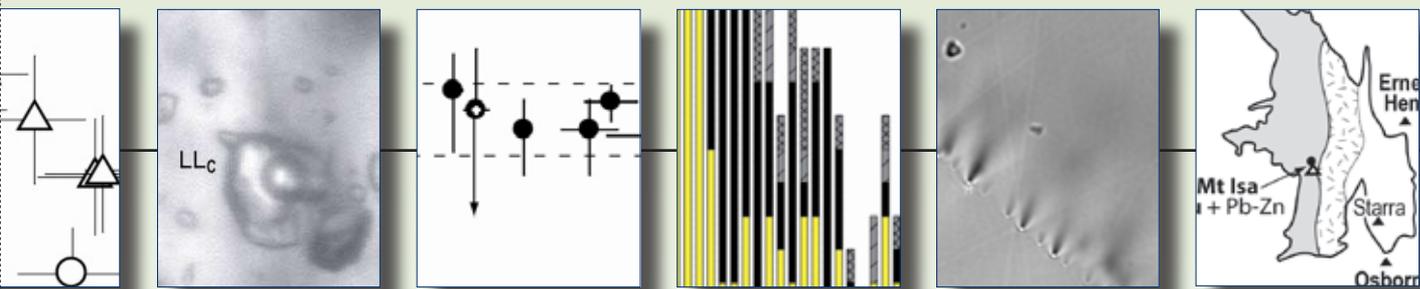


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Mineralising Systems History Program

(Incorporating)

H6 Project Final Report 2008



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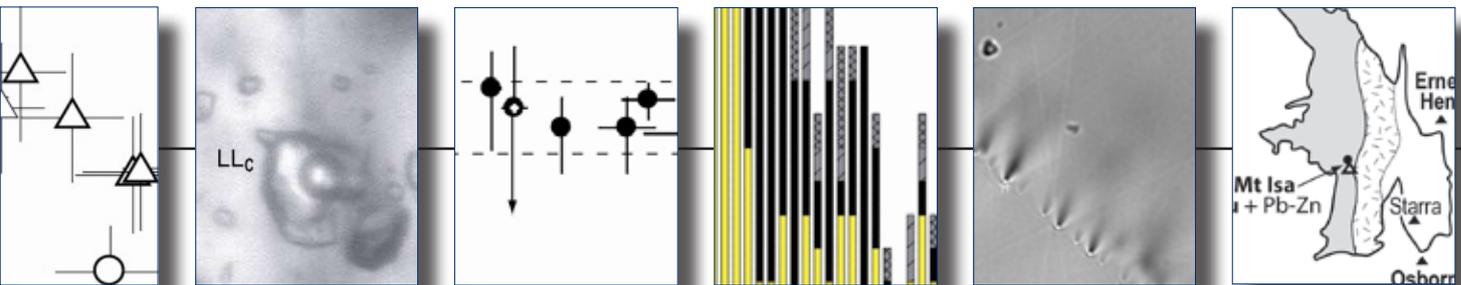
pmd*CRC

Mineralising Systems History Program

- H1** Application of Re-Os isotopes to Geochronology, Ore Forming models and Exploration Models
- H2** Pb-Pb step-leaching as a possible means of dating mineralisation, metamorphism and deformation.
- H4** $^{40}\text{Ar}/^{39}\text{Ar}$ Dating of Mineralisation, Metamorphism and Deformation
- H6** $^{40}\text{Ar}-^{39}\text{Ar}$ geochronology and halogen and noble gas geochemistry of mineralising systems

(Incorporating)

H6 Project Final Report 2008



Compiled by Mark A Kendrick

The School of Earth Sciences, The University of Melbourne, Australia

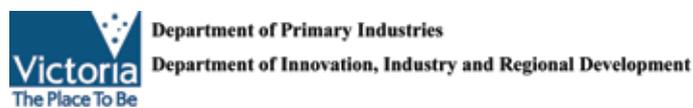
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Appendix A4: Evaluation of Ar-Ar fluid inclusion ages

Kendrick, Miller, and Phillips, 2006b, Part II: Evaluation of ^{40}Ar - ^{39}Ar quartz ages: Implications for fluid inclusion retentivity and determination of initial $^{40}\text{Ar}/^{36}\text{Ar}$ values in Proterozoic samples.: *Geochimica et Cosmochimica Acta* 70, 2562-76.

Appendix B: H6 Publications**Appendix B1: The Mt Isa Copper Deposit**

Kendrick, Duncan and Phillips (2006) Noble gas and halogen constraints on mineralising fluids of metamorphic versus surficial origin: Mt Isa, Australia: *Chemical Geology* 235, 325-351.

Appendix B2: The Ernest Henry IOCG Deposit

Kendrick, Mark and Phillips (2007) Mid-crustal Fluid Mixing in a Proterozoic Fe oxide-Cu-Au deposit: Evidence from Ar, Kr, Xe, Cl, Br, I, Ernest Henry, Australia: *Earth and Planetary Science Letters* 256, 328-343.

Appendix B3: The Osborne IOCG Deposit

Fisher and Kendrick (2008) Metamorphic Fluid Origins in the Osborne Fe oxide-Cu-Au deposit, Australia: Evidence from noble gases and halogens: *Mineralium Deposita*, in press.

Appendix B4: Sources of Regional Na-Ca alteration Fluids

Kendrick, Baker, Fu, Phillips and Williams (2008) Noble gas and halogen constraints on regionally extensive mid-crustal Na-Ca metasomatism, the Proterozoic Eastern Mt Isa Block, Australia: *Precambrian Research*, in press.

Appendix C: H6 Publications in preparation**Appendix C1: Sources of CO₂ in the Mary Kathleen Fold Belt**

Kendrick, Oliver and Phillips (in prep.) Tracing the sources of CO₂ in metamorphic belts with Ne and Ar: A fluid inclusion case study, northeast Australia.

Appendix C2: The Wernecke IOCG Prospects

Kendrick, Honda, Gillen, Baker and Phillips (in press). New constraints on regional brecciation in the Wernecke Mountains, Canada, from He, Ne, Ar, Kr, Xe, Cl, Br and I. *Chemical Geology*.

Appendix C3: The Analysis of Scapolite

Kendrick and Phillips (in prep.). Quantitative extraction of noble gases by in vacuo crushing: Implications for Ar-Ar dating and measurement of scapolite Br/Cl and I/Cl.

Appendix C4: Ar constraints on the 'Walshe Model' of gold mineralisation

Kendrick, Walshe and Petersen (in prep.) Global links between gold and mantle degassing of ^{40}Ar plus methane: A 2.65 Ga case study.

