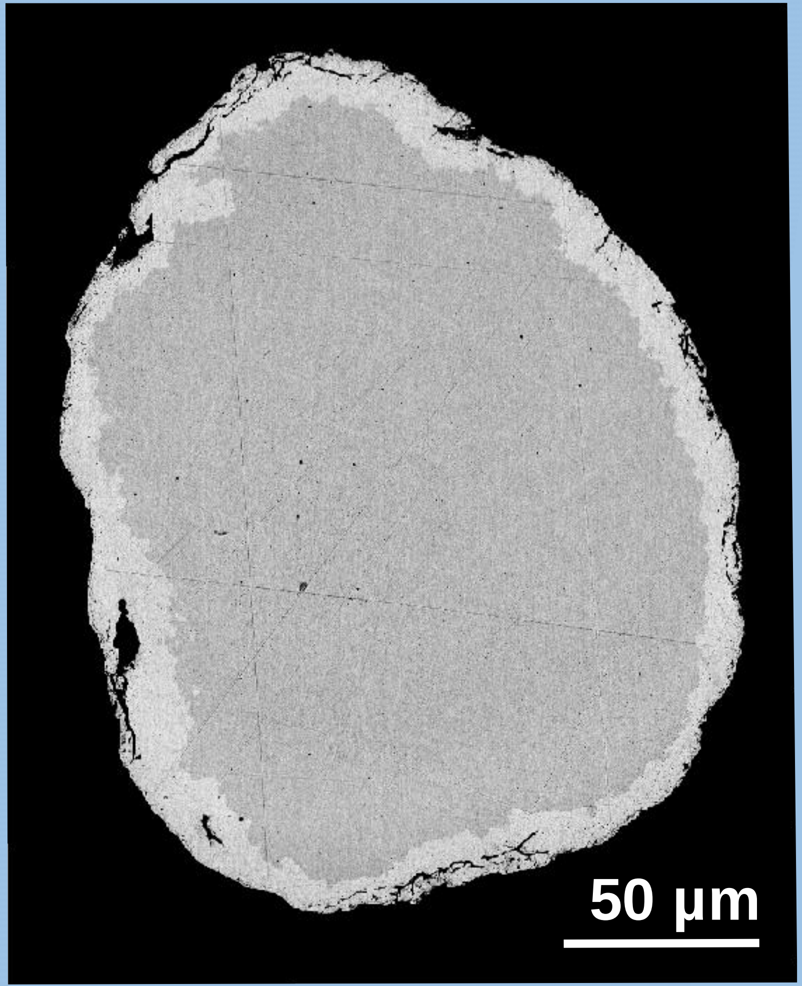
Surface coatings of Fe and Mn oxides commonly form on gold particles during residence in sediment.



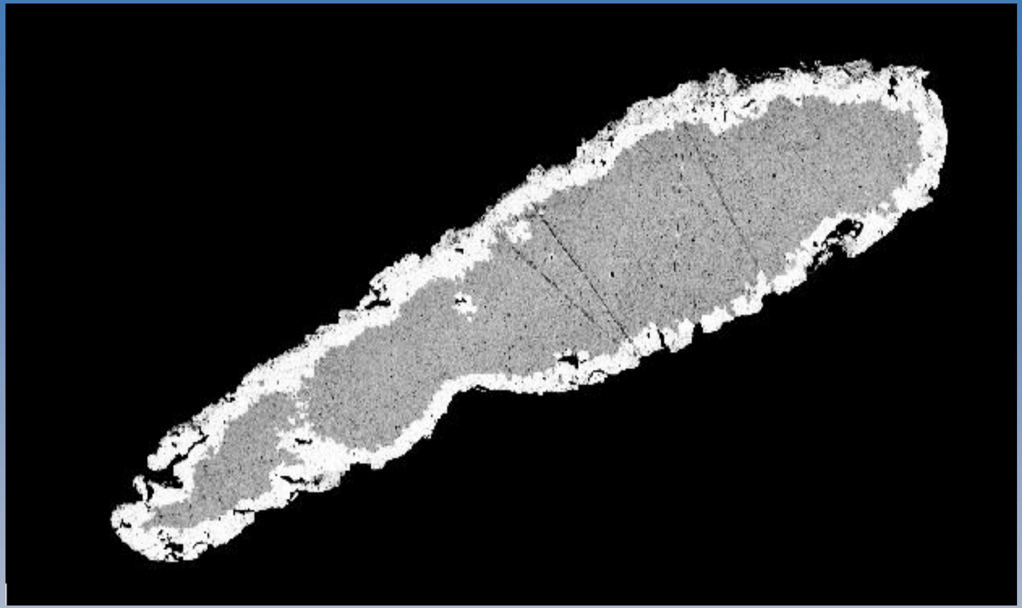


Coatings of pure gold-micron scale are very common.

