H4: $^{40}\text{Ar}/^{39}\text{Ar}$ dating of mineralisation, metamorphism and deformation

1) pyrite mica dating (pmd)
2) Fluid inclusion dating and geochemistry

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Testing the “fools clock”:
dating pyrites using $^{40}\text{Ar}/^{39}\text{Ar}$

John Miller
What are we dating?

Using $^{40}\text{Ar}/^{39}\text{Ar}$ technique to date muscovite/sericite included in pyrite: pyrite acts as an armour protecting included mica from later heating ($^{40}\text{Ar}$ loss), later hydrothermal alteration and reactor induced $^{39}\text{Ar}$ recoil loss.
Brief background to $^{40}\text{Ar}/^{39}\text{Ar}$ dating

- Uses decay of $^{40}\text{K}$ (parent) to $^{40}\text{Ar}$ (daughter)
- Samples irradiated in nuclear reactor to convert some $^{39}\text{K}$ to $^{39}\text{Ar}_K - ^{39}\text{Ar}_K$ used as proxy parent
- Both daughter and proxy parent isotopes are gases and can be released from sample by step heating using a laser or furnace to produce an age spectrum

Closure Temperature Concept

Daughter product is a gas which can diffuse out of mineral if temperature is too high ($^{40}\text{Ar}$ loss)
Age may represent cooling below a closure temperature & not crystallisation
Brief background to $^{40}$Ar/$^{39}$Ar dating

$^{39}$Ar recoils ~0.1 μm during sample irradiation

With small grain sizes (<10 μm) this can cause $^{39}$Ar recoil loss from grain. This produces age gradients and elevated apparent ages at low temperature steps

Geological heating event causing $^{40}$Ar loss
(diffusion of daughter isotope from grain)

Heating event (or slow cooling of sample) can cause diffusion of $^{40}$Ar from grain ($^{40}$Ar loss), leading to younger $^{40}$Ar/$^{39}$Ar ages (i.e., not dating grain crystallisation).
Previous Pyrite dating

• Smith et al., (2001) successfully dated single pyrite crystals
  • Advantages: very small sample size (compared to bulk sampling for dating sulphides by Re-Os); single crystal dating can identify heterogenous data; pyrite protects mica from geologic argon loss and reactor induced $^{39}$Ar recoil (Smith et al., 2001; Geology, v. 29, p. 403-406).

Why hasn’t it become a common method?

• Earlier work by York et al. (1982) produced discordant isochrons - pyrite systematics not really understood
• Sulphur contaminates the extraction line
Kanowna-Belle (KB) and Mt Charlotte have completely different noble gas characteristics marked by different total gas ages and release profiles.

Significance of older ages - are they real or not?

Oldest age step for KB matrix sericite - highlights danger in just dating matrix mica with $^{40}\text{Ar}/^{39}\text{Ar}$.
Highlight systematics of pyrite inclusion dating (using 3 examples)

• (1) Pyrite date with same age as matrix (Mount Charlotte, Type 1 alteration, MC263 301’)

• (2) Date on pyrite from 440 Ma gold lode with complete hydrothermal over print of matrix by a younger short-lived event (Stawell)

• (3) Date on pyrite from system with major thermal overprint post gold mineralisation that caused major $^{40}$Ar loss from matrix mica (Kanowna-Belle sample from drill hole GDD438 (351.1 to 351.3 m)
EXAMPLE 1 - Step-heating experiments on Mt Charlotte Pyrite (Yilgarn Au deposit)

Repeateable experiments with gas loss at low-T steps & age plateaux at High-T steps

Example Spectra

MC-1/10
Age plateau
2595 ± 14 Ma

Gas loss

11 combined spectra

High-T steps

Gas loss at Low-T steps

MATRIX MICA
2601 ± 13 Ma

Kent & McDougall, 1995

Kent & McDougall, 1995
2601 ± 13 Ma

91-234 24 Sublevel Charlotte ore body

Fraction $^{39}$Ar released

Fraction $^{39}$Ar released

Age (Ma)

Age (Ma)
High-T steps - removes gas loss affecting low-T steps = age close to observed plateaux ages