HISTORY PROGRAM EXECUTIVE SUMMARY

The Mineralising Systems History program was designed to develop enabling technologies for the study of ore deposit and fluid histories, and provide new infrastructure/ analytical capabilities in Australia.

The program was conceived because most world-class ore systems formed during discrete hydrothermal events in terranes which experienced widespread and repeated fluid flow over protracted time periods. The project aimed to develop a range of geochemical, geochronological, stable and radiogenic isotope techniques that could be applied to mineral systems and would help constrain both the timing of 'discrete hydrothermal events' and the origin of the hydrothermal fluids responsible for ore formation. The program was designed to be integrated with the three Terrane Projects of the *pmd**CRC which were developing mineral systems frameworks for understanding the context of the range of world class ore deposits that were the focus of the History Program.

Improved age dating of mineral deposits was considered key to advancing our understanding of Australian ore deposits which have historically been difficult to date. Therefore the Mineralising Systems History program encompassed the Re-Os, Pb-Pb and Ar-Ar techniques, which are the geochronological techniques most commonly applied to ore deposits, and ore-related alteration. In addition, combined noble gas and halogen analysis of fluid inclusions, which is an extension of Ar-Ar methodology, was investigated as a new way to trace fluid origins and 'fingerprint' fluids related to mineralisation. Each of these techniques provided the focus of a discrete project within the program, these included:

Project H1 – Re-Os dating of sulphide minerals.

Project H2 – Pb-Pb step-leach dating of ore-related minerals.

Project H4 – Ar-Ar dating of sericite, pyrite and fluid inclusions.

Project H6 – Fluid inclusion noble gas and halogen analysis.

The H1, H2 and H4 projects ran during the first half of the *pmd**CRC, finishing at the end of 2005. The analysis of noble gases and halogens was developed during the final stages of the H4 project in 2005 and was continued into the latter part of the *pmd**CRC as the H6 project. This executive summary precedes the H6 final report and includes a short resume of the main reports generated by each of the component projects. Further information is available in the project final reports or on the *pmd**CRC TWIKI website.

Project Team

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Reid Keays	

H1: Application of Re-Os isotopes to geochronology, ore forming processes and exploration.

Project Leader: Bruce Schaefer

Rhenium and osmium are chalcophile elements that are partitioned from ore fluids into most sulphide minerals during ore deposition. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio can be used to distinguish mantle and crustal Os sources and the radioactive decay of ^{187}Re to ^{187}Os provides the basis for Re-Os age dating.

The H1 project was designed to test common sulphide minerals including chalcopyrite, pyrite and sphalerite as geochronometers. Molybdenite Re-Os ages can provide robust constraints on the age of mineralisation. However, molybdenite is not a common sulphide mineral and because Os is incompatible in molybdenite it does not allow the source of Os to be determined. The H1 project sought to increase the applicability of Re-Os dating to the more ubiquitous sulphide minerals, and because these minerals contain common Os, this had the potential advantage that the source of Os would be constrained.

Samples were collected from the Ernest Henry, George Fisher and the Mt Isa deposits in the Mt Isa Inlier. Sample preparation procedures were developed at Monash University and measurements were made using the TIMS instrument at La Trobe University, and subsequently Macquarie University (Bruce Schaefer). The work encountered two major difficulties: firstly, it was found that commonly Re and Os concentrations of sulphide minerals are so low (ppb to parts per trillion) that it was necessary to analyse large samples and combine mineral separates with whole rock samples. Secondly, the mineral separates and whole rock samples did not define true isochrons, but 'scattered' errorochrons that are difficult to interpret.

For example, the Ernest Henry system preserved a pervasive older, inherited component which did not fully equilibrate with the mineralising assemblage as it was forming. In contrast, apparent ages obtained for the Mt Isa copper deposit and the George Fisher deposit (~1440 Ma) post-date the Isan Orogeny by up to 100 Ma and are much younger than expected for mineralisation. While it is possible that these ages reflect a late onset of mineralisation (Gregory et al., 2004), the similarity of the Re-Os ages, and regional Ar-Ar cooling ages, more likely indicate open system behaviour of Re and Os in sulphide minerals (especially sphalerite and chalcopyrite) to low temperature. Finally, investigation of metabasaltic and doleritic units from the Mt Isa Inlier revealed extensive open system behaviour on a whole rock scale with respect to Re-Os, again probably associated with cooling from the Isan Orogeny to produce ages of ~1450 Ma.

In the course of this study it was found that while Re and Os contents of various mineral phases were highly variable, often in a non-systematic manner, arsenopyrite and magnetite are often the best candidates for geochronological studies since they preserve significant fractionations in Re/Os and are more robust than phases such as pyrite, galena and sphalerite.

In conclusion, the technique proved less reliable than alternative approaches for dating mineralisation and further work is required to fully understand the mobility of Re and Os in common sulphides. Currently it is uncertain if mantle-like $^{187}\text{Os}/^{188}\text{Os}$ ratios obtained for Mt Isa and George Fisher are representative of the Os source during mineralisation.

HI Main Reports

- Gregory M., (2006) Recognising and quantifying fluid flow events around the Mt Isa base-metal deposits, Qld, Australia. PhD thesis Monash University
- Gregory M., Wilde A., Keays R., and Schaefer B., (2004) Preliminary Re-Os dating of the Mt Isa Cu ores, Northwest Queensland. Predictive Mineral Discovery Cooperative Research Centre – Extended abstracts from the June 2004 Conference. Geoscience Australia Record 2004/9. (Eds Barnicoat and Korsch)
- Keays and Schaefer (2004) HI - Application of Re-Os Isotopes to geochronology, ore forming models and exploration models. **pmd**CRC*** poster.

H2: Pb-Pb step-leaching as a possible means of dating mineralisation, metamorphism and deformation in complex terrains

Project Leader: Janet Hergt

Uranium and Thorium are present in trace amounts in common silicate and ore minerals and Pb-Pb ages can be obtained by measurement of the various Pb isotopes produced by radioactive decay of U and Th (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$). The Pb-Pb step-leaching method is advantageous compared to conventional Pb-Pb, or some other 'mineral isochron' approaches of age dating, because it enables an isochron age to be obtained from grains of an individual mineral type. In this regard it is analogous to the Ar-Ar step-heating method, but a different suite of minerals, some of which have higher closure temperatures, can be analysed. In contrast, conventional 'mineral isochrons' require coexisting minerals to have formed in isotopic equilibrium and they are notoriously difficult to apply to ore deposits or complex open systems in metasomatic/metamorphic terranes.