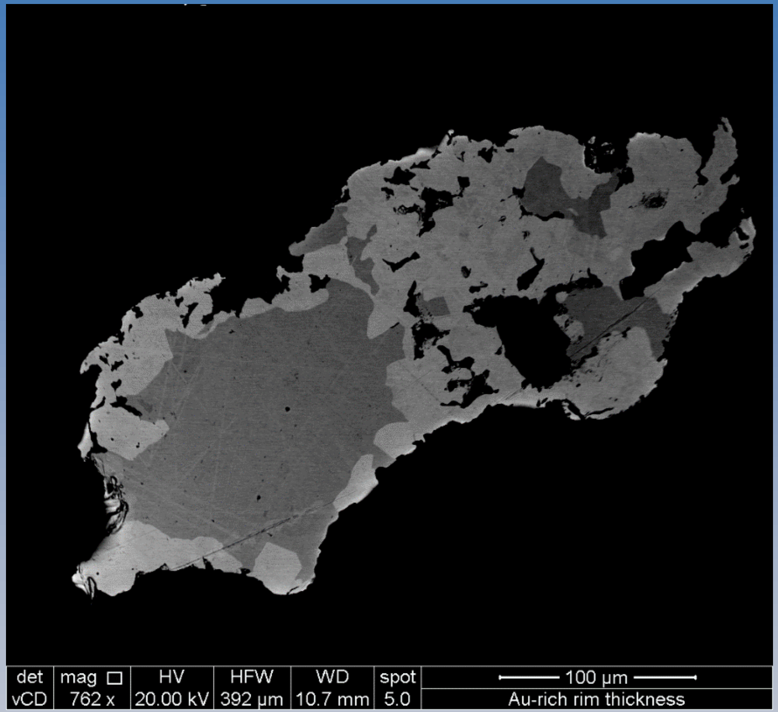
Gold- rich rims

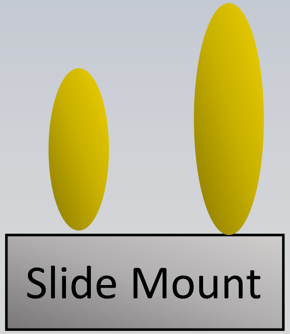


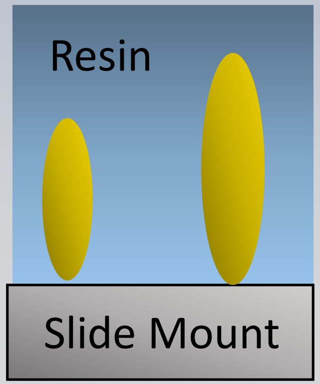
A note about Gold-rich Rims: 1

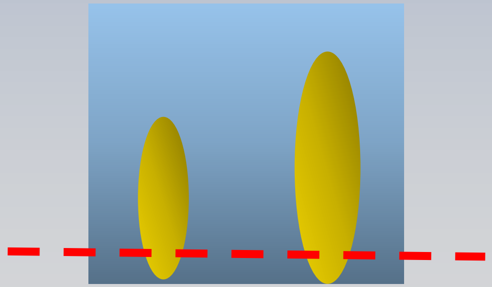


Section through placer gold particle mounted ‘edge on’ : thickness ≈ true thickness

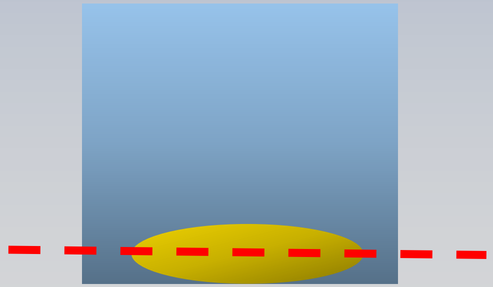








Line of section polish



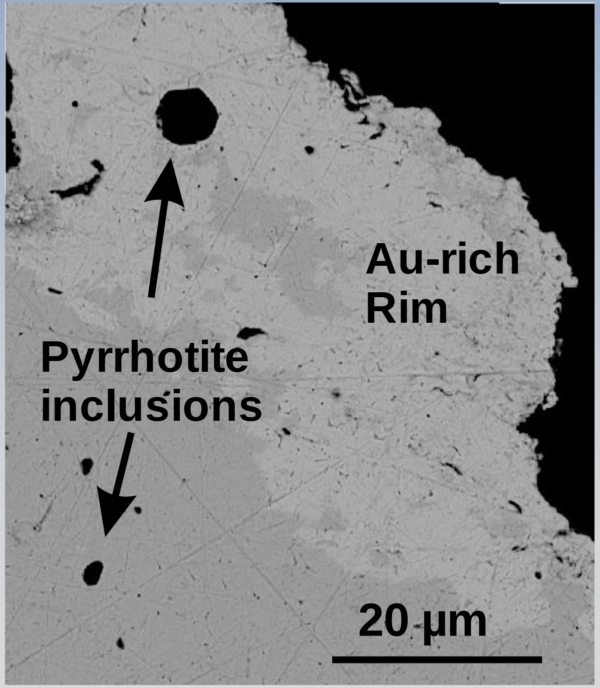
How ‘thick’ is this rim?

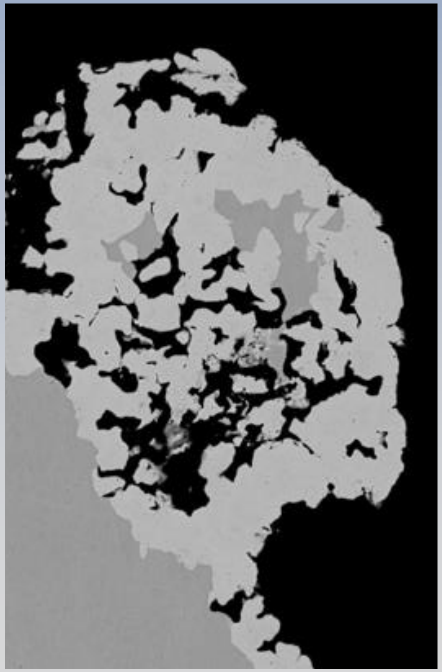
A note about Gold-rich Rims: 2

Two components

Ag- depleted zone:

Addition of pure Au





Conflation of 2 distinct processes has lead to hypotheses of rim (and particle) growth by Au addition:

