

STRUCTURAL GEOLOGY GEOPHYSICS GEOCHEMISTRY HYDROTHERMAL PATHWAYS PROJECT GENERATION DUE DILIGENCE EXPLORATION & MINING

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#### **Principles of geochemistry**

General and hydrothermal systems

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These notes form core ingredients to workshops provided on site and on-line by Nick Oliver of HCOVGlobal. They are not intended as a replacement for a full course, but can assist in understanding background principles. The materials in here were generated over a 30 year period through teaching and training in several institutions and in industry – many thanks to all my collaborators and employers over the years. The contents should be regarded as informational and the use of the materials for any teaching or corporate decisions should not be undertaken without my permission, and is subject to disclaimers. Contact nickoliver@hcovglobal.com if you'd like more information.

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### Some fundamentals regarding commodities & approach

# Primary orthomagmatic (Ni, Cr, PGE) and syn-sedimentary or syn-volcanic (e.g. SEDEX, VHMS) ores:

- Initial metal source obscure and usually only relevant at terrain-selection scales
- 'feeders' usually horribly overprinted and difficult to unravel (structural history)
- Primary metal distributions commonly modified by deformation and metamorphism (remobilization)
- Necessary focus on igneous or sedimentary processes, after unravelling structure (i.e. lithogeochemistry with assumption that structure has folded/faulted early contacts)
- Potential for remobilization to change ore distributions to align with/be controlled by structure, but <u>usually</u> the earlier layering controls can be revealed
- In some, but not all of these systems, there may be broad-scale syn-ore zoned alteration systems with carbonates and silicates that will subsequently behave mechanically differently to sulphide ores



# Ores formed largely by long distance metal extraction and focus into key structures (most hydrothermal deposits, Au, Cu-AU, U etc)

- Initial metal source is usually assumed to be 'distal' but potential local sources are commonly ignored, and this statement holds for different ingredients (ore, alteration)
- 'feeders' remain difficult to identify, particularly because their apparent simplicity in some systems (e.g. Sirkka line near Kittila) leads people to assume they should all be like that
- Structural controls are crucial, but ores formed early, and later deformed strongly, commonly cause non-constructive argument and paranoia (general rule of the geology of Plant Earth: the older the ores are, the more likely they are to have suffered post-ore modification)





## Summary

- Selection or review of methods, QAQC
- "Fix-up" strategy
- Which elements are important the need for an "immobile element reference frame"
- Defining structural problems in a geochemical sense (veins, shears, folds, ore shapes etc)
- Develop efficient workflow



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## Selection or review of methods, QAQC



#### Discuss/determine the likely value of the geochemical program to your overall exploration and resource defined

Cost/benefit analysis

- program to your overall exploration and resource definition strategy
- Consider this in the context of the total cost of your likely drill program
- If your project looks very encouraging in any market, start with lots of geochemistry and wind back later
- Early foresight in this area saves \$ later, particularly for resource models and reporting compliance (JORC, NI 43-101 etc)







### Analytical methods: simple summary

- You get what you pay for: if your system is geochemically complex, taking initial shortcuts will come back to haunt you; Fight for your rights to decent geochemistry!
- Comprehensive XRF & solution ICPMS is the most robust but not considered cost effective for many exploration programs (> USD50 per sample), but it's the best
- Solution ICP MS with 4 acid digest is 'industry standard', 50 elements ~USD25/sample, usually with extra fire assays (for gold). ICP-AES is also needed for metal- or very S-rich systems (e.g. VMS, bonanza Cu where high upper detection limits are desirable for some elements). But ICP-AES only can be problematic if you are looking for the peripheral signals of systems with zoned elements close to their detection limits (e.g. Sb, Bi, Te) or you're concerned with really sorting out protoliths (e.g. REE, Y, Ce)
- pXRF machines are increasing in quality, can be used routinely (with care)

### Four Acid Digestion With ICP-MS Finish

Four acid digestion quantitatively dissolves nearly all minerals in the majority of geological materials. However, barite, rare earth oxides, columbite-tantalite, and titanium, tin and tungsten minerals may not be fully digested.

Despite the potentially incomplete digestion of REEs, the leachable portion of these elements may hold important exploration vectoring information and can be chosen as an add-on.

### Four Acid Digestion With ICP-AES Finish

Four acid digestions are able to dissolve most minerals, but although the term "near-total" is used, not all elements are quantitatively extracted in some sample matrices.

CODE	AN	ALYTES & RA		PRICE PER SAMPLE					
	Ag	0.01-100	Cu	0.2-10,000	Na	0.01%-10%	Sr	0.2-10,000	
ME-MS61 0.25g sample ME-MS61m 0.75g sample	Al	0.01%-50%	Fe	0.01%-50%	Nb	0.1-500	Ta	0.05-100	
	As	0.2-10,000	Ga	0.05-10,000	Ni	0.2-10,000	Te	0.05-500	
	Ba	10-10,000	Ge	0.05-500	Р	10-10,000	Th	0.01-10,000	
	Be	0.05-1,000	Hf	0.1-500	Рb	0.5-10,000	Ti	0.005%-10%	€22.75
	Bi	0.01-10,000	In	0.005-500	Rb	0.1-10,000	TI	0.02-10,000	022.75
	Са	0.01%-50%	Κ	0.01%-10%	Re	0.002-50	U	0.1-10,000	
	Cd	0.02-1,000	La	0.5-10,000	S	0.01%-10%	٧	1-10,000	€30.75
	Ce	0.01-500	Li	0.2-10,000	Sb	0.05-10,000	W	0.1-10,000	
	Со	0.1-10,000	Mg	0.01%-50%	Sc	0.1-10,000	Y	0.1-500	
	Cr	1-10,000	Mn	5-100,000	Se	1-1,000	Zn	2-10,000	
	Cs	0.05-500	Мо	0.05-10,000	Sn	0.2-500	Zr	0.5-500	
ME-MS61r	Dy	0.05-1,000	Gd	0.05-1,000	Nd	0.1-1,000	Tb	0.01-1,000	62.0.45
	Er	0.03-1,000	Но	0.01-1,000	٩ſ	0.03-1,000	Tm	0.01-1,000	€28.45 Full suite
	Eu	0.03-1,000	Lu	0.01-1,000	Sm	0.03-1,000	Yb	0.03-1,000	i di sulle