Pb-Pb step-leaching (PbSL) is a digestion technique based on sequential acid treatment of a mineral resulting in the selective recovery of radiogenic and common Pb components from the crystal lattice. This makes it possible to obtain a Pb-Pb age from a single-phase via the generation of 'unmixing' isochrons. Developed originally by R. Frei and colleagues at Bern, it was clearly important to investigate the application of this technique to ore deposits.

The primary goal of the project was to determine how robust the PbSL technique is in dating the growth/ equilibration of specific mineral phases, to establish and refine analytical protocols at the Melbourne University facilities, and improve understanding of when the technique can be applied. The initial focus of the project was on common metamorphic minerals (primarily garnet but also staurolite) in a variety of lithological settings. Samples were collected from the Southern Cross region of Broken Hill, where existing high quality geochronological data were already available, enabling detailed technique evaluation (Tonelli, 2002). This work showed that important metamorphic silicates such as garnet, staurolite and tourmaline, can be successfully dated using PbSL. Furthermore, when these minerals formed at different times the ages can be combined with petrologic observations to constrain the P-T evolution through time.

In the Southern Cross region, garnet in metapelitic rocks provided reliable D1 ages that were not reset by subsequent deformation and metamorphism. In contrast, garnets from amphibolites and the ore-lode horizon, failed to yield age information. These mixed results are believed to reflect the U and Th contents of the garnets which are highest in the metapelites and lowest in the amphibolites. In addition, micro-inclusions (e.g., of monazite) in garnets complicated interpretation of the results. If these inclusions were equilibrated with the garnet, meaningful ages resulted, but if the inclusions were not in equilibrium, the quality of the isochron was degraded. Importantly, 3D visualisation of Pb isotope data, obtained by step-leaching, enables the presence and 'equilibration state' of inclusions to be identified. This enabled filtering of compromised data which would not have been possible by conventional Pb-Pb methods.

The second goal of the study was to test the reliability of PbSL in directly dating common ore minerals including: chalcopyrite, pyrite, pentlandite/pyrrhotite and magnetite. This was theoretically possible because many low-Pb sulfides have surprisingly high U contents (and initial U/Pb ratios). The technique was applied to well-constrained samples from a number of Australian and other mineral deposits covering a range of mineralisation styles (Mount Isa, Copper Blow, Ernest Henry, Osborne, Cadia-Ridgeway, Minnie Moxham and the Bushveld Complex: Bassano, 2007). Unfortunately the apparent ages obtained proved unreliable, having unacceptably large

uncertainties, and being younger than expected in most cases. Detailed examination of the trace element characteristics of the mineral samples indicated the disappointing results are attributed to two factors: first, U- and/or Pb-bearing mineral impurities are common in the matrix of sulphide and oxide minerals. Although uncommon, these inclusions can introduce inherited components giving unusual, anomalously old ages. Secondly, the more typical anomalously young ages, are attributed to open system behaviour of Pb in most sulphide and oxide minerals down to low temperatures (similar behaviour was suggested for Re and Os previously). The anomalously young apparent ages obtained for Australian samples are broadly consistent at ~1.1 Ga, and probably reflect major tectonic reorganisations and magmatism, believed to have occurred at this time. Importantly, this work revealed that even in the rare cases where an ore mineral gave an apparently well-constrained isochron, the apparent age did not reflect the formation event. Thus, caution should be exercised in the interpretation of ore mineral PbSL ages reported in the literature if independent constraints are unavailable. Finally, the technique was applied to metasomatic tourmaline in the Western Fold Belt of the Mt Isa Inlier (Duncan et al., 2006; Bassano, 2007). This work confirmed that robust PbSL ages can be obtained for silicate minerals, and together with new U-Pb zircon ages, they have redefined the age of peak metamorphism in the Western Fold Belt (Duncan et al., 2006). Peak metamorphism is now correlated throughout the Mt Isa Inlier and is indicated to have occurred at ~1595-1560 Ma.

H2 Main Reports and publications

- Tonelli M., (2002) An evaluation of Pb step leaching geochronology as applied to high grade metamorphic terranes PhD thesis Melbourne University
- Bassano K., (2007) A feasibility study of the application of the Pb-Pb isotope step-leaching technique to ore minerals. PhD thesis Melbourne University
- Duncan et al., (2006) Geochronological constraints on tourmaline formation in the Western Fold Belt of the Mount Isa Inlier, Australia: evidence for large-scale metamorphism at 1.57 Ga? *Precambrian Research* 146, 120–137.

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

Project Leader: David Phillips

The Ar-Ar dating method is based on the radioactive decay of ^{40}K to ^{40}Ar and the common occurrence of K alteration around ore deposits makes it applicable to constraining many types of ore-related alteration. The H4 project was focused on improving age constraints in low-grade orogenic gold systems of the Yilgarn Terrane in Western Australia and in the Tasmanides of Victoria. The key achievements of the H4 project were the establishment of $^{40}\text{Ar}/^{39}\text{Ar}$ methods to date mica-bearing pyrite grains, an improved interpretive framework for fine-grained sericite samples which are prone to Ar-loss during later overprinting events, and the development of analytical methods for fluid inclusion noble gas and halogen analysis (see H6).

Laser fusion of mica in pyrite combined with stepped heating of sericite samples provided a new chronological framework for Au-deposits at Stawell in Victoria and Mt Charlotte plus Kanowna Belle in Western Australia. Mica-in-pyrite ages for Stawell are ~440 Ma, compared to matrix-mica ages of ~400 Ma. Similarly, mica in pyrite ages for Mt Charlotte and Kanowna Belle are within error of the preferred mineralisation ages (~2.6–2.63 Ga), and are older than matrix mica ages of <2.5 Ga. These data indicate combined mica-in-pyrite and matrix-mica (sericite) Ar-Ar ages can provide information on both the age of mineralisation and constrain the duration of retrograde alteration in low-grade gold deposits.

Furthermore, detailed evaluation of matrix-mica age spectrum plots from samples with known age provided a new framework for identifying when these ages have been affected by ^{39}Ar -recoil or ^{40}Ar -loss. These artifacts are the two biggest problems that limit the application of sericite geochronology to constraining the timing of mineralisation. Therefore identifying the significance of these artifacts in the literature is an essential step to refining terrane scale age correlations and developing regional models.