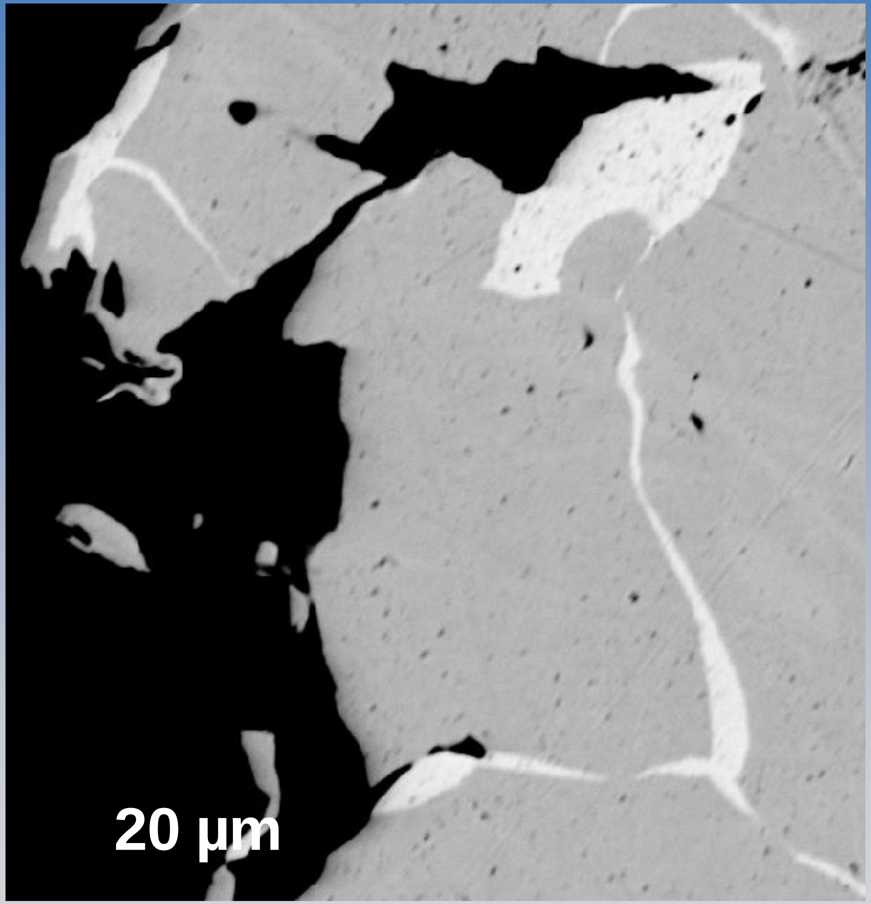
Nuggets growing

New gold

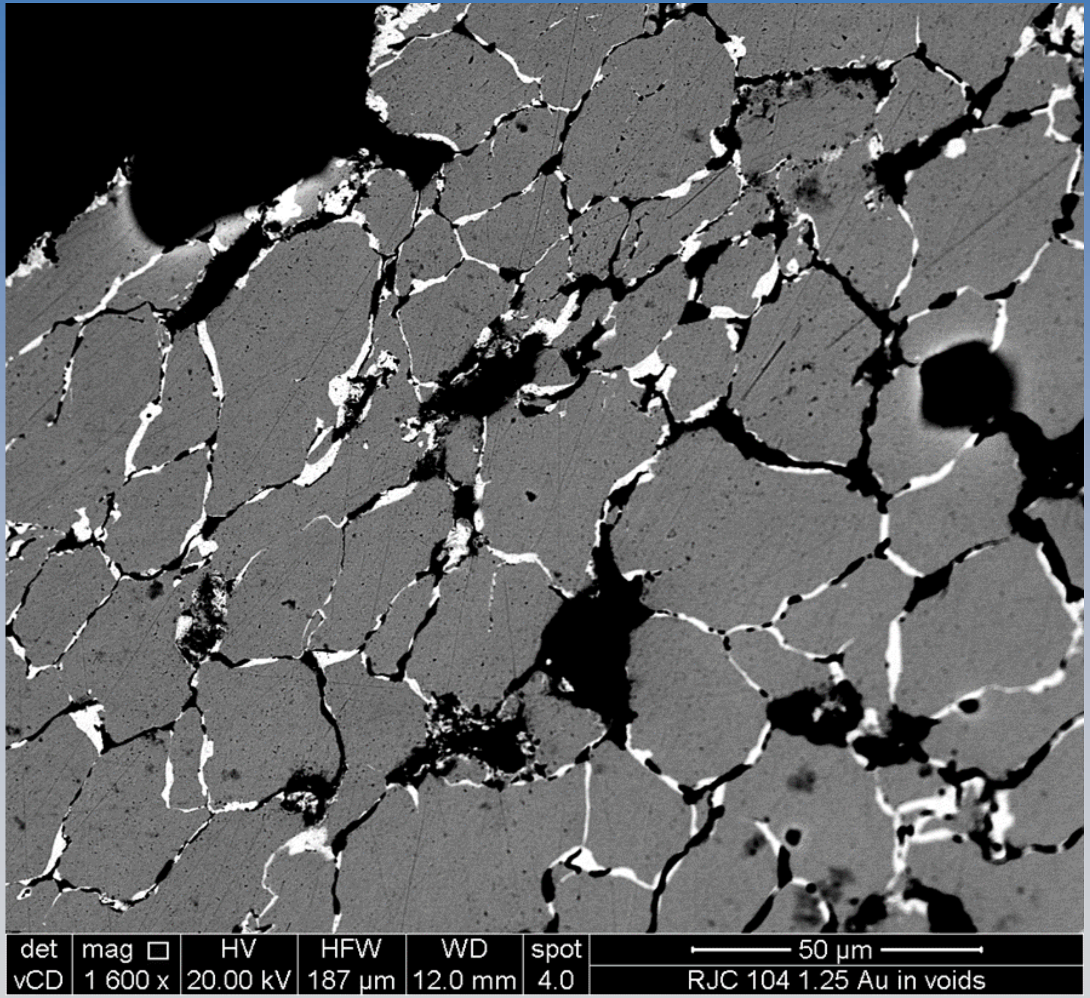
Really thick rim

Modification of original particle: surficial environment

Gold Rich films

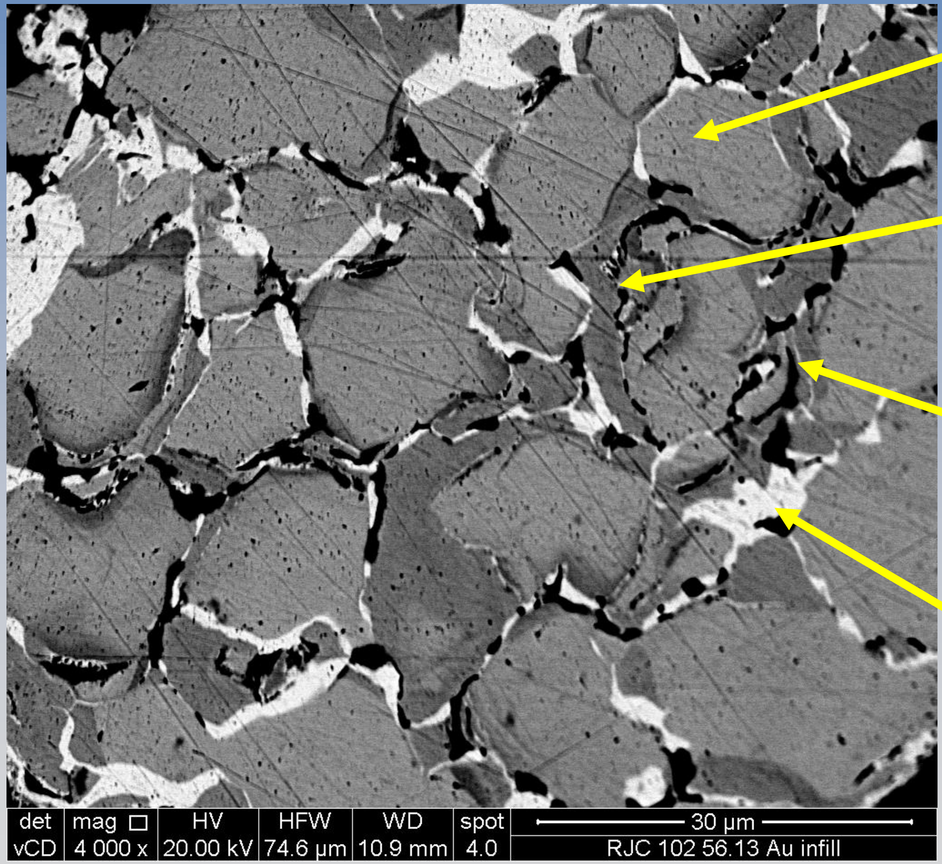


Gold from ore: Lone Star Klondike



Commonly encountered in gold particles from weathered regolith. Pure Au films follow fluid conduits along grain boundaries- often associated with voids that suggest pure Au is infill.

