Cyclic Magmatic-Hydrothermal Process in Porphyry Cu Systems

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Acknowledgments
Outline

- Genetic models of PCD
- Key questions
  - Fluid exsolution
  - Triggers of mineralization
  - Timescales
- My research
- Implications and future work
Why Cu
What is a Porphyry Copper Deposit?

- Related to porphyritic intrusions
- Large tonnage
- Low grade
- Bulk mineable
- Stockwork hosted ore
- Large scale of hydrothermal alteration
- Supergene enrichment
Why Porphyry Cu?

75 % Cu
50 % Mo
20 % Au
All of the Re

Chuquicamata, Chile with 66.37 Mt Cu, 1.81 Mt Mo and 300 t Au

Map from Google Earth
Where are they?

Insights into continental growth

Richards, 2013, NG
Insights into volcanic monitoring
Link deep magmatic process to hazard prediction-mineral exploration
From source to sink

- Fluid exsolution
- Sulfide deposition
What do we know

Expanding vapour plume

Porphyry ore deposit

Groundwater circulation

Dense brine sinks/spreads laterally

Mixing zone

Shallow crust

200 °C

400 °C

600 °C

800 °C
Fluid exsolution at depth

Continue or Pulsed?
Expression of deep fluid at the surface
How do “we” collect them?
- Transportation in oxidized state

- Mineralization in reduced state
From oxidized fluid to reduced ore

Hypothesis 1: disproportionation of SO$_2$

\[ 4\text{SO}_2(g) + 4\text{H}_2\text{O}(aq) \rightarrow 3\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{S}(aq) \]

Richards al., 2013, GCA
From oxidized fluid to reduced ore

Hypothesis 2: anorthite reacts with SO$_2$

$$3\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{SO}_2 + \text{H}_2\text{O}_4 \rightarrow 3\text{CaSO}_4 + 3\text{Al}_2\text{SiO}_5 + 3\text{SiO}_2 + \text{H}_2\text{S}$$

Henley et al., 2015, NG
From oxidized fluid to reduced ore

Hypothesis 3: new flux of reduced gas
From oxidized fluid to reduced ore

Hypothesis 4: mix with meteoric water
From oxidized fluid to reduced ore

Hypothesis 1: disproportionation of $SO_2$

$$4SO_2(g) + 4H_2O_{(aq)} \rightarrow 3H_2SO_4_{(aq)} + H_2S_{(aq)}$$

Hypothesis 2: anorthite reacts with $SO_2$

$$3CaAl_2Si_2O_8 + 4SO_2 + H_2O \rightarrow 3CaSO_4 + 3Al_2SiO_5 + 3SiO_2 + H_2S$$

From oxidized fluid to reduced ore

Hypothesis 3: new flux of reduced gas

Hypothesis 4: mix with meteoric water

Blundy et al., 2015, NG.
George Box:

Essentially, all models are wrong, but some are useful.
What is the lifetime of a deposit?

Highly variable, why?

Chiaradia et al, EG 2014
Key questions

- Fluid exsolution process
- Trigger for mineralization
- Duration of ore formation

Examine them on the world-class Qulong PCD
Why Qulong?

- **Large but simple**
  - one mineralization center

- **Young**
  - Utilize the power of high precision geochronology

- **High altitude**
  - maximize the differences between magmatic & meteoric fluids
The precision of geochronology

Chiaradia et al, EG 2014

- volume = 2500000 μm³, U = 250 ppm
- double volume or double U
- half volume or half U
Oxygen isotope variation with altitude

$^{16}$O evaporates easier than $^{18}$O

$^{18}$O is preferentially removed by precipitation
- Magmatic fluid
  \(^{18}\text{O}\) enriched
  \(\delta^{18}\text{O} = 8 \, \%\)

- Meteoric water
  At high altitude
  \(^{18}\text{O}\) depleted
  \(\delta^{18}\text{O} = -20 \, \%\)
Coupling high-precision geochronology and O isotopes
Largest in China (11 Mt Cu + 0.6 Mt Mo)

Post-collisional setting (~16 Ma)

Li et al., Geology, 2017
Relative timeframe of Qulong

A) Rongmucuola pluton → P porphyry → Aplite → X porphyry → breccia → breccia → Mineralization → decreasing relative age → Post-ore diorite

Li et al., EG, 2017
Sulfide veins and alteration assemblages
Records of fluid exsolution & evolution

Li et al., EG, 2017
Defining the timeframe of magmatism

Single zircon grain U-Pb dating

CA-ID-TIMS

Most precise dating tool for magmatism
Dating magmatism at the kyr level

Chemical Abrasion Isotope Dilution TIMS
- The lifetime of magmatic system is ~2 Myr
- Extended (~1 Myr) periods of quiescence
Define the timeframe of mineralization

Single molybdenite vein Re-Os

ID-N-TIMS

Most precise and date metals directly
1. **Sample Digestion**
   - Carius tube
   - 220 °C, 48 hours
   - Sample + tracer in CrVI - H2SO4
   - Freeze and open tube

2. **Os Separation**
   - Solvent extraction and back extraction
   - CHCl3
   - Acid media
   - Os in CHCl3
   - Os in HBr

3. **Os Purification**
   - Micro-distillation
   - 80 °C, 4 hours
   - Capture Os in HBr
   - Dry and dissolve Os in CrVI-H2SO4
   - N-TIMS

4. **Re Separation and Purification**
   - Solvent extraction and ion exchange purification
   - Re separation
   - Dry and convert to NaOH
   - (CH3)2CO
   - NaOH
   - Re extracted in (CH3)2CO
   - Dry and convert to HNO3, load on resin
   - N-TIMS

Li et al., unpublished
Different stages of alteration & mineralization phases at Qulong

Li et al., EG, 2017
High precision dating for Mineralization

- Rapid metal deposition in $\sim 266 \pm 13$ kyrs
- Mineralization only linked to P porphyry (conduit)

Li et al., EG, 2017
Why highly variable?