Finally, detailed evaluation of fluid inclusion Ar-Ar ages indicated they do not provide a reliable means of dating Precambrian ore deposits. However, a new methodology for investigating the Ar, Kr, Xe, Cl, Br and I composition of complex fluid inclusion assemblages was proven on Mt Isa samples. Combined noble gas and halogen analysis

has proven a valuable technique for understanding fluid origins and was developed further in the H6 project.

H4 Main Reports and publications

- Phillips D., (2002-2005), H4 Final report: $^{40}\text{Ar}/^{39}\text{Ar}$ dating of mineralisation metamorphism and deformation. five chapters/papers, including:
 - Phillips and Miller (2006) $^{40}\text{Ar}/^{39}\text{Ar}$ dating of mica from thermally overprinted Archaean gold deposits, *Geology* 34, 397-400.
 - Kendrick et al., (2006) Part I. Decrepitation and degassing behaviour of quartz up to 1560 C: Analysis of noble gases and halogens in complex fluid inclusions assemblages. *Geochimica et Cosmochimica Acta* 70, 2540-2561.
 - Kendrick et al., (2006) Part II: Evaluation of $^{40}\text{Ar}/^{39}\text{Ar}$ quartz ages: Implications for fluid inclusion retentivity and determination of initial $^{40}\text{Ar}/^{36}\text{Ar}$ values in Proterozoic samples. *Geochimica et Cosmochimica Acta* 70, 2562-2576.

H6: Development of methods for measuring noble gases and halogens in fluid inclusions and applications for tracing fluid source

Project Coordinator: Mark A Kendrick

The noble gas and halogen composition of fluid inclusions can provide new information on the origin of ore fluids. The noble gases and halogens have isotopic/elemental compositions that vary by orders of magnitude between the crust, mantle and hydrosphere and are less prone to resetting by wall-rock interaction than stable isotopes. The H4 and H6 projects established a noble gas and halogen analytical facility that would otherwise have been unavailable to industry and researchers in Australia. The results from this facility have had major impact on our understanding of fluid processes in two important mineral districts within Australia and the techniques developed have been proven as valuable tests for deposit/exploration models.

Fluid origins have been investigated in 'Isa-Style' copper deposits and iron-oxide-copper-gold deposits of the Mt Isa Inlier, including Mt Isa, Ernest Henry, Osborne, Eloise,

Starra and Lightening Creek. In addition, regional alteration in the Mary Kathleen Fold Belt and the Cloncurry District was investigated to test its relationship to IOCG mineralisation and several breccia prospects in the Wernecke Mountains of Canada were investigated as an analogue to the Isan IOCG.

In contrast to previous interpretations based on stable isotope data, this work has demonstrated the involvement of upper-crustal sedimentary formation waters in all of the ore deposits studied and that fluid interaction with halite (or scapolite) was an important source of salinity for IOCG fluids. In addition, deeply-derived metamorphic fluids were closely associated with Cu mineralisation at Mt Isa and magmatic fluids were involved in several of the IOCG deposits. However, the data suggest regional granitoids are more important as heat engines that drive fluid convection than as sources of mineralising fluids. This data has contributed to a new deposit model that emphasises the importance of wall-rock interaction.

In the final part of the project, the technique was applied to orogenic-gold mineralisation in the St Ives Gold Camp. Preliminary analyses appear to confirm that mixing between mantle-derived methane and magmatic SO₂ could be a trigger for mineralisation in gold-only ore

deposits (Neumayr et al., 2007). However, further work is required for unambiguous validation.

H6 Main Reports and publications

- Kendrick M.A., (2006-2008) H6 Final report: Combined noble gas and halogen analysis of fluid inclusions: eight appendices/papers (this volume) including:
 - Kendrick et al. (2008) Noble gas and halogen constraints on regionally extensive mid-crustal Na-Ca metasomatism, the Proterozoic Eastern Mt Isa Block, Australia: Precambrian Research, in press.
 - Fisher and Kendrick (2008) Metamorphic Fluid Origins in the Osborne Fe oxide-Cu-Au deposit, Australia: Evidence from noble gases and halogens: Mineralium Deposita, in press.
 - Kendrick et al., (2007) Mid-crustal Fluid Mixing in a Proterozoic Fe oxide-Cu-Au deposit: Evidence from Ar, Kr, Xe, Cl, Br, I, Ernest Henry, Australia.: Earth and Planetary Science Letters 256, 328-343.
 - Kendrick et al. (2006) Noble gas and halogen constraints on mineralizing fluids of metamorphic versus surficial origin: Mt Isa, Australia: Chemical Geology 235, 325-351.

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Development of methods for measuring noble gases and halogens in fluid inclusions and applications for tracing fluid source

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Acknowledgements

The large amount of work undertaken in the H6 project was made possible by collaborations with the Fluids F3, Isa I7 and Yilgam Y4 projects.

The key collaborators include David Phillips, Geordie Mark, Tim Baker, Pat Williams, Nick Oliver, John Walshe, Rob Duncan, Louise Fisher, Bin Fu, Dave Gillen, Klaus Petersen and Masahiko Honda. Stanislav Szczepanski is thanked for technical assistance in the noble gas laboratory throughout the project.

**DEVELOPMENT
OF METHODS
FOR MEASURING
NOBLE GASES
AND HALOGENS
IN FLUID
INCLUSIONS AND
APPLICATIONS
FOR TRACING
FLUID SOURCE**

Project team: Mark A. Kendrick and David Phillips

I. Introduction

The H6 project further developed infrastructure and methods for the analysis of noble gases and halogens in fluid inclusions (Fig 1). The project has had significant impact on our understanding of Australian ore deposits and this report aims to provide an overview of the key findings. The project work has resulted in several publications that describe the work in much greater detail and these are included in appendices B and C.

The H6 project was conceived because the noble gases and halogens can provide new information on the origin of ore fluids that are essential to the development of new deposit models. In particular, the noble gases and halogens are complementary to stable isotopes but have some advantages because they are less susceptible to resetting during wall-rock alteration and they have far more variable compositions (Table 1).

The main halogen and noble gas parameters (there are more than 20 noble gas isotopes) used to distinguish different fluid types are summarised in Table 1. The $^{40}\text{Ar}/^{36}\text{Ar}$ value is a key parameter which varies by more than an order of magnitude between >30,000 in deeply-derived magmatic or metamorphic fluids, to as little as 300–2000 in upper crustal sedimentary formation waters. Neon and He isotope ratios enable mantle components to be distinguished, and the halogen Br/Cl and I/Cl values constrain fluid evolution and acquisition of salinity. Additional background information is provided in the introduction to each of the appendices.