Interpreting complex alloy features in terms of particle modification



1. First phase: homogenous alloy

2. Grain boundary migration yielding Ag-rich alloy sympathetic to grain boundaries

3. Alloy removal at surface along grain boundaries

4. Partial infill with pure Au

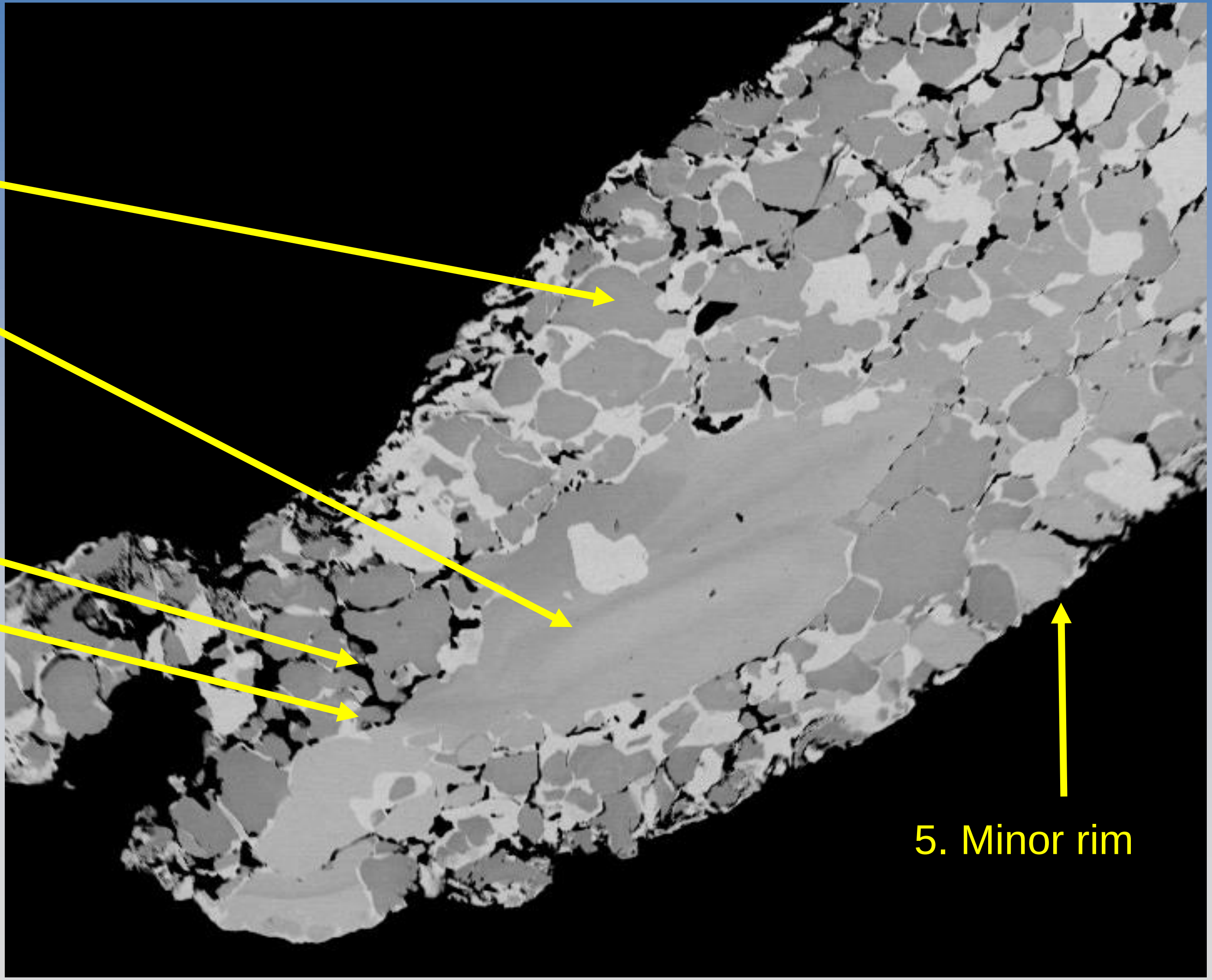
Interpreting complex alloy features in terms of particle modification: 2

1. First phase: homogenous alloy

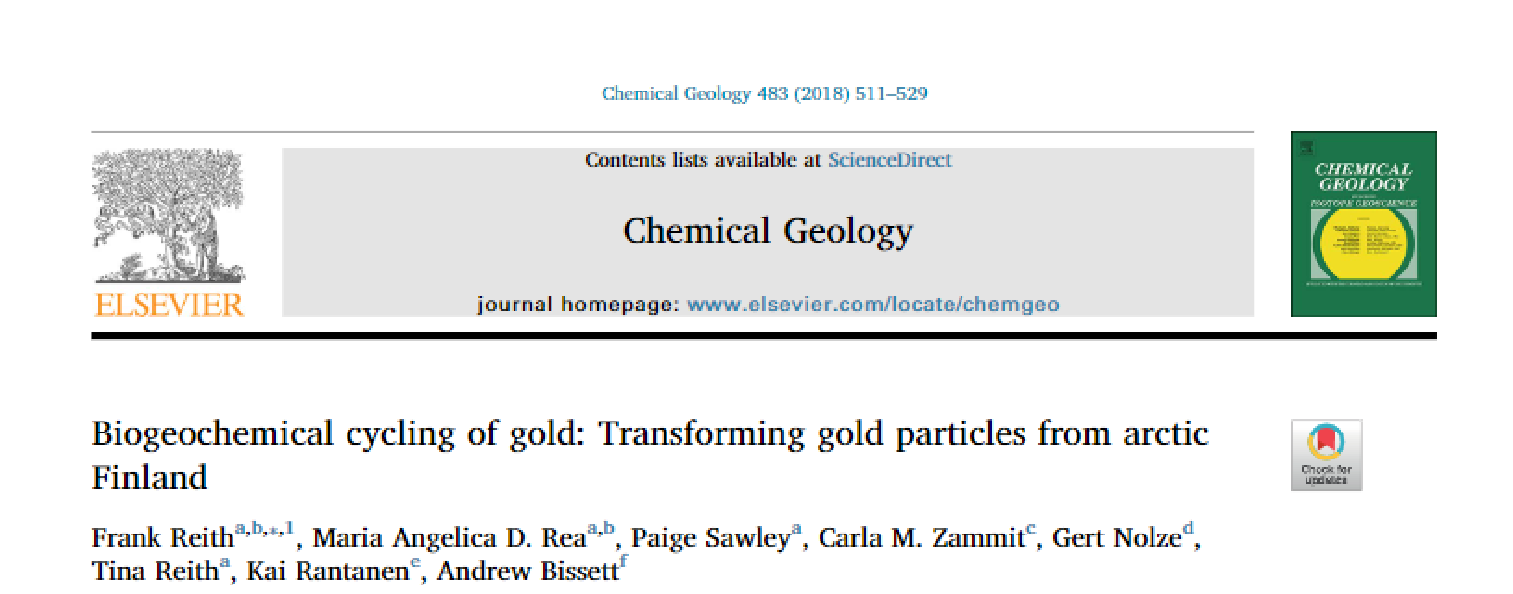
2. Modification of initial alloy

3. Alloy removal at surface along grain boundaries

4. Partial infill with pure Au



Which brings me to


Chemical Geology 483 (2018) 511–529

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

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Biogeochemical cycling of gold: Transforming gold particles from arctic Finland