Make sure you go through the laboratory website to check detection limits etc. These sites don't really give a full guide as to what methods are best for what materials, this requires persistence and experience to solve. Look at the difference in elements and detection limits here relative to the price. ICPMS is 50 or 80% more expensive but <u>way</u> better than that price difference suggests

CODE	AN	ALYTES & RA		PRICE PER SAMPLE					
	Ag	0.5-100	Cr	1-10,000	Na	0.01%-10%	Ti	0.01%-10%	
ME-ICP61	Al	0.01%-50%	Cu	1-10,000	Ni	1-10,000	TI	10-10,000	€12.15 complete package
	As	5-10,000	Fe	0.01%-50%	Ρ	10-10,000	U	10-10,000	
sample	Ba	10-10,000	Ga	10-10,000	Рb	2-10,000	V	1-10,000	10
ME-ICP61m	Be	0.5-1,000	Κ	0.01%-10%	S	0.01%-10%	W	10-10,000	€6.60 plus 0.60/element
	Bi	2-10,000	La	10-10,000	Sb	5-10,000	Zn	2-10,000	
0.75g sample	Са	0.01%-50%	Mg	0.01%-50%	Sc	1-10,000			
Jumpic	Cd	0.5-1,000	Mn	5-100,000	Sr	1-10,000			€20.15
	Со	1-10,000	Мо	1-10,000	Th	20-10,000			

\*To include Hg in the suite of elements above, please request method ME-ICP61m

# Key strategies when commencing a new geochemical program (e.g. first stage drilling)

- Find the 'best' hole. Set this aside as a hole for maximum initial analytical detail (analysis or re-analysis). If budget permits (and it should), analyse the entire hole (half core pulps 0.3 to 2m intervals). Then you are well positioned to make the best possible decision about what methods and how much 'barren' material should be routinely included in geochemical analysis. Even if you already have a big database, it may be desirable to (re)analyse a "master hole" (see next slides)
- Find the **least mineralized hole**: this may contain the best information on the 'background'. Do this first!
- Find an **'average' hole**. Comparison between these 3 holes should form the basis for drill- and geochemistry-program development
- If you need to drill the best targets first (the usual case), use initial successes to make the case for an 'early spend' on 4-acid digest multielement ICPMS on 'the best' hole. A USD10000 early spend on geochemistry will reap rewards later – it's only 50 to 80m of 'missed out' drilling

### General geochemical workflow (on prior datasets)

- QAQC, what have you got? Do you need to level or even omit some results? Assess existing geochemical data diversity, work out what method(s) to use next
- Separate elements out into 4 categories (examples further down):
  - Lithogeochemical indicators ("immobiles")
  - Vein/mineralization indicators
  - Alteration indicators
  - Useless (too close to detection limit) or less interesting elements

### General geochemical workflow (on prior datasets)

- QAQC, what have you got? Do you need to level or even omit some results? Assess existing geochemical data diversity, work out what method(s) to use next
- Consider carefully the need to re-analyse with a superior method in order to 'enhance' your old 'bad' data



### General geochemical workflow (on prior datasets)

- Use immobile element ratios to assist with lithogeochemistry
- Apply conditional formatting in Excel to look for lithogeochemical boundaries and veins/faults/shears
- Sort remaining elements
- Decide how this data will eventually move into a 3D, targeting or mining environment

All now easier with ioGAS

# QAQC/data check summary

- Try to track down detection limits but will be obvious from data
- Spreadsheet use conditional formatting to quickly 'reject' elements with too much data < detection limit</li>
- Map plot data by date, laboratory or method, check for false boundaries
- ioGAS etc 'level' different datasets but the common denominator is the worst data
- Reject some data, then 'catchup' e.g. pXRF campaign or other re-assay
- Re-assay a crucial hole with top-quality geochemistry to decide what to do next

# Bad data examples

- Different methods used for different materials
- All used aqua regia, so very poor % digest
- You can tell this at a glance by looking at the Al and Na these are felsic to intermediate volcanics



A cross (X) or question mark (?) in the following slides reflects the degree of uncertainty in the data quality. Lines with coincident or near-coincident slopes are best, and allow confidence in interpreting results between the 4 different sample types (colours at left).





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Normal Score

-1

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Normal Score

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Normal Score

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#### Attribute Map



Some soils from western Turkey. There is an As-Sb anomaly on the NW of the area, but it is possibly compromised by a change in laboratory. Note in particular the pale blue to dark blue transition (= 4 ppm Sb) is fairly coincident with the boundary between the two laboratories' analyses. A new dataset will make this problem worse – unless it is used to 'correct ' the old data and provide a 'levelled' dataset.