The H6 project encompassed three main areas of work. These included:

- i) application and continued development of combined Ar, Kr, Xe, Cl, Br and I analysis of ore deposit fluid inclusions;
- ii) evaluation and testing of He and Ne isotope applications in Proterozoic samples; and
- iii) investigations of scapolite to develop halogen monitors for improved halogen analysis, and better understanding of possible halogen fractionation in the mid-crust.

The first part of this report focuses on Mt Isa and Iron Oxide Copper Gold (IOCG) deposits, and is divided into two sections based on the first two areas of work. The next section involves analyses of scapolite and is largely developmental, with only indirect application to Mt Isa. The final section is focused on orogenic gold mineralisation in the Yilgarn Terrane.



Fig 1. The fluid inclusion dedicated noble gas mass spectrometer at the University of Melbourne, established by the **pmd***CRC, is one of only two such facilities world-wide capable of simultaneous noble gas and halogen analysis. This instrument provides a new way to distinguish ore fluids (see table 1).

Table I. Noble gas and halogen parameters used to distinguish different fluid types

	ASW		Formation Waters		Meteoric Fluids		Magmatic Fluids	
	Meteoric	Seawater	Bittern Brine	Halite Diss.	Meta-sed (Corella)	Basement-derived	A-type related	Mantle-derived
Argon								
$^{40}\text{Ar}/^{36}\text{Ar}$	300		< 2000		< 2000	> 30,000	> 30,000	40,000
^{36}Ar ppb	1.7-2.7	1.3-2.1	~3-100		~1-20	<3	~3-12	0.1
$^{40}\text{ArE}/\text{Cl}$			~ 10^{-5} - 10^{-6}		~ 10^{-5} - 10^{-6}	~ 10^{-3} - 10^{-4}	~ 10^{-3} - 10^{-4}	~ 10^{-3} - 10^{-4}
Neon and Helium								
$^{20}\text{Ne}/^{22}\text{Ne}$	9.8		9.8 to ~8		<9.8	<9.8	<9.8	12.5
$^{21}\text{Ne}/^{22}\text{Ne}$	0.029		0.029-0.09		>0.029	>0.029	>0.029	>0.029
$^3\text{He}/^4\text{He}$ (Ra)	1		0.05		0.05	0.05	0.05	8
Mixed								
$^4\text{He}^*/^{40}\text{Ar}^*$	--	--	5.7-40		5.7	5.7	5.7	2.0
$^4\text{He}^*/^{21}\text{Ne}^*$	--	--	17-200 $\times 10^6$		17.1 $\times 10^6$	17.1 $\times 10^6$	17.1 $\times 10^6$	
$^{84}\text{Kr}/^{36}\text{Ar}$	2.0		1.8			1-2		
Halogens and salinity								
Br/Cl ($\times 10^{-3}$)	-	1.5	1.5-11	0.1- 0.3	0.1- 0.3	0.1 - 30	1-2	1-2
I/Cl ($\times 10^{-6}$)	-	0.8	~10-1000	0.5 - 2?	0.5 - 2	0.5 – 500?	10-80	10-80
NaCl Wt%	~0	3.5	~30	30-70	<70	5-20	<70	5-30

Nb – all ratios are molar. ASW = air-saturated water (includes meteoric and seawater). Metamorphic volatilisation fluids have compositions determined by the source rock. 1Ra = 1.4×10^6 = the atmospheric $^3\text{He}/^4\text{He}$ value.

2. Application and continued development of combined Ar, Kr, Xe, Cl, Br, I analysis to ore deposit fluid inclusions
(Appendices B1 to B4):

Mt Isa Copper (Kendrick et al., 2006)

The world class Mt Isa copper deposit (Fig 2) was studied to allow a better understanding of both the ore deposit and the noble gas technique. Different techniques for extracting noble gases from two-phase fluid inclusions, including in vacuo crushing and stepped heating, were evaluated. This approach enabled a more detailed comparison of results with previously published noble gas studies than would otherwise have been possible.

In addition, equations and new methods for graphical presentation of noble gas data, including $^{40}\text{Ar}/^{36}\text{Ar}$ versus ^{36}Ar plots (Fig 3), were developed. These plots allowed the identification of mixing between basement-derived metamorphic volatilisation fluids, that are most closely associated with copper mineralisation in quartz fluid inclusions, and sedimentary formation waters that dominate in dolomite fluid inclusions (Fig 3).

Ernest Henry (Kendrick et al., 2007)

Ernest Henry is the largest IOCG deposit within the Mt Isa Inlier. Fluid inclusions in this deposit have $^{40}\text{Ar}/^{36}\text{Ar}$ values of up to 30,000 (Fig 4), which provides strong isotopic evidence for the involvement of magmatic fluids. The involvement of magmatic fluids has been

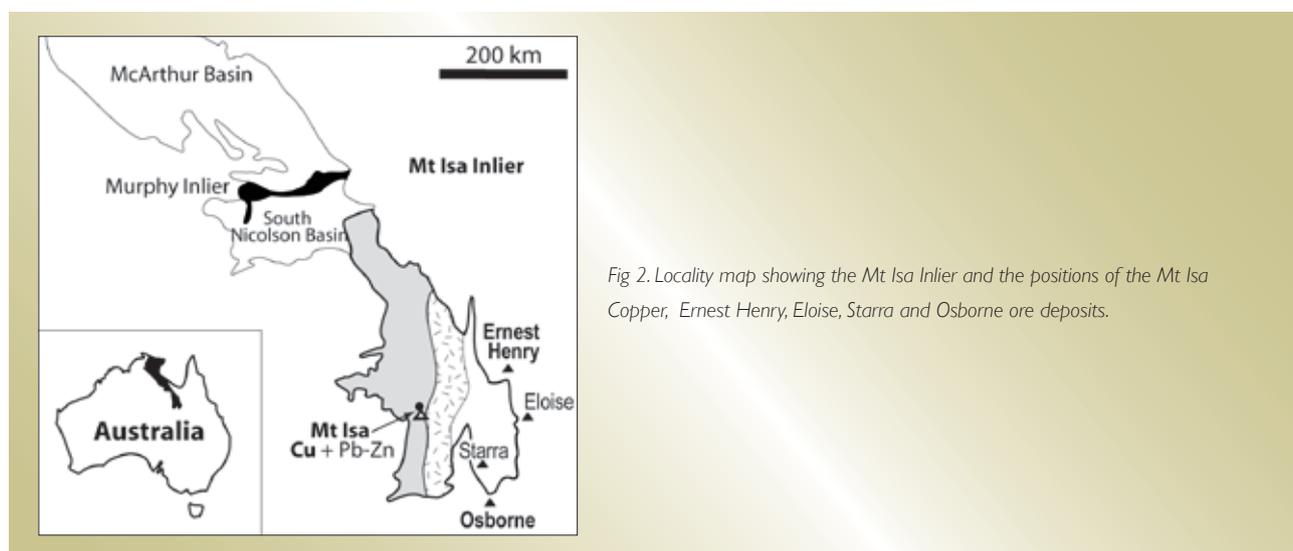


Fig 2. Locality map showing the Mt Isa Inlier and the positions of the Mt Isa Copper, Ernest Henry, Eloise, Starra and Osborne ore deposits.