**Mount Charlotte - High-T steps only**
(MC-1; Size of step weighting if more than one step)

- **Mean** = 2592.3 ± 6.8 [0.26%] 95% conf.
  - Wtd by data-pt errs only, 0 of 12 rej.
  - MSWD = 0.80, probability = 0.65
  - (error bars are 2σ)
EXAMPLE 2 - standard $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating experiments, Stawell Mine, Western Victoria

- Dating of matrix minerals highlighted 3 main ages
- 500 Ma metamorphism, 440 Ma alteration & 400 Ma plutonism

Most gold at 440 Ma with minor intrusion-related gold at ca. 400 Ma
Pyrite dating of major historical lode at the Stawell Mine

Hangingwall lode, Magdala gold deposit, western Victoria.

Sample JM-23f

Deformed turbidites
Volcanogenic rocks
Basalt

Gold Lode/Fault
Historical (1860-90) stope
Late Fault
Dating of matrix sericite (not 440 Ma)
Interpreted to be intrusion-related overprint

Sample JM-23f

Matrix sericite & chlorite

Pyrite

Sericite

SEM image of pyrite with sericite inclusions.

Note steps averaged assuming $^{39}$Ar recoil redistribution only (minimal <1% $^{39}$Ar loss)
(400 Ma = age of Stawell pluton)
Dating of pyrite from same sample (JM-23f)

Gas loss at low-T steps & age plateaux at High-T steps

Example Spectra

JM-23f - pyrite Laser step-heating of 11 grains

Age (Ma)

Fraction $^{39}$Ar released

JM-23f-10

Age (Ma)

Fraction $^{39}$Ar released

JM-23f-11

Age (Ma)

Fraction $^{39}$Ar released
Majority of High-T steps are not within $2\sigma$ error of matrix sericite age (~400 Ma) but are within error of known mineralisation age (440 Ma).

Mean pyrite age of 436±3 Ma includes high temperature steps within $2\sigma$ error of each other. Younger age steps are attributed to partial resetting and/or exposed inclusions.
EXAMPLE 3 - Step-heating experiments on matrix sericite from Kanowna-Belle (GD-2)

Spectrum discordant with evidence for major $^{40}$Ar loss at Low-T steps with age gradient at High-T steps - OLDEST age steps are 2500 Ma

Massive $^{40}$Ar gas loss at Low-T steps

Age gradient

Kanowna-Belle Muscovite Sample GD2
Step-heating experiments on Kanowna-Belle Pyrite (Yilgarn Au deposit)

Spectra have discordant age gradients - loss event in matrix not observed

If gradient is caused by $^{40}\text{Ar}$ diffusion to pyrite/mica inclusion boundary during Proterozoic heating event (average of all steps will have meaning)
Kanowna-Belle total gas ages - (individual pyrites)

Box heights are $2\sigma$

GD1 Pyrite
Kanowna-Belle
Total gas ages

Oldest age step for KB matrix sericite
• $^{40}\text{Ar}$ lost from mica due to geologic heating (or $^{39}\text{Ar}$ recoil loss) is inferred to remain in interstitial space on pyrite/inclusion boundary.

• Mica inclusions on pyrite rim or adjacent to fractures are susceptible to any resetting that affects matrix mica. This produces variable over print of each pyrite (some pyrite grains are more open systems than others).
Summary

- **Example 1)** Mt Charlotte matrix and pyrite same age
- **Example 2)** High-T steps on Stawell pyrite preserved older age (~440 Ma) even with complete overprint of matrix at ca. 400 Ma
- **Example 3)** Kanowna-Belle retained $^{40}$Ar inside pyrite that was lost from matrix mica during Proterozoic heating event
- Pyrite is a variably closed system
- Highlights danger in relying too much on dating wall rock alteration using $^{40}$Ar/$^{39}$Ar i.e. it may be dating later (younger) event
- **Potential of dating matrix sericite and pyrites to cover multiple periods of alteration in one sample**
- Method can be applied to terranes projects provided pyrite has mica inclusions (petrography critical)
$^{40}\text{Ar}/^{39}\text{Ar}$-$\text{Kr}$-$\text{Xe}$ application development

Mark Kendrick
Analytical problems

- *In vacuo* crushing + stepwise heating
- Daughter mineral fractionation.
- Bulk analysis – samples containing multiple generations of fluid inclusion.
- Minimising air contamination.
Solution