Two other examples where bad initial decisions on analytical methods and changing laboratories ends up with 'rubbish' soil geochemistry surveys. Note the E-W and N-S 'boundaries' between different levels of metals, reflecting different times of analysis or laboratories. Massive amounts of wasted effort in very tough terrains.

## Intro - spreadsheets/data: cleaning up

- Keep the raw data; copy into working sheets
- Bad analyses
  - Do repeats
  - Check lab standards reports
  - Consider an internal standard
- BD's or NA's or negative numbers
  - Set at half the detection limit
  - Or set to very low number
  - Decision on which may affect means or medians
- Check totals: are they consistent with the missing elements (commonly Si, H, O, C)?
- Learn permissible ranges for 'normal' rocks, can web-search quickly
  - E.g. > 45% SiO2 except ultramafics, < 20% Fe2O3 unless BIFs, < 15% Al2O3 except in soils or supergene/laterite, < 10% CaO except in limestones, 0.2 to 8% K2O in most rocks, Cu usually 5 to 200 ppm, Cr usually < 500 ppm except in mafics etc etc

An easy view of the periodic table of the elements: scales of element mobility/immobility

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# Element mobility – the key to just about everything

Element mobility here mostly refers to the response of elements to dissolution and transport in hydrothermal fluids.

Elements commonly considered 'immobile' in hydrothermal systems are very important (and mobile) in magmas and in clastic sedimentary processes. Their variation sometimes defines ore systems themselves (e.g. Ni-PGE orthomagmatic, placer deposits). These variations must be clearly understood when dealing with hydrothermal overprints.

# Principles of element mobility

Three categories of elements: Firstly,

Conservative elements that don't like to move much

- Use these to define protoliths
- Use these to look at variability in primary (orthomagmatic, SEDEX etc) systems
- Use these to benchmark hydrothermal changes (alteration, veins, breccias, shear zones)
- Examples: Ti, Al, Mg, REE, Zr, Sc, Y





Three categories of elements: Secondly,

#### **Elements that love to move**

- Easily dissolved from rocks
- Easily precipitated into veins or breccia matrix
- Often define ore-forming systems
- Examples: Si, Ca, Fe, Cu, Au, S



Three categories of elements: Thirdly, Elements that love to move but cannot do so without connecting with another element



#### Master and Miss Feldspar, pardon the Get Smart



Al (Max) K (99)

- May be easily dissolved from a rock
- But due to charge, ionic radius and field strength issues, must combine with another element, preventing it from independently precipitating in veins etc.
- Examples: K, Na, Rb
- "need" Cl (to travel) and Al (to precipitate), i.e. as feldspars, micas in alteration

# Typical immobile elements: HFSE, do not readily complex, 'tight' with their electrons

- For most aqueous chloride-bearing fluids: immobile = Ti, Zr, Y > Al, Ga, Mg > REE, Cr, V, Ni > Fe, Mn, Cu, Si, P, S, Au > Ca, Sr, Pb, Zn > Na, Rb, K = mobile
- For CO2-rich fluids Si may be immobile or nearly so
- For seawater interaction with basalts, Mg can be mobile
- For F- or P-rich fluids P, REE, siderophiles, Al, U, Zr may be mobile
- For B-rich fluids anything goes.

Reaction zones (replacement, alteration, metasomatism)





# Scales of element mobility

### Define scale pertinent to ore system: closed system = not ore-forming, open system = ore-forming

Is the metal source observable – and if so, at what scale, or is the source "deep"?



# SCALE & SOURCE: Where does the metal come from?



# SCALE & SOURCE: Where does the metal come from?

Both paragenesis and 'remobilization' come into play in these concepts





In this example, you don't know if the quartz and hematite in the vein was derived from external sources, as there is plenty of Fe and Si in the adjacent rocks. So this is (potentially)<sub>co</sub>closed system"<sub>iciples, do not copy/transmit without permission</sub>

Near Mt Whaleback iron ore mine, Pilbara district, Australia

#### Guessing scales of mass transfer by knowing rock and mineral chemistry

## Qz-To vein

### lo alteration

**Granite** 

#### Guessing scales of mass transfer by knowing rock and mineral chemistry

**K2O** 

Si<sub>02</sub>

## Qz-To vein

### the alteration

But if you run (imagine) profiles of K and Si across the vein/alteration pair, you can see a pattern by which the apparent Kalteration is caused simply by extraction of silica from the altetred granite, and re-deposition in the vein

#### Guessing scales of mass transfer by knowing rock and mineral chemistry

**K2O** 

Si<sub>02</sub>

### Qz-To vein



### To alteration

However, when you look at the boron (represented by the black mineral tourmaline), you can see it is added to the vein and the alteration zone. So Si and K may be 'closed system', whereas B is 'open system'. You would need a detailed geochemical transect to check this possibly closed system Si-K

transfer.