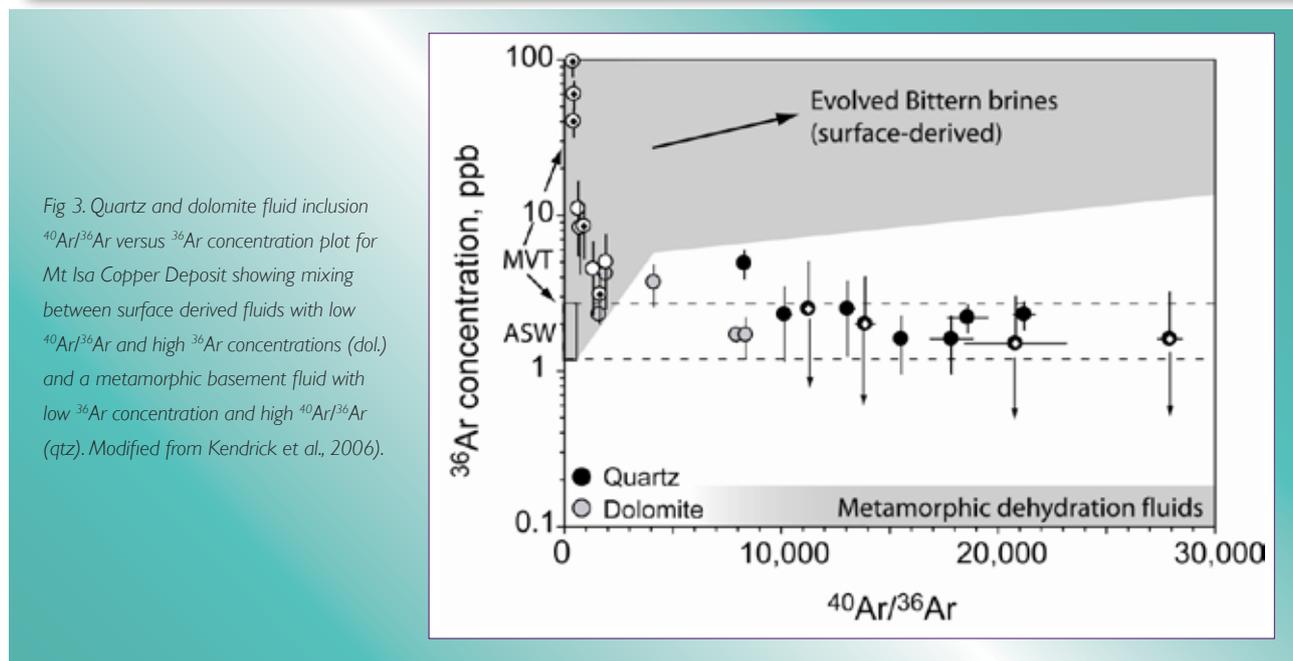


Fig 3. Quartz and dolomite fluid inclusion $^{40}\text{Ar}/^{36}\text{Ar}$ versus ^{36}Ar concentration plot for Mt Isa Copper Deposit showing mixing between surface derived fluids with low $^{40}\text{Ar}/^{36}\text{Ar}$ and high ^{36}Ar concentrations (dol.) and a metamorphic basement fluid with low ^{36}Ar concentration and high $^{40}\text{Ar}/^{36}\text{Ar}$ (qtz). Modified from Kendrick et al., 2006).