Chiaradia et al, EG 2014
Over-interpretation of low precision data

Precision sensitive

$r^2 = 0.6031$

Li et al., EG, 2017
Link absolute time and fluid evolution

TIME
Re-Os

Quartz fluid inclusion

Hematite
Opaque minerals

Quartz oxygen isotope
Cooling history of Qulong PCD

- $0.55 \pm 0.11 \, ^\circ C/kyr \ (r^2 = 0.797)$
- $1.19 \pm 0.82 \, ^\circ C/kyr$
- $1.27 \pm 0.53 \, ^\circ C/kyr$

$\times$ samples with depths $> 211 \, m$

Li et al., EG, 2017
- **Pulsed ore formation**
- **Rapid and cyclic cooling** (0.5 vs 0.2 °C/kyr)
- **Single pulses last tens of kyr** (38 ± 11 and 59 ± 10 kyr)
Avoid overprinting

Constrain oxygen isotope diffusion

Oxygen isotope exchange equilibrium between fluid & quartz

Li et al., Geology, 2017
Oxygen isotope archive in absolute time

Li et al., Geology, 2017
Oxygen isotope archive in absolute time

Understand ore-forming process in real time
Involvement of non-magmatic fluid

$\delta^{18}O$ (‰)

1st pulse  2nd pulse  3rd pulse

Age (Ma)

16.15  16.05  15.95  15.85

$\delta^{18}O_{\text{fluid}}$

Li et al., Geology, 2017
Dynamic Interplay between magmatic and meteoric water

- Magmatic fluid
  $^{18}\text{O}$ enriched

- Meteoric water
  $^{18}\text{O}$ depleted
Cyclic ore-forming fluid evolution

\[ \delta^{18}O \text{ (‰)} \]

1st pulse  2nd pulse  3rd pulse

\[ \delta^{18}O_{\text{fluid}} \]

Age (Ma)

16.15  16.05  15.95  15.85

Li et al., Geology, 2017
Fluid exsolution at depth

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How do “we” collect them?
**From oxidized fluid to reduced ore**

**Hypothesis 1: disproportionation of SO₂**

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**Hypothesis 2: anorthite reacts with SO₂**

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**Hypothesis 3: new flux of reduced gas**

**Hypothesis 4: mix with meteoric water**
From oxidized fluid to reduced ore

Hypothesis 4: mix with meteoric water
How does meteoric water work?
Magic temperature window for mineralization

420 – 285 °C

- Thermal conduction is inefficient
- Ore formation requires rapid cooling
- Fluid mixing is efficient and straightforward

Li et al., MD, 2017 and unpublished
- Progressive decrease of magmatic fluid flux
- Most magmatic fluid released in the first pulse

Li et al., Geology, 2017
Episodic fluid release from source pluton associated with fractionation crystallization
A common process in PCD?
Presence of multiple pulses

Williamson et al., NG, 2016; Tapster et al., EPSL, 2016; Cook et al., TiGeoCh, 2014; Sillitoe, EG, 2010; Weis et al., Science, 2012.

Presence of meteoric water
Take home message

- Tracing fluid evolution in absolute time
- Single mineralization pulse lasts tens of kyr
- Gradual cooling of source pluton
- Multiple pulses in PCD
- Rapid cooling requires meteoric water
Essentially, all models are wrong,

Hopefully mine is useful.
Thanks for your time!
Published data for magmatism & mineralization

- Low precision, poor reducibility
- Unaddressed systematic bias

Can not be used to address the timescale

Li et al., MD, 2017
Crystallization T and magmatic O IC

mean = 6.14 ± 0.39 ‰
\( n = 23, \ 2 \ SD \)

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\( n = 23, \ 2 \ SD \)

measured zircon \( \delta^{18}O \) values

calculated quartz-zircon equilibrium temperature
674 ± 151 °C (2 sigma)

mean = 8.78 ± 0.65 ‰
\( n = 27, \ 2 \ SD \)

measured quartz \( \delta^{18}O \) values

Li et al., Geology, 2017
δ¹⁸O of different fluids at Qulong

Meteoric water
-15.6 ‰

Magmatic water
7.6 ‰

δ¹⁸O of water (‰)

Fluid source determination

7.6 ‰

-15.6 ‰

100% Magmatic water

Mixing ratio

100% Meteoric water

Li et al., Geology, 2017
Interplay between magmatic and meteoric water

- **Before mineralization**
  - Free meteoric water circulation

- **During mineralization**
  - Magmatic fluid fluxing dominates

- **After mineralization**
  - Meteoric water re-dominates

Li et al., Geology, 2017