# Worked practical exercise

What came in? What went out? What stayed at home? Where are Kay and Al?
Vein: mostly Pyrrhotite FeS, with qtz, pyrite and gold

Alteration: Siderite + quartz FeCO3 + SiO2

#### Magnetite Quartz BIF Fe3O4 + SiO2

#### **Quick exercise:**

#### Determine the scale of element mobility here:

- 1. CO2
- 2. Fe
- 3. S

Paragenesis and remobilization, metal sources

- Why does everyone try to hide when the word 'remobilization' is uttered
- What is the value of paragenesis?
- What is the value of geochronology?
- Scale, scale, scale

# Ways to physically change original rock chemistry

 Deformation-related segregation of soft or soluble minerals from hard or insoluble ones





#### Near Mt Whaleback iron ore mine, Pilbara district

#### Boudinage in marbles, Cloncurry IOCG district

#### **Boudinage and separation**

#### Paracatu gold deposit, Brazil (Oliver et al., Econ. Geol. 2015)



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#### Folding-related thickness changes







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# Specific introduction of new compc by deformation

Albitic shear zone

Calcite vein arrays





#### "Classic" vein + alteration scenarios

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#### "Classic" replacement of original rocks (in this case after most of the obvious deformation)

Cuiaba gold mine, Minas Gerias, Brazil

Textures: commonly difficult, misleading, poorly interpreted and over-sold if scale not considered





Cannington – "Broken Hill-type" Ag-Pb-Zn-(Cu-Au) ores, metamorphosed at ~ 700°C'. The sequence of original mineral deposition is seriously obscured by the metamorphism





Sphalerite-garnet skarns, 'sold' as "Broken-Hill type", but cut the peak metamorphic fabrics at a range of scales. Delicate skarn textures preserved (would not survive peak metamorphism and deformation, which does this:)



An ore deposit for peace-loving types (e.g. Late Mesozoic to Cenozoic porphyries)



First beat the mixture until shortened



Apply a shearing motion on the dough until flattened



Corollary: the older the rocks, the less likely you are to be able to determine the original source-transport-trap features

Remobilization and geochronology

### What is remobilization?



An event occurring after the main time of interest that results in redistribution of elements of interest





#### PARAGENESIS



Needs: scale definition, understanding of original rock chemistry, understanding of prograde/retrograde mineral stabilities and likely paths, and separation of minerals out into infill vs alteration etc.

# Traps for the unwary 1) diffusion processes in already-altered rocks 2) overprinting 3) scales of mass transfer

3) scales of mass transfer

Eloise Cu-Au mine, Cloncurry district, Australia



The top vein has a brown alteration halo and does not change its internal chemistry as it cuts the different layers. The bottom vein is thicker, but it changes from calcite to pyrrhotite as it cuts across original, foliated layers that are calciterich and pyrrhotite-rich, respectively. This suggests the ingredients in the vein were extracted by diffusion from the adjacent rock, not from fluid flow and mass transfer greater than the scale of observation. The additional useful information is that the background rock is foliated, whereas the vein is unfoliated and unfolded (or boudinaged). This means that there is a time gap between a ductile deformation and the formation of the vein – in other words the vein cannot have been a 'feeder' for the calcite and sulphide alteration in the surrounding foliated rocks.

## How do garnets grow in a schist?

### What is the difference here?

#### arsenopyrite

#### pyrrhotite

Small arsenopyrite crystals – for example perhaps the core of this crystal – can dissolve and reprecipitate as porphyroblasts in metamorphosed sulphidic shales. The timing of growth of the porphyroblast is not a good indication of the timing of introduction of the arsenic. You can see a long history of sulphide precipitation and probable dissolution – note the ragged edges of the arsenopyrite and the location of the pyrrhotite and chalcopyrite in the strain shadows. It's possible that dissolution of the arsenopyrite provided sulphur for the later precipitation of sulphides – perhaps by interacting with a relatively S-poor fluid containing Cu (e.g. chlorite solution)?

#### Paragenesis can be difficult, personal and potentially misleading



#### How to really use paragenesis

- Assume that polydeformed rocks are likely to mislead you, particularly Precambrian ones
- If you can't afford geochron that spans a range of blocking temperatures – oh well you're in trouble, but
- Try to assume that new mineral growth could mean either new introduction of chemicals to the system, <u>or</u> reworking of old chemistry
- Define the problem you are looking at over a range of scales: otherwise your work may be meaningless

How to really use paragenesis

- Don't listen to consultants or academics that push one geochronological method or a unique model for the larger ore system you are in (e.g. all Archean lode gold deposits form by .....).
- <u>Every</u> Precambrian ore deposit I've worked on has shown some evidence of remobilization, and much effort is wasted in tail-chasing particular parts of the paragenesis to suit a pre-conceived model

### Solving paragenesis problems

- Don't use more micro-scale paragenesis
- Geochronology, but.....
- Consider <u>differential</u> element mobility
- Consider the scale over which the elements could have moved
- Broaden the paragenetic scope to m, 100m, km, 10km
- Don't ignore regional metallogenic context

Turning your messy geochemical data into a geochemistrystructure work-horse

- 1. Lithogeochemistry vs logging
- 2. Finding veins/breccias and replacement
- 3. Characterising faults and shears
- 4. Ensuring the best path to get the information into 3D

# Lithogeochemistry in deformed rocks: three fundamental purposes

- Improve the understanding of the geology in 2D and 3D – a crucial check on logging and mapping, and indispensable in weathered or strongly altered rocks
- 2. An essential tool for targeting in Ni, PGE, SEDEX and VHMS because the lithofacies control the metal intrinsically
- 3. Last and definitely not least: a fundamental tool for discriminating rock variability from alteration, veining and breccias in hydrothermal systems
- 4. Commonly perceived as wasted money by management, because they're ..... (insert abuse)

# Lithogeochemistry and veins in deformed rocks

- What rock observations speak to the need for geochemistry? What can you learn without geochem?
- How well have you logged protoliths? How much does it matter to you?
  - Distinguish protoliths from alteration (and veins) in geochemical database
  - Don't make the mistake of assuming your metals of interest are the only elements needed in the geochemical package
- The rock almost always contributes mass to the mineral system even at hand-specimen scales (i.e. an altered granite is still a granite, but how/why/what?)