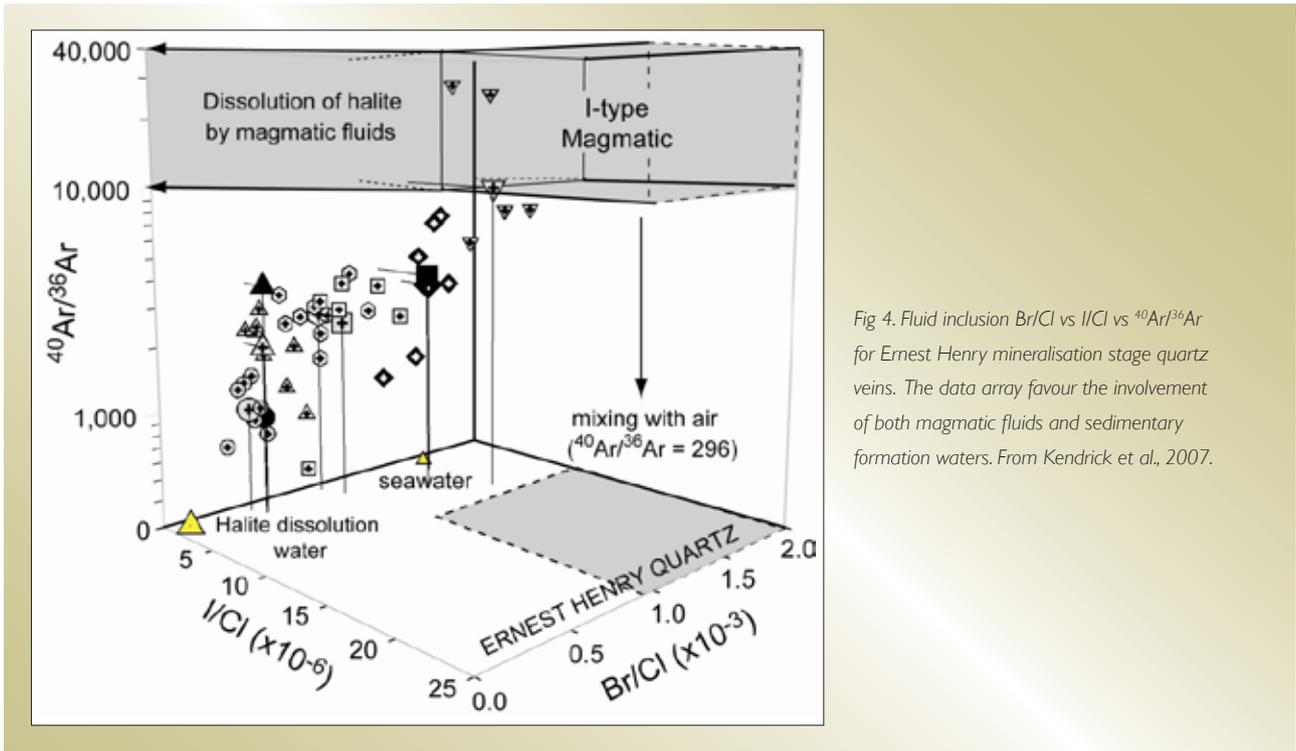


Fig 4. Fluid inclusion Br/Cl vs I/Cl vs $^{40}\text{Ar}/^{36}\text{Ar}$ for Ernest Henry mineralisation stage quartz veins. The data array favour the involvement of both magmatic fluids and sedimentary formation waters. From Kendrick et al., 2007.

suggested previously, on the basis of textural interpretations and stable isotope data. The involvement of magmatic fluids is compatible with the 1525 Ma U-Pb titanite ages for mineralisation that suggest synchronicity with the 15 km distant Mt Margaret granite (Mark et al., 2006a; Mark et al., 2006b).

In contrast to stable isotopes, the noble gas and halogen data are characterised by variability (Fig 4) and cannot be

explained by the exclusive involvement of magmatic fluids. Instead, the variable signatures are most easily explained by mixing between magmatic fluids and halite dissolution sedimentary formation waters. The heterogeneity of the noble gases and halogens reveals a level of complexity that was previously unrealised. The involvement of at least two distinct fluids could have been overlooked previously because magmatic fluids and sedimentary formation waters have very similar stable isotope compositions (Mark et al.,

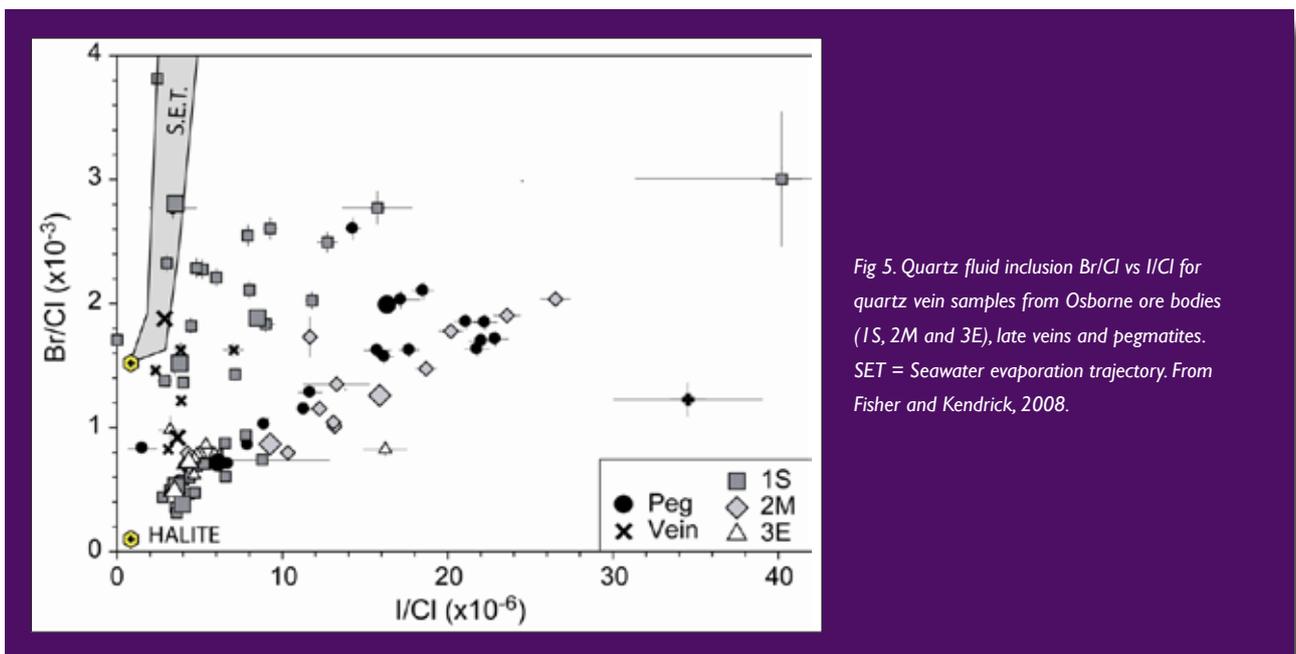


Fig 5. Quartz fluid inclusion Br/Cl vs I/Cl for quartz vein samples from Osborne ore bodies (1S, 2M and 3E), late veins and pegmatites. SET = Seawater evaporation trajectory. From Fisher and Kendrick, 2008.

2006a). This study illustrates the importance of applying multiple techniques to ore deposits and demonstrates that halite or scapolite dissolution was an important source of chlorine in IOCG ore fluids.

Osborne (Fisher and Kendrick, 2008)

The Osborne deposit is the second largest IOCG deposit in the Mt Isa Inlier and was selected as an analogue to Ernest Henry. In contrast to Ernest Henry, the preferred mineralisation age is a peak-metamorphic (~1595 Ma), and much of the Fe oxide was present in the host rock prior to Cu-Au mineralisation. The maximum $^{40}\text{Ar}/^{36}\text{Ar}$ value determined for Osborne fluid inclusions was ~2200. This is an order of magnitude lower than determined for Ernest Henry fluid inclusions and favours the involvement of sedimentary formation waters and locally derived metamorphic fluids only. The noble gases suggest basement-derived magmatic fluids were not involved in the Osborne IOCG deposit.

Therefore, the peak metamorphic timing of mineralisation and the noble gas data both suggest that the abundant CO_2 fluid inclusions trapped in this deposit are more likely to represent metamorphic fluids derived from the Corella Fm. than a mantle-derived magmatic fluid component. The

halogen composition of fluid inclusions is extremely variable radiating from values close to the composition of halite (Fig 5). Therefore, as for Ernest Henry, evaporites are indicated as an important source of salinity.