Frank Reith[a,b,*,1], Maria Angelica D. Rea[a,b], Paige Sawley[a], Carla M. Zammit[c], Gert Nolze[d], Tina Reith[a], Kai Rantanen[e], Andrew Bissett[f]

The most recent work on placer gold particles in Finland

Bio films drive a progressive compositional change in gold particles

Paper contains a load of good science- evidence for Au expulsion from bacteria is compelling

I have no reason to doubt gene sequencing procedures or identification of biofilm community taxa

BUT……..

Hypothesis of the paper

F. Reith et al. Chemical Geology 483 (2018) 511–529

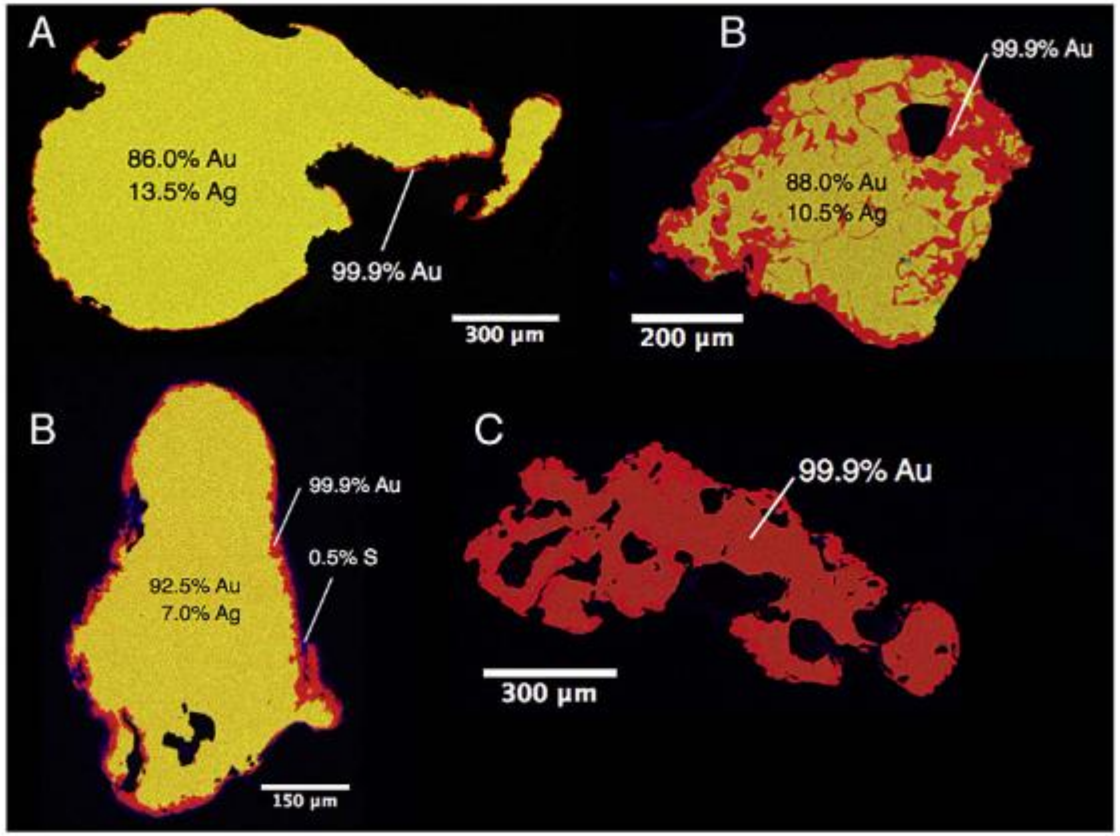


Fig. 8. Electron microprobe maps, Au (red) and Ag (green), showing the progressive transformation of Au particles. (A) A particle composed of a homogenous Au–Ag alloy with a partial layer of secondary high purity Au; (B, C) increasingly transformed Au-particles, and an almost entirely transformed particle (D). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Au-Ag Alloys

≈ Pure gold

A : Hypogene particle

B: initial modification by addition/alteration of gold at Surface

C: extension of alteration to particle interior

D: transformed particle

Problems with this hypothesis..

Conflates textures that form during unrelated processes, to propose an overarching generic dynamic system

Completely ignores the relevance of observations/conclusions from studies that routinely observe sections of 1000’s of gold particles

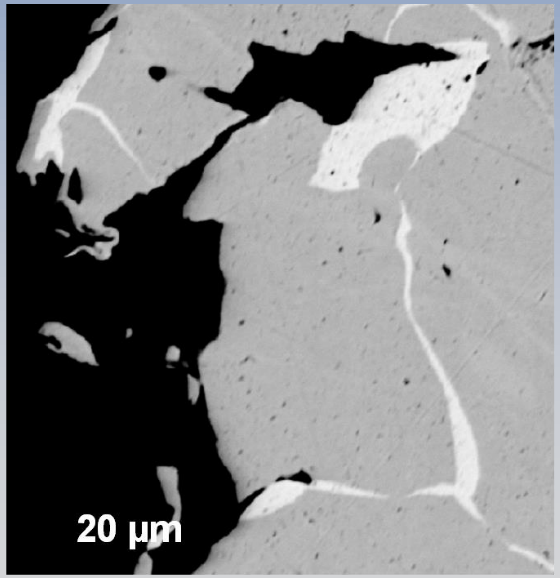
Origins of rims/ ‘overthickened rims’

(Stewart et al 2017)

Transport induced strain engenders recrystallization – end result flaky (deformed particles) commonly mostly pure gold

Which when mounted flat and polished suggest ‘huge’ rims..

Timing of formation of Au films vs rims)



Rob’s problem: Reith et al. help establish an unquestioning attitude to the relative importance of ‘gold growth’

Journal of Geochemical Exploration, 39 (1991) 303–322 303
Elsevier Science Publishers B.V., Amsterdam

Gold in bedrock and glacial deposits in the Ivalojoki area, Finnish Lapland

Matti Saarnisto[a], Esko Tamminen[b] and Matti Vaasjoki[a]
[a]*Geological Survey of Finland, 02150 Espoo, Finland*
[b]*Geological Survey of Finland, Box 77, 96101 Rovaniemi, Finland*

(Received April 20, 1989; accepted for publication March 13, 1990)

This all seems very sensible- based on observations of many gold particles

Certainly scope for a detailed study of placer gold in Finnish Lapland to illuminate nature of source(s)

Recap

We can place formation of various features to different point in the history of a gold particle.