# Lithogeochemistry: Excel and ioGAS (+ some fancy options)

- Use conditional formatting in Excel with colour scales as shown below
- Sort elements into likely immobile (lithotype defining elements), metals of interest, alteration elements, 'other'
- Run immobile element ratio calculations through your spreadsheet, put these columns next to the immobile elements
- This will allow you to check your logged rock types, or define new rock types that cannot be seen easily in drill core
- After you do this, you can look at alteration and veining within individually defined rock units, and extract more/less altered pairs with the same protolith to compare in detail

В	DH	1	J	R	S .	τU	V	W	Z	AA	AB	AC /	AD AB	AF	AG	AH	AL	AJ A	K Al	. AN	A AN /	AL AQ	AR	AS /	AT AU	A٧	AW	AX	AY	AZ	BA BE	BC	BD	BE	BF	BG	BH BI	BJ	BK
Rock	holeid	from	to	Mg/Ti :	SelY M	g/A Al/T	і мыл	i Y/Mg	Ce/P	LN Ce/P	v <i>r</i> ti o	eLa-Uti	TL	o ALJ	o Ce_p	La_p	ть_р и		∟p V_j	or Mg	L SC_PP	m S/Ti	InS/Ti I	InAu	Sr_PP	n Na_p	. Ca_p	» К_рс	t S_pet	Rb_p B	Ba_ppm	Au_ppm	Ад_рря	Zn_ppr	Си_рря Р	'b_ppm /	∿а_рј Ві_рј	: Cd_PL	Mo_p
			LITHOTYPE RATIOS										LITHOTYPE ELEMENTS							AU & SULFUR			ALTERATION						OTHER MINERALIZATION										
DAC		07.0	00.0																																			_	
BHS DAS		87.2	88.2	6.1	2.62 0	.37 16.3	3 4.4	3.7	0.007	-5.005	500	5.7	0.5	0 8.1	8.7	3.5	0.35	0.10 (	0.3 25	0 3.0	3 29.6	6.38	1.85	-4.61	283	2.14	4.43	9 1.40	3.19	50.8	126	0.01	0.28	132	173.8	9.2	27 0.06	0	1.78
BAS		88.2	89.2	6.8	2.67 0	.42 16.:	3 4.8	3.6	0.007	-4.949	534	7.3	0.5	0 8.1	9.5	3.9	0.37	0.10 0	0.3 26	7 3.4	1 33.1	7.42	2.00	-3.51	288	2.5	4.7	7 1.81	3.71	62.4	163	0.03	1.04	176	238.0	30.2	61 0.64	1	0.97
BAS	_	89.2	90.2	7.2	2.34 0	.41 17.	7 4.6	3.7	0.007	-4.967	535	1.9	0.4	6 8.1	8.7	3.6	0.38 0	.20 0	0.3 24	6 3.3	3 28.6	4.93	1.60	-4.61	282	2 2.2	5 5.13	3 0.50	2.27	15.0	108	0.01	0.32	121	239.9	29.2	18 0.34	0	1.80
BAS	_	90.2	91.2	8.2	2.68 0	.46 18.	.1 4.1	7 3.1	0.007	-4.986	531	1.2	0.4	5 8.1	8.4	3.4	0.35 0	.20 (	0.3 23	9 3.7	71 30.8	7.71	2.04	-2.53	180	1.74	3.40	2.05	3.47	72.6	178	0.08	2.05	1234	207.1	30.9	62 1.44	13	0.79
BAS		91.2	92.2	9.0	2.75 0.	.49 18.	5 4.5	5 2.9	0.007	-4.925	566	0.8	0.4	4 8.1	9.2	3.8	0.37 0	.20 0	0.4 24	9 3.9	6 31.4	7.91	2.07	-2.66	132	1.46	5 2.94	\$ 3.01	3.48	104.3	298	0.07	3.77	5986	300.6	48.7	91 2.60	70	1.00
BAS		92.2	93.0	9.0	2.60 0	. <b>4</b> 9 18.	.1 4.8	3.1	0.007	-4.938	563	0.7	0.4	5 8.1	9.1	3.8	0.40 0	.20 0	0.4 25	6 4.0	3 32.7	2.98	1.09	-3.91	203	1.73	3.16	5 3.31	1.34	113.0	366	0.02	2.52	2027	331.3	45.8	39 3.70	23	0.99
BAS		93.0	93.8	7.8	2.66 0	.47 16.0	6 4.5	5 3.2	0.007	-4.916	510	0.6	0.4	9 8.1	9.0	3.8	0.39 0	.20 (	0.4 25	0 3.8	4 32.2	5.98	1.79	-3.22	255	5 1.83	4.00	2.67	2.93	87.3	335	0.04	1.89	1467	155.0	62.4	45 1.38	15	0.88
BAS		93.8	94.6	8.3	3.01 0.	46 18.	.1 4.5	2.8	0.008	-4.779	571	5.2	0.4	5 8.1	10.4	4.4	0.33 0	.20 (	0.3 25	7 3.7	3 31.6	11.11	2.41	0.61	48	0.58	0.98	4.53	5.00	129.2	222	1.84	9.14	7010	386.6	346.0	286 4.84	85	1.15