Eloise, Starra and Lightning Creek

Samples from the Eloise and Starra IOCG deposits were collected to test if their fluid inclusion noble gas and halogen composition were similar to fluid inclusions in the syn-magmatic Ernest Henry deposit or the syn-metamorphic Osborne deposit. Samples were collected from breccias at Lightning Creek because it was considered this area was dominated by magmatic fluid processes and the analyses would allow the magmatic signature identified at Ernest Henry to be more tightly constrained.

Fluid inclusion microthermometry showed most of the samples from Eloise and Starra were typical of IOCG fluid inclusion assemblages, comprising a mixture of variably saline aqueous and carbonic fluid inclusions. However, one sample from Eloise was dominated by a unusually high abundance of CO_2 fluid inclusions. Surprisingly, the samples from Lightning Creek were all dominated by low salinity secondary liquid-vapour fluid inclusions that are not usually linked to magmatism.

Table 2. Summary of maximum $^{40}\text{Ar}/^{36}\text{Ar}$ values in Cloncurry District Deposits

Deposit	Age (Ma)	Max $^{40}\text{Ar}/^{36}\text{Ar}$	Interpretation/significance
Ernest Henry	~1530	29,000	Syn-magmatic deposit with large magmatic component
Osborne	1595	2200	Syn-metamorphic deposit lacking a magmatic component
Eloise	~1530 ?	4500	A minor CO_2 -rich component with possible magmatic origin supports late-Isan age or late-Isan reworking
Starra	~1530 ?	3300	Slightly elevated $^{40}\text{Ar}/^{36}\text{Ar}$ arguably indicates the presence of a very minor magmatic component
Lightning Creek	~1530 ?	1500	Secondary fluid inclusions provide evidence for non-magmatic fluid flow through high permeability hydrothermal breccias

Reference values

Mantle	40,000
Sed fm. Water	<2000
Meteoric	300

Age refs in (Mark et al., 2006a)

The spread in Br/Cl and I/Cl values were similar for samples from all localities and Ernest Henry/Osborne. These data reflect fluid interaction with evaporites (scapolite or halite) rather than the fluid source. Fluid inclusions in Starra and Eloise samples had $^{40}\text{Ar}/^{36}\text{Ar}$ values intermediate of Osborne and Ernest Henry (Table 2). The maximum $^{40}\text{Ar}/^{36}\text{Ar}$ value of ~3300 at Starra and 4500 at Eloise favours a dominant fluid origin from sedimentary formation waters but does not preclude a minor magmatic component. Further work is required to constrain the timing of mineralisation in these deposits (cf. Mark et al., 2006a) and (Oliver et al., 2008). However, the highest $^{40}\text{Ar}/^{36}\text{Ar}$ value of 4500 determined for Eloise was on the sample dominated by CO_2 fluid inclusions, suggesting the possible involvement of a CO_2 -rich magmatic fluid. If this is the case, late-Isan syn-magmatic mineralisation would be favoured. Further work, including Ne isotope analysis will clarify the origin of CO_2 fluid inclusions at Eloise.

The low salinity fluid inclusions in the Lightning Creek

samples had $^{40}\text{Ar}/^{36}\text{Ar}$ values of 300-1500. These low values do not favour a relationship to A-type magmatism. The presence of these non-magmatic fluid inclusions in a hydrothermal breccia could indicate that after formation, the magmatic-hydrothermal breccias, became high permeability pathways for non-magmatic fluids.

Regional albitisation; Mary Kathleen and Cloncurry Districts (Kendrick et al., 2008)

Na-Ca alteration (albitisation) is common throughout the Eastern Fold Belt but is concentrated along the Pilgrim and Mt Dore Fault Zones (Fig 6). Several lines of evidence suggest that regional Na-Ca alteration and IOCG mineralisation are related, including: the overlapping timing of much of the alteration and mineralisation at ~1530 Ma; and the argument that constituents characteristic of ore assemblages, including K and Fe, were scavenged from Na-Ca altered rocks (Oliver et al., 2004); and the similarity of mixed aqueous-carbonic fluid inclusion assemblages in IOCG deposits and regional alteration (Fig 7).

This study evaluated the ability of the noble gases and halogens, as conservative fluid tracers, to test if Na-Ca alteration fluids in the Cloncurry District and Mary Kathleen Fold Belt had similar origins to ore related fluids in the Cloncurry District. The data demonstrate independent fluid origins for Na-Ca alteration in the Mary Kathleen Fold Belt and Cloncurry Districts, but support a genetic relationship between ~1530 Ma Na-Ca alteration and IOCG mineralisation in the Cloncurry District.

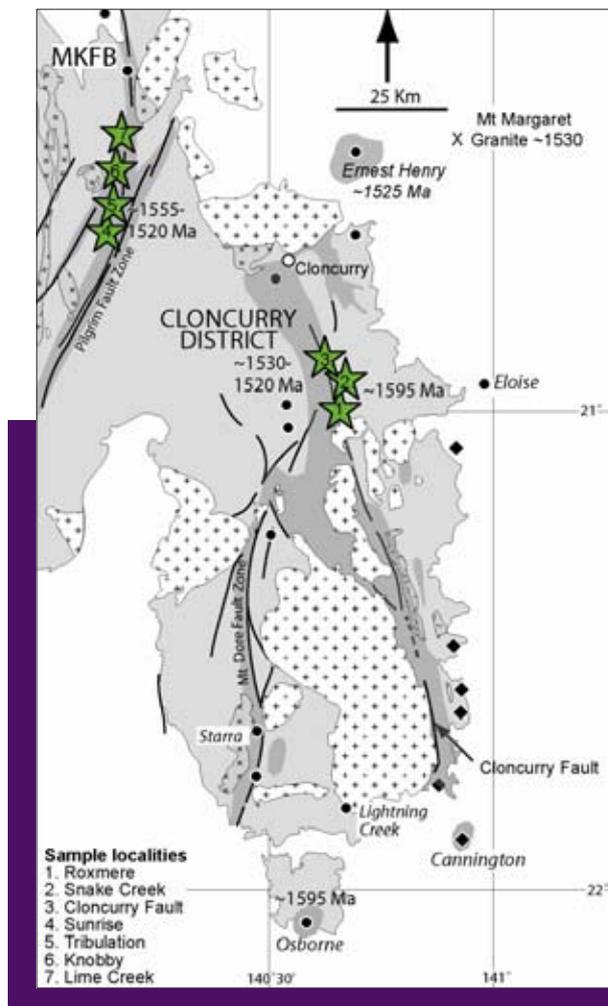


Fig 6. Schematic map showing areas of intense Na-Ca alteration concentrated along faults in the Eastern Fold Belt. Based on maps in (Mark et al., 2004; Oliver, 1995).