What are the implications of this understanding for;

1. Methodologies adopted for particle studies

2. Gaining robust data through different analytical methods

Gold particle studies: design of methodology:

1. How many gold particles are necessary?

    1. To characterise alloy by EMP – 30 is usually adequate

    UNLESS we have a population where more than one mineralizing event is represented, (placer or lode populations)

    We only know this once we start analysing….

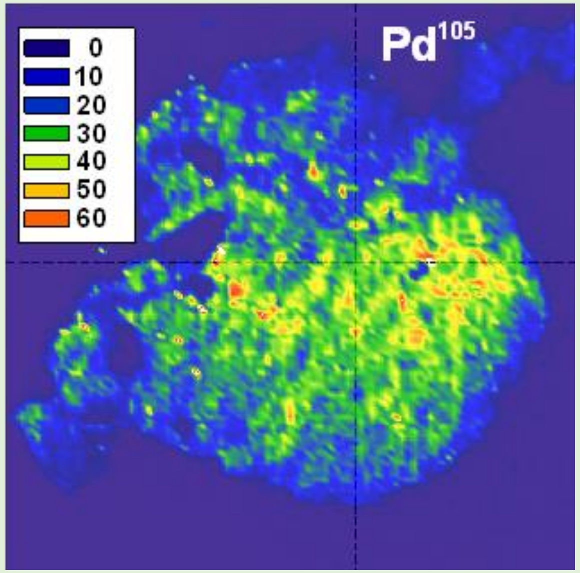
    2. Inclusions are typically observed in around 10% of polished sections (only known after analysis…..)

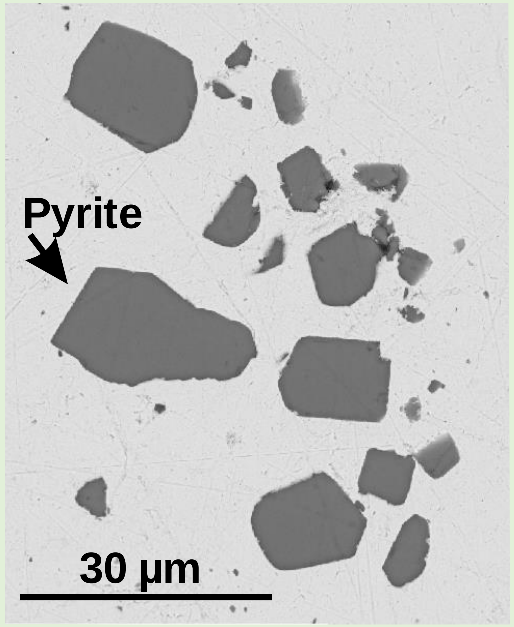
    We need 15 records of inclusions to characterize a single population: so a target of 150 particles is reasonable

Gold particle studies: implications of gold heterogeneity

Is compositional profile of placer gold compatible to that from proximal lode?

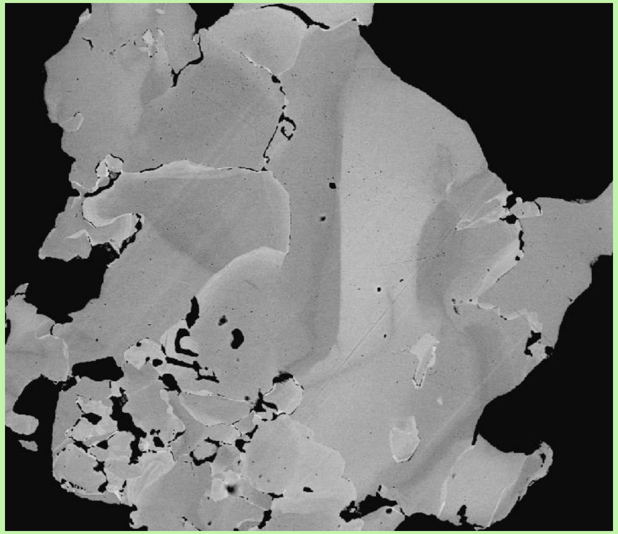
Where placer sources remain undiscovered can we determine the deposit type of the source?





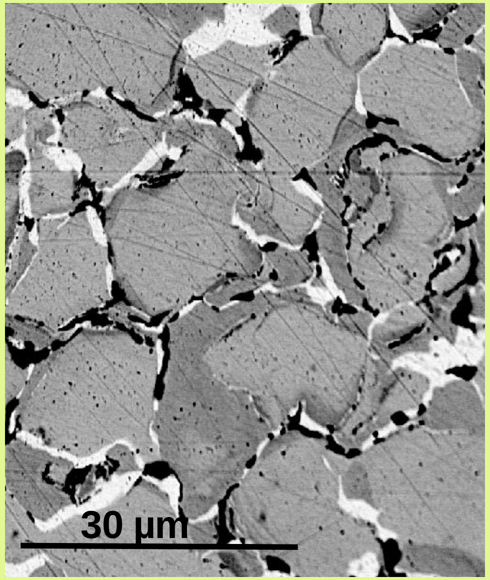
Consider only features from primary mineralizing environment

Can we gain information on the gold depositional environment from particle heterogeneity?



Consider features from primary mineralizing environment together with modified alloy

Can we illuminate chemical mobility of gold in the surficial Environment?