V		94.6	95.3	12.8	3.97 0.	.20 62.	7 7.3	2.2	0.010	-4.598	769	8.6	0.1	3 8.1	4.5	2.1	0.13 0	.00 (	0.0 10	0 1.6	7 14.3	38.46	3.65	4.41	32	0.23	3.04	1.91	5.00	58.5	40	81.98	143.00	1452	2812.0	410.4	3259 41.20	25	3.97
BAS		95.3	96.3	9.3	2.24 0	.58 16.0	0 4.7	2.9	0.009	-4.754	512	7.1	0.	51 8.1	11.3	4.9	0.40 0	.20 0	0.3 26	1 4.7	2 30.4	7.98	2.08	-3.00	174	1.43	3.7	1 3.09	4.07	107.3	369	0.05	3.15	1440	276.5	53.4	65 1.05	16	1.10
BAS	-	96.3	97.1	8.5	2.52 0	.50 17.0	0 4.6	3.1	0.008	-4.853	546	7.7	0.4	8 8.1	9.7	4.0	0.38	0.10 (	0.3 26	2 4.1	0 31.7	7.85	2.06	-0.31	23	1 1.70	4.03	2.03	3.77	72.4	206	0.73	3.84	757	702.7	35.4	68 1.20	9	2.29
BAS	-	97.1	98.0	8.1	2.88 0	49 16 :	3 6.2	2.9	0.008	-4.815	554	2.8	0.5	0 8.1	10.4	4.2	0.38 0	20 0	0.4 27	7 4.0	3 33.7	10.00	2.30	-3.91	272	1.90	5.6	1 2.21	5.00	75.3	224	0.02	143	216	247.1	30.5	46 0.91	1	0.99
BAS	+	98.0	99.0	7.3	192 0	44 16	6 32 5	27	0.020	-3.901	273	3.8	0.4	9 81	30.2	14.8	0.38 0	40	17 13	4 35	7 18 2	8.20	2 10	-183	36	0.5	2.8	5 5 0 9	4.02	182.9	346	0.16	2.73	759	171.8	57.3	503 3.67	12	168
BAS		99.0	100.0	7.8	184 0	57 131	6 226		0.020	3 910	207	10.9	0.6	0 8 1		14.9	0.37.0	40	16 12		5 19.0	7.05	195	.9.52	444	0.86	2.51	2.69	4.92	161.5	442	0.08	0.53	959	122.8	43.7	96 3.08	12	1.05
BAS	-	100.0	101.0	0.0	2.04 0	42 49	0 02	, <u>c.c</u>	0.020	5.091	525	0.0	0.0	0 0.1.	20.1	2.0	0.31 0		1.0 10	0 4.0	0 05.0	6.00	1.00	4.44	115	0.00	1 1 1		4.20	145.4	000	0.00	2.30	970	079.0	40.1	46.2 4.90	10	1.00
DAG		101.0	102.0	0.2	2.04 0	40 00	0 0.5	· 2.5	0.000	-5.031	555	0.0	0.4	0 0.1: E 0.4	0.0	0.0	0.30 0	.20 0	0.0 Z0	0 3.5. E 0.0	2 25.5	44.00	0.66	4.00	40	0.42		9 4.54 0 40	2.50	145.4	500	0.00	3.20	005	213.0	42.1	103 1.30	10	1.10
DAG	<b>-</b>	102.0	102.0	11.3	5.24 0.	40 23.3	o 23.	1.2	0.007	-4.340	414	-5.5	0.3	0 8.1	5.8	2.3	0.15 0	.20 (	J.4 14	5 3.3	4 24.1	14.28	2.00	-1.20	- 35	0.4	1.03	3.48	5.00	13.3	506	0.30	4.64	305	01.1	106.1	163 3.13	11	1.88
DAS		102.0	103.0	20.8	7.12 0	.58 35.4	4 11.3	5 0.9	0.006	-5.119	665	1.4	0.2	3 8.1	3.1	1.2	0.13	0.10 0	0.0 15	3 4.7	8 29.2	20.30	3.01	0.59	- 28	0.52	2 1.2	1 3.32	4.67	51.6	552	1.80	4.30	1416	227.6	115.7	389 3.76	19	3.11
BAS		103.0	104.0	17.0	4.71 0	.52 32.0	6 10.8	5 1.5	0.014	-4.271	604	10.9	0.2	5 8.1	7.7	3.6	0.21	0.10 0	0.0 19	1 4.2	4 30.6	20.00	3.00	-0.65	2	1 0.38	0.68	3.31	5.00	105.8	646	0.52	3.96	2329	134.1	52.0	227 4.41	34	230
BAS		104.0	104.8	15.5	4.88 0.	.38 40.3	8 16.0	1.7	0.018	-3.994	680	-1.5	0.2	0 8.1	11.7	5.4	0.20 0	.30 0	0.6 13	6 3.0	3 25.4	25.00	3.22	0.01	- 28	0.40	1.03	5 3.73	5.00	103.8	292	1.01	8.93	364	230.9	101.3	538 5.99	4	2.74

### Spreadsheets/data: cleaning up

- Exceeding upper limits
  - Check the data, look for 5%, 10% or 50% especially for elements which commonly top-out in ICPMS e.g. Fe, S, Zn
  - Set at some % higher than the upper limit, but not beyond reason e.g. can't get > ~ 60 wt % Fe (not FeO) unless pure hematite.....
  - Consider re-analysis (e.g. ICP-OES repeats for certain elements that top-out in ICPMS)
- Don't consider elements that have a large proportion of analyses at detection limit (unless really important): common culprits – Be, Li, Ga, Re, Os

