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

1) pyrite mica dating (pmd-dating)
2) fluid inclusion dating and geochemistry

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Previous Pyrite dating

- Smith et al. (2001) dated single pyrite crystals from basalts.
- Advantages:
  - very small sample size.
  - single crystal dating can identify heterogenous data.
  - pyrite armours mica from argon loss and reactor induced $^{39}$Ar recoil. (Smith et al., 2001; Geology, v. 29, p. 403-406).

Why is this not a common dating method?
- Earlier work by York et al. (1982) produced discordant results - pyrite systematics not fully understood.
- Sulphur contaminates the extraction line
- Pyrite is very ‘hot’ after irradiation

Solution to the above problems:
- Remove sulphur during the experiment.
- Improve sample characterisation.
- Combine step-heating and in vacuo crushing experiments
- Analyses of single pyrite grains
Testing time for the “fools clock”:

$^{40}\text{Ar}/^{39}\text{Ar}$ dating of pyrite
**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 \( ^{39}\text{Ar}_{\text{K}} \) - \( ^{39}\text{Ar}_{\text{K}} \) 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
A Word on Errors

• Errors: precision vs accuracy
  – Inter-lab calibration (Precision):
    • Berkeley lab: \( R^{GA}_{FC} = 3.596 \pm 0.11\% \) (2\( \sigma \))
    • U Melbourne: \( R^{GA}_{FC} = 3.599 \pm 0.22\% \) (2\( \sigma \))
  
• Accuracy of \(^{40}\text{Ar}/^{39}\text{Ar}\) method is limited by decay constant uncertainties (±1%).

• Precision ± 0.1%:
  – 2600 ± 2.6 Ma

• Accuracy ± 1%:
  – 2600 ± 26 Ma
Brief background to $^{40}\text{Ar}/^{39}\text{Ar}$ dating

$^{39}\text{Ar}$ recoils $\sim 0.1 \, \mu\text{m}$ during sample irradiation

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

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

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

$^{40}$Ar/$^{39}$Ar technique dates white mica inclusions in pyrite. Pyrite armours the micas from later heating, hydrothermal alteration and recoil. Combined step-heating and crushing experiments have the potential to date the pyrite and fingerprint the fluid sources (e.g. crustal vs. mantle; meteoric water vs brines, using noble gases and halogens - Cl, Br, I).
40Ar/39Ar Analyses of Pyrite
Three examples:

• (1) Pyrite date with same age as matrix (Mount Charlotte, Type 1 and Type 3 alteration).
• (2) Date on pyrite from 440 Ma gold lode with complete hydrothermal overprint of matrix by a younger short-lived event (Stawell).
• (3) Date on pyrite from system with major thermal over-print post gold mineralisation that caused major 40Ar loss from matrix mica (Kanowna-Belle sample from drill hole GDD438 (351.1 to 351.3 m).
EXAMPLE 1 - Step-heating experiments on (Type 1) Mt Charlotte Pyrite.

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

Example Spectra

Gas loss at Low-T steps

High-T steps

11 combined spectra

MC-1/10
Age plateau
2595 ± 14 Ma

Kent & McDougall, 1995

2601 ± 13 Ma

MATRIX MICA

91-234 24 Sublevel Charlotte ore body

Gas loss

Age (Ma)

Fraction $^{39}$Ar released

Fraction $^{39}$Ar released
High-T steps - removes gas loss affecting
low-T steps = mean age ~ 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)
Mt Charlotte Type1 pyrite: isochron (High-T steps) = 2596 ± 9 Ma (2σ)

Laser probe analyses

\(^{40}\text{Ar}/^{36}\text{Ar}\) = 293.3 ± 3.3

Age = 2596 ± 4.7 Ma (1σ)
Age = 2596 ± 9.1 Ma (1σ; +J)
MSWD = 1.33
EXAMPLE 1b - Step-heating experiments on (Type 3) Mt Charlotte Pyrite.