Consider only features formed in surficial environment

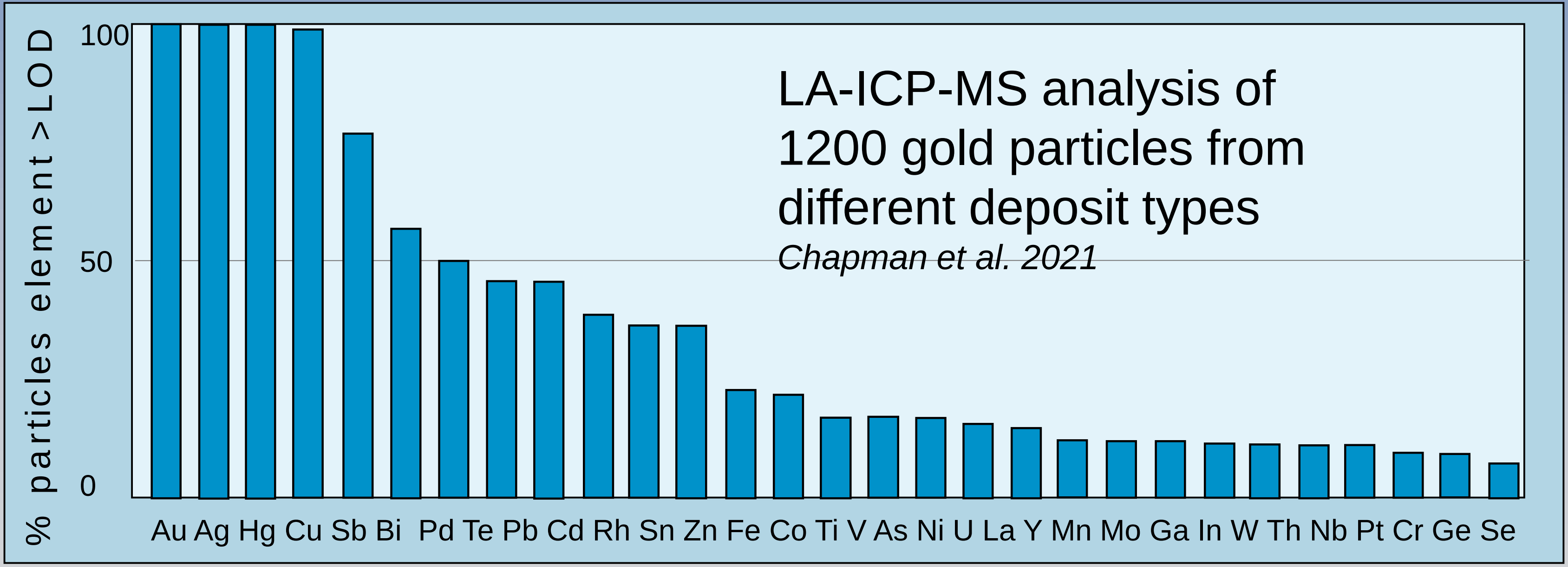
Does the low LOD for elements afforded by LA-ICP-MS systems offer more discriminants than analyses by EMP?

Hypothesis:

LOD for all elements is far lower than with EMP

Therefore we have more discriminants

Therefore we need less particles



1. LA systems provide quantitative data for Cu and Hg in every case
2. We do not increase the range of generic discriminants
3. Focussed studies may benefit from extra discriminants
4. Populations of particles are still required to generate a meaningful characterization as a chance analysis of a 'cluster' can generate unrepresentative results.

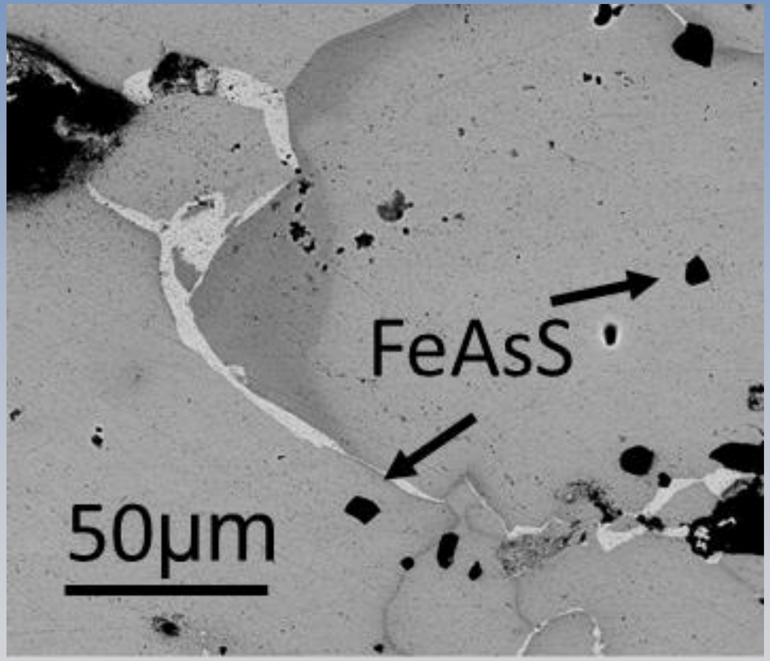
Our hypothesis does not withstand scrutiny

Gold heterogeneity and analytical methods: Major features

Analytical methods generate compositional data either from the whole gold particle or a sample of it. Different approaches provide different degrees of control over influences on the analytical values generated.

Whole particle analysis. Generates weighted average of all alloys/ inclusons (and surface coatings).

LA-ICP-MS spot analyses: (Polished sections) Subtle alloy variation not visible by optical Microscope. Inclusions can be avoided/targeted as appropriate.



SEM EDS systems. (Polished sections), can identify inclusion species, and Au/Ag ratio but not alloy Cu and Hg contents.

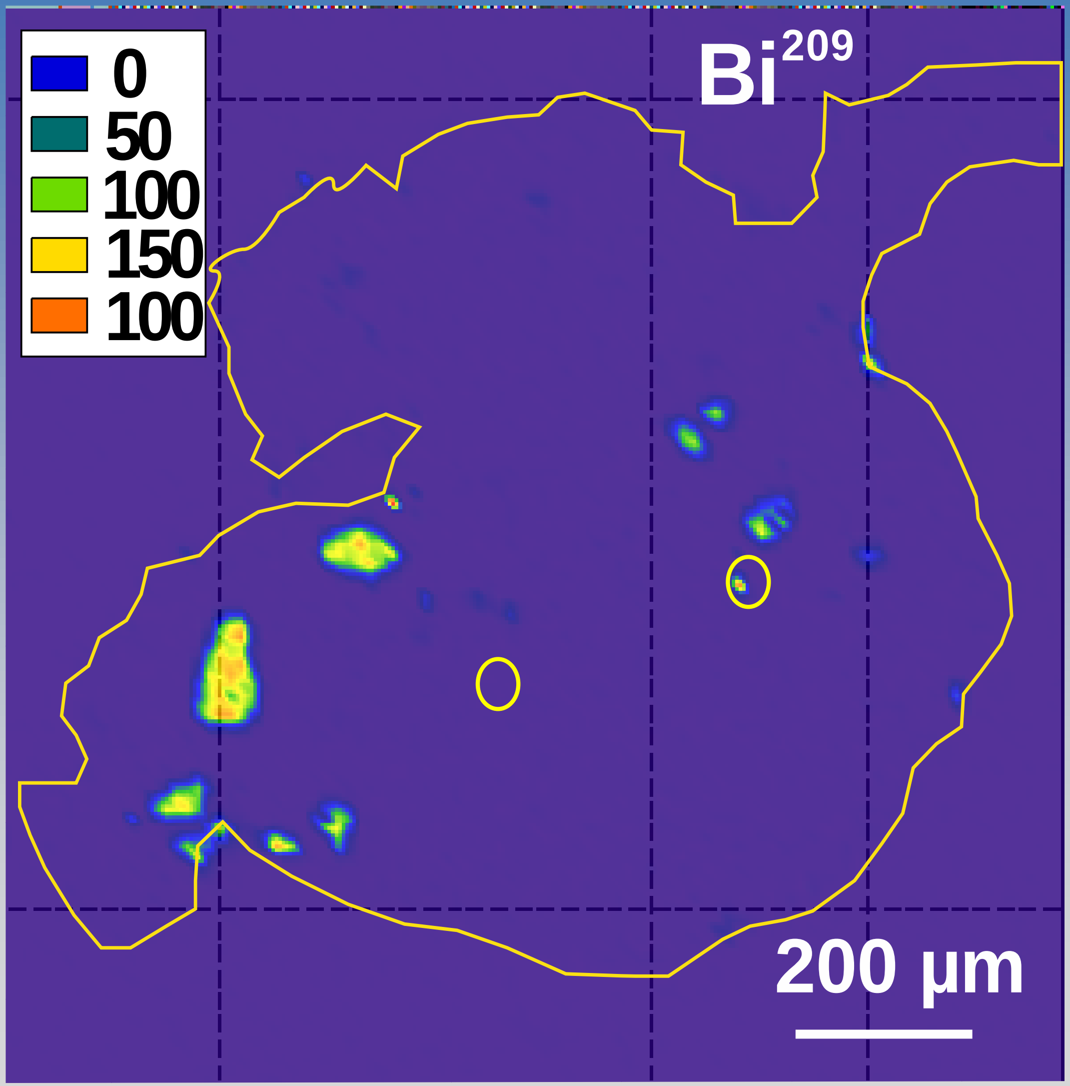
EMP analysis. (Polished sections), permits choice of sample point from BSE image but cannot observe alloy heterogeneity wrt Hg and Cu during site selection.