# Spreadsheets/data: initial formatting

- Use conditional formatting column by column (use format paster)
- Move columns into 4 categories:
  - Main ore target elements
  - Lithotype defining elements
  - Alteration-related elements
  - Ones you don't care about really but might use later

# Spreadsheets/data: defining protoliths

- Assemble the columns that show similar conditional formatting and start with Ti, Al to look for similar (immobile) elements
- Calculate some immobile element ratios
- Conditionally format these too
- Focussing on the immobile element ratio columns, mark your lithogeochem boundaries on the spreadsheet
- Compare with logged lithotypes

### Principle 1

- if you (more-or-less) trust the logging/mapping, use it as a guide when you overlay the geochemistry. ioGAS makes this easy with its attribute manager (colour, shape, size can be adjusted quickly)
- But you also need to trust the geochemistry: consistency, reliable assays for refractory/immobile elements, same lab or inter-lab corrections etc



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### Principle 2

- Use lithogeochemistry, visualized, to assist drillhole-to-drillhole correlations
- Super-easy in ioGAS
- OK and visually appealing in Excel
  - Select/arrange elements to highlight key lithogeochem elements (what are these?)
  - Conditional formatting



#### Log these!

Black rocks Black rocks Black rocks Black rocks Black rocks Black rocks Black rocks

Ser.

3

Black rocks Black rocks Black rocks Black rocks Black rocks Black rocks Black rocks

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																	Al2O3_9 C	r_ppm 🔽 Ni	_ppm 🔽 Tic	02_% 💌 S	iO2_% 🔽 F	e2O3_ 🔽 N	gO_% C	aO_% 💌
									Al2O3_9 0	r_ppm💌 N	li_ppm 🔽 Ti	02_%	iQ2_% 🔽 F	e2O3_🔽 N	1gO_%🔽 (	CaO_% 💌	15.69	231	101	0.58	62.42	4.03	3.29	2.57
AI203	Cr	ppm Ni	ppm T	i02 % - S	iO2 %	Fe203		CaO % 🔽	10.28	1174	605	0.34	48.56	8.26	13.17	4.72	11.39	771	540	0.46	49.15	7.65	10.89	5.88
_	85	1371	812	0.34	40.53	9.59	15.31	7.37	7.35	1762	981	0.3	42.39	11.05	21.21	4.26	8.79	1023	775	0.36	42.75	9.48	15.65	6.91
	6.01	1693	1004	0.73	27.4	10.79	20.63	4 46	7.23	1406	1076	0.28	41.38	11.34	22.31	4.16	8.58	1088	845	0.39	43.80	10.54	15.84	5 05
	5.81	1828	1195	0.23	39.88	11.96	24.96	3 31	6.59	1443	1046	0.26	40.49	11.24	22.49	4.73	7.97	1055	990	0.32	42.04	10.85	20.49	4 77
	5.64	1979	1212	0.23	20.00	11.00	25.55	2 0	6.4	1515	1086	0.25	39.97	11.5	23.79	4.33	7.26	1481	1113	0.29	41.95	11.55	22.18	4.04
	5.7	2055	1240	0.2	20.0	11.03	25.33	2 / 2	5.8	1785	1299	0.22	39.8	11.81	24.86	4.16	5.59	1299	1028	0.22	41.02	11.9	20.66	5.64
	5.60	2000	12240	0.2	40.14	11.77	25.44	2.42	6.03	1585	1196	0.23	40.26	11.94	25.41	3.61	6.15	1428	1193	0.24	42.01	12.21	23.8	3.68
	5.60	2105	1221	0.22	20.22	11.0	25.22	3.42	5.88	1665	1142	0.23	41.55	11.58	25.03	3.48	6.23	1420	1301	0.26	41.85	12.43	24.28	3.25
	5.09	2104	1220	0.21	39.23	11.82	25.34	3./	5.88	1774	1170	0.23	42.49	11.67	24.57	3.14	6.24	1349	1189	0.24	41.05	12.04	23.95	3.84
	5.07	2085	1220	0.22	40.93	12.07	25.22	2.71	6.09	2238	1210	0.24	41.05	11.85	24.95	3.46	6.23	1334	1190	0.24	41	12.02	23.88	3.8
	5.80	2095	1224	0.23	40.71	11.80	25.18	3.44	6.6	2136	11/9	0.26	42.05	11.74	24.62	3.06	6.22	1076	1209	0.23	39.8	12.09	23.58	4.3
	6.01	2018	1220	0.23	41.01	11.86	25.09	3.43	6.6	1983	1149	0.25	41.49	11.76	24.56	3.24	6.11	1063	1174	0.23	40.54	12.33	23.57	4.21
_	5.96	1801	1189	0.23	40.35	11.74	25.25	3.59	6.65	1/34	1135	0.26	40.87	11.75	23.72	3.88	5.05	1022	1188	0.26	40.93	12.77	23.94	3.9
	6.89	2271	1183	0.28	43.09	11.91	24.85	2.45	0.7	1328	1078	0.28	41.13	10.22	23	4.11	7.05	1264	906	0.5	40.5	11.54	22.27	4.17
	6.69	1959	1081	0.26	41.5	11.32	23.66	3.75	7.02	1001	002	0.31	41.57	10.52	10.71	4.30	7.88	1031	721	0.36	44.08	11.43	18.51	5.04
	6.82	2110	1044	0.28	41.29	11.02	22.82	4.14	8 28	1211	830	0.32	41.04	10.55	19.28	J.55 /1.98	7.61	753	697	0.34	45.14	11.01	17.71	5.34
	7.27	1949	969	0.29	41.45	10.95	21.21	4.87	8.18	1326	777	0.34	42.17	10.7	17 33	6.24	8.38	659	588	0.39	46.1	10.95	16.9	4.69
	8.81	1914	900	0.4	41.6	10.62	18.68	4.5	8 72	1236	721	0.35	42.17	10.1	16.8	6.18	9.02	644	568	0.43	47.6	11.16	16.18	4.39
	7.1	1662	886	0.28	39.99	10.49	19.81	4.9	9.37	1279	694	0.38	42.65	9.73	15.81	6.20	9.68	611	491	0.42	18.18	10.65	15.08	4.73
	6.57	1863	982	0.25	38.58	10.13	18.98	5.35	5.57	1275	004	0.00	42.00	5.75	10.01		9.75	525	459	0.47	48.06	10.82	14.42	5.7
	7.53	1448	778	0.3	39.26	9.75	17.76	5.54									10.41	483	413	0.52	48.51	10.77	13.11	5.43
	8.65	1346	708	0.35	41.49	9.52	16.38	6.01									11.34	447	339	0.55	48.88	10.16	11.36	6.02
	9.44	1320	658	0.38	43.3	9.32	14.93	6.35									13.5	252	184	0.59	51.12	8.21	7.2	6.49