• Stepwise heating alone will decrepitate different fluid inclusions at different temperatures.
• Fractionation avoided due to daughter mineral dissolution.
• Larger samples to give high ‘resolution’ from many steps.
Eloise Cu-Fe-O-Au, Mnt Isa

Br/Cl (x10^{-3}), I/Cl (x10^{-6}) and K/Cl

Group 3 is the site of K-daughter mineral

EL 48179
Further evidence for 5 groups

$^{40}\text{Ar}_e/\text{Cl}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ values

Boiling/devolatilisation

F-values (Fractionation values), $F = 1$ atmosphere,

L - phase

$F > \text{ASW} \ (2-3)$ enriched in heavy noble gases

V - phase

$F <$ depleted in heavy noble gases

As expected from, Tdcp V dom FI at high T, L dom FI at low T
Group 3 is the site of K-daughter mineral.

F > 1 - L dominated

F < 1 - V dominated

40Ar/36Ar = 295.5

40Ar/36Ar = 295.5

Br/Cl, I/Cl, and K/Cl.

Temperature °C
Salinity origin

![Graph showing salinity origin with I/Cl (x10^-6) and Br/Cl (x10^-3) axes. S.E.T., Diamond, PCD, and Fumerole are labeled on the graph. Halite Dissolution water is indicated.](image)
Salinity origin

Br/Cl (x10^{-3}) vs. I/Cl (x10^{-6})

- S.E.T.
- PCD
- Diamond
- Fumerole
- Halite Dissolution water
- Mantle > 40,000
- Crust 295 < C > 38,000
- Atmosphere/ASW = 295 -- HD
Halite dissolution water

Br/Cl fractionated by L-V partitioning?

Multi-phase K-rich, HD
Salinity origin

- Type 1, LVD, K-rich
- Type 3, LV CO₂
- Type 8, LV 2s
- S.E.T.
- PCD
- Diamond
- Fumerole
- Halite Dissolution water
Age information for Eloise?

**Older apparent ages due to excess $^{40}\text{Ar}_E$**

- Younger than $1790 \pm 270$ Ma
- Older apparent ages due to excess $^{40}\text{Ar}_E$

**True age = $1514-1530$ Ma** (Baker et al. 2001)

**Diagram:**
- $K/36\text{Ar}$ vs $40\text{Ar}/36\text{Ar}$
- Data points for:
  - EL7a crush
  - EL7a step heat
  - EL7b step heat only
  - EL9 step heat only

**Note:**
- The graph shows the relationship between $K/36\text{Ar}$ and $40\text{Ar}/36\text{Ar}$, with data points indicating different samples and their corresponding ages.
When is age information available?

Same experiments different sample material

AW02-002 Cu-related quartz vein from the western succession.
High K/Cl >> 1

Variable $^{40}\text{Ar}_E/\text{Cl}$

$^{40}\text{Ar}/^{36}\text{Ar} = 700 - 2400$
Sample
AW02-002
Isochron

Slope = 9.082 ± 1.0 x10^6
Age = 981 ± 138 Ma
^40^Ar/^36^Ar = 1797±300
MSWD = 1878
3D isochron

$^{40}\text{Ar}/K = 1.00 \pm 0.04 \times 10^{-5}$

$^{40}\text{Ar}/^{36}\text{Ar} = 293 \pm 83$

$^{39}\text{Ar}/^{36}\text{Ar} = 267 \pm 36$

MSWD = 8.3,

Age = 1055 \pm 56 \text{ Ma}$
Air corrected 2D mixing

\[ \frac{^{40}Ar^*}{K} = 1.005 \pm 0.03 \times 10^{-5} \text{ (95% conf)} \]

MSWD = 6.4,

Age = 1059 ± 43

The age has a precision of 4%
Comparison with Eloise…
Comparison with Eloise…

![Graph showing Br/Cl and I/Cl ratios with different labels and markers.](image-url)
Conclusions

• Composition of multiple fluid inclusion types in complex samples.
• Mnt Isa Cu-related fluids (qtz) very different to Cu-Fe-O-Au deposit fluids.
• Age of qtz vein determined at 1059 +/- 43 Ma. Believed to represent age of Cu mineralisation.