**Mount Charlotte Deposit**

**Type 3 Pyrite**

**High Temperature Step**

Mean = $2613.5\pm5.2$ [0.20%] @ Wtd by data-pt errs only, 0 of 9 in MSWD = 0.94, probability = 0.4 (error bars are 2σ)

Plateau age = 2629.5±9.8 Ma (2σ, including J-error of 0.002%) MSWD = 0.83, probability = 0.43 Includes 69.8% of the 39Ar

Mount Charlotte Deposit
MC3 Pyrite #5

Plateau age = 2606.5±7.0 Ma (2σ, including J-error of 0.002%) MSWD = 1.4, probability = 0.24 Includes 98.7% of the 39Ar

Mount Charlotte Deposit
MC3 Pyrite #8
Mt Charlotte Pyrite
Summary

- Excellent results for Type 1 pyrite -
  - Age $2596 \pm 9$ Ma ($2\sigma$)
- Limited $^{40}$Ar loss.
- Atmospheric $^{40}$Ar/$^{36}$Ar ratio for trapped component of gas observed from isochron diagram.
- Type 3 pyrite grains - slightly older ages(?)
  - Mean age = $2614 \pm 5$ Ma ($2\sigma$)
Example 2 - standard $^{40}$Ar/$^{39}$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 from Au lode
Not 440 Ma - interpreted to be intrusion-related overprint

Sample JM-23f

Matrix sericite & chlorite

Pyrite

Sericite

SEM image of pyrite with sericite inclusions.

JM-23f - sericite
Total gas age = 401.2 ± 1.7 Ma
Age gradient indicates sample affected by $^{39}$Ar recoil

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

Gas loss at low-T steps & age plateaux at High-T steps
Majority of High-T steps are not with 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.
**Stawell Summary**

- High-T steps on Stawell pyrite preserved older age (~440 Ma) even with complete overprint of matrix at ca. 400 Ma.
- Highlights danger in relying too much on dating wall rock alteration using $^{40}\text{Ar}/^{39}\text{Ar}$ 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.
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

Cumulative $^{39}$Ar Percent
Step-heating experiments on Kanowna-Belle Pyrite

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

Gradient is caused by $^{40}$Ar diffusion to pyrite/mica inclusion boundary during Proterozoic heating event.
Crush experiments give apparent age of 6976 Ma. Thus average of all steps will approximate age.
• $^{40}$Ar lost from included mica due to geologic heating (or $^{39}$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)
Box heights are 2 $\sigma$

TOTAL GAS AGES
Mount Charlotte (Red) - Kanowna-Belle (Blue)

Significance of older ages - are they real or not?

Oldest age step for KB matrix sericite - highlights danger in just dating matrix mica with $^{40}\text{Ar}/^{39}\text{Ar}$

Purple dashed line = oldest age steps for matrix sericite
Summary

- Potential of dating matrix sericite and pyrites to cover multiple periods of alteration/heating in one sample
- Pyrite is a variably closed system - single grain analyses highlight that some pyrites are more reset than others
- Work highlights danger in relying too much on dating wall rock alteration using $^{40}\text{Ar}/^{39}\text{Ar}$ i.e. it may be dating later (younger) event
- Method can be applied to terranes projects provided pyrite has mica inclusions (petrography critical)
40 Ar/39 Ar step-heating experiments on Revenge & Fimiston Lode Pyrites.

**Fimiston Lode Pyrite**

- Mean = 2617.8 ± 6.9 [0.26%] 2σ
- Wtd by data-pt errs only, 1 of 7 rej.
- MSWD = 1.2, probability = 0.28

(box heights are 2σ)

**Revenge Pyrite**

- Mean = 2619.8 ± 7.0 [0.27%] 2σ
- Wtd by data-pt errs only, 2 of 8 rej.
- MSWD = 1.6, probability = 0.16

(box heights are 2σ)

(Total-gas age = 2617 ± 15 Ma; 1σ)
(High Temp age = 2637 ± 16 Ma; 1σ)
Summary of Yilgarn Pyrite Ages

- Mount Charlotte (MC1) 2595 ± 9 Ma (2σ; ±15 Ma, incl J-err)
- Mount Charlotte (MC3) 2614 ± 5 Ma (2σ; ±9 Ma, incl J-error)
- Kanowna Belle (GD1) 2633 ± 22 Ma (95%; ±25 Ma, incl J-error)
- Fimiston Lode (F-1) 2618 ± 7 Ma (2σ; ±14 Ma, incl J-error)
- Revenge (R-1) 2620 ± 7 Ma (2σ; ±15 Ma, incl J-error)
Future work

- $^{40}\text{Ar}/^{39}\text{Ar}$ dating of pyrite samples from other well-constrained gold deposits.
- Combine step-heating analyses of single pyrite grains with crushing experiments to determine trapped argon isotopic composition.
- Integrated noble gas (He, Ne, Ar, Kr, Xe) and halogen (Cl, Br, I) analyses of well-constrained pyrite samples to fingerprint age/fluid sources - must be linked to structural/alteration framework.
- Dating other phases containing potassic inclusions (e.g. other sulphides, magnetite, etc.).