Lithogeochemistry, of quality, typically outstrips most groups' efforts at 'best practice' logging. This is detail of ultramafic cumulate layering within a single logged rock type at Sunrise Dam Gold Mine.



## Principle 3

- Once lithogeochemical groups are identified:
  - Can distinguish alteration effects
    - Formal comparison of less- and more-altered equivalents via "isocon" diagrams
    - More statistical comparison by use of attribute system in ioGAS
  - Can isolate and utilize effects of veins by recognizing dilution of immobile elements

# veins within geochemical data



## Veins and alteration zones (same principles for hydrothermal breccia)

Textures preserved, one mineral pseudomorphed by new ones

Textures partly preserved, but most original minerals destroyed

All textures and original minerals destroyed



Vein: commonly coarser and simpler than surrounding alteration

## Precursor rock variability and sampling strategies (field or mine – and you are doing the sampling)



- Size of sample relative to banding/bedding in sample
- Spatial relationships of vein to alteration
- Do we include the vein?
- Is a 5-6 comparison possible or does the outcrop/shearing etc obscure the detail?

# Dealing with 'random' samples: typical drill data or an 'inherited' database



- What if a dataset already exists and is passed on to you?
- What if the data is regular intervals from drill core?
- How do we deal with the data if we did not gather it ourselves?

## Element mobility – the key to quantifying geochemical changes

Sample	A	В
SiO2	98%	99%
TiO2	1.9%	0.95%



The geochemical dilution of an immobile element is ~ inversely proportional to the amount of veining 81

A CONTRACTOR

### How can you tell whether the TiO2 is moving, the silica, or both?

Sample	Α	В	TiO2	I	TiO2	
Campio			Al2O3		Al2O3	
SiO2	92%	96%				
TiO2	1.9%	0.95%	SiO2		SiC	2 Quartz vein or breccia
AI2O3	6%	3%				infill

A

B

# The slope of the line defining the best fit to the immobile elements is proportional to the total mass change

For an individual pair of samples

Sample	A	В
SiO2	98%	99%
TiO2	1.9%	0.95%
AI2O3	0.2%	0.1%
Zr	200	100
	ppm	ppm



- Dilution of immobiles = mass gain (dilation)
- Enrichment of immobiles
  = mass loss (dissolution)

K3 far west long section, looking down and NW: <u>logged %qtz not</u> <u>best Au-vein descriptor</u>

-Colour

Shape K3 only? Size

Au ppm Progressive

Au\_ppm to 0.026 [30.00%]
 Au\_ppm to 0.099 [60.00%]

Au\_ppm to 0.253 [80.00%]
 Au\_ppm to 0.517 [90.00%]

Au\_ppm to 1.025 [95.00%]
 Au\_ppm to 2.59 [98.00%]
 Au\_ppm to 217.0 [100.00%]



An epithermal Au-Ag mine in western Turkey (Kestanelik): logged qtz % suggests high Au in both veins and in wallrocks





You would think that logged % quartz would be easy – but look at the core

Estimate % hydrothermal quartz. Take your time.

Estimate % hydrothermal quartz. Quick! The boss is looking over your shoulder!

#### Estimate % hydrothermal quartz. Outside. In the heat, and do 400m today



FGAT20

### Yeah of course that's schist. What % quartz?



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This result says that the quartz veins are thick and continuous, and there are only localized zones of high Au in the hanging walk of this vein ont copy/transmit without permission

### Nick's favourite immobile element

## Titanium

- Used in toothpaste, paint, some white food products.....
- Moderately abundant in many rocks, 0.01 to 2%
- Highly variable in sedimentary and igneous processes
- Yet almost invariable in hydrothermal processes
- You can make high speed objects with titanium: aircraft, bicycles, tennis racquets, motorcycles, armour-piercing projectiles
- I have seen only one or two cases where hydrothermal Ti mobility > 10cm can be demonstrated – usually in carbonatitic fluids (almost melts anyway) or in high pressure metamorphic fluids involving boron or fluorine



## Even though we're interested in Au, Cu, Fe, As, Zn etc, the 'answer' lies in the immobile elements!