Gold heterogeneity and analytical methods: Trace elements

Not observable by **EMP/SEM.**

Incorporated into **whole particle analysis** (along with everything else).

Characterised fully by **LA-ICP-ToF-MS** analysis.

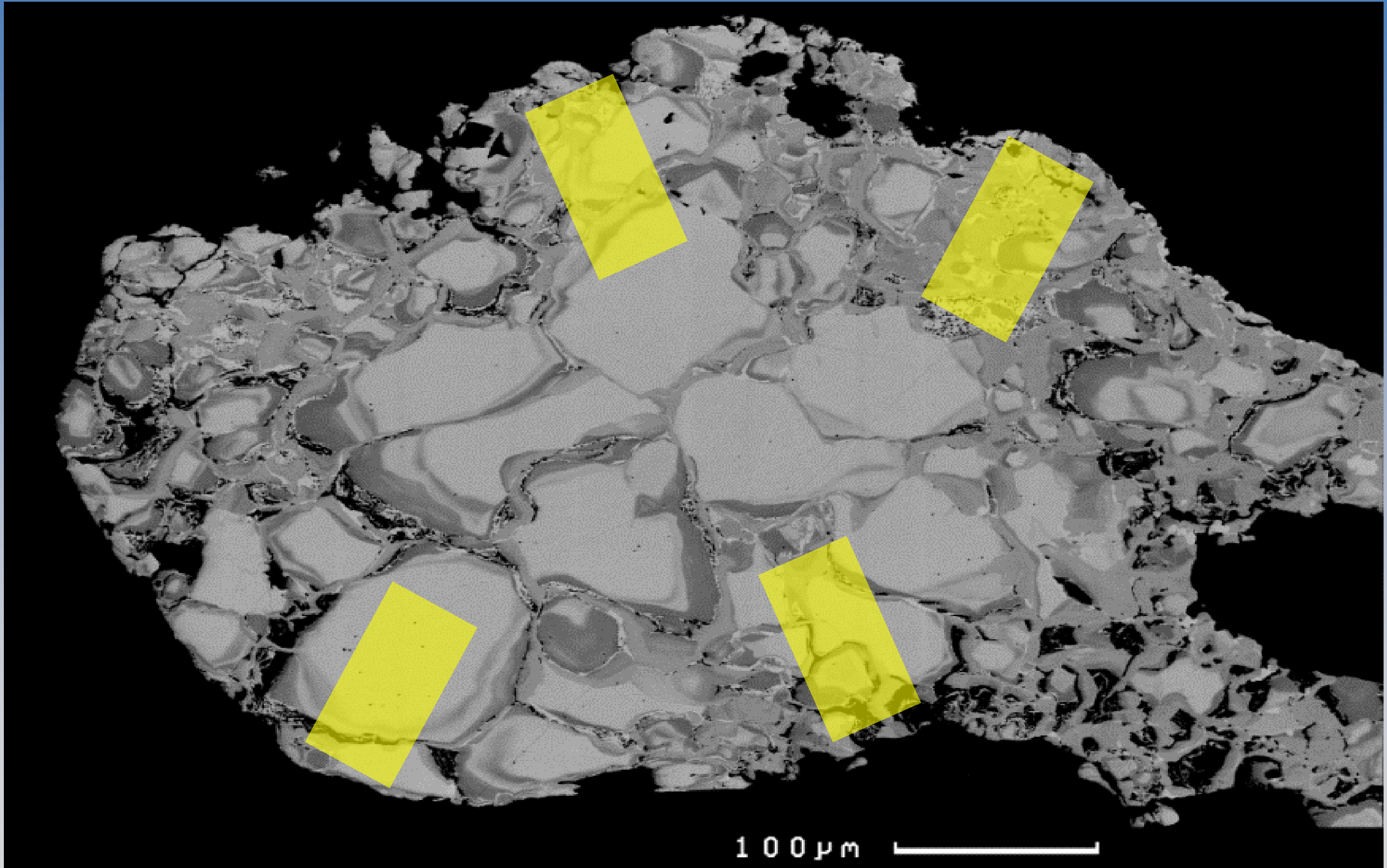


Heterogeneity Inferred from **quadrupole LA-ICP-MS analysis**, But heterogeneity may yield unrepresentative results according to chance positioning of spot (yellow circle). Trace element signatures of inclusions are possible.

Gold heterogeneity and analytical methods: analysis of surface or of interior via surface

Particle surface composition is not representative of the whole so XRF analysis of particles is inappropriate.

Some studies drilling through the rim by laser to access the particle core.



Think of a number ….

Conclusions

Gold can be highly heterogeneous but we can ascribe specific microfabrics to either time of formation or subsequent events

Gold particle studies that focus on specific environments (i.e. primary mineralization or surficial mobility of gold) must focus on the relevant features of a gold particle

Easy to generate spurious data if the heterogeneous nature of natural gold is ignored

Potential problems may be avoided by appropriate workflow, informed choice of analytical approach and study of sufficient particles

More detailed information in Chapman et al. 2021 Mineralium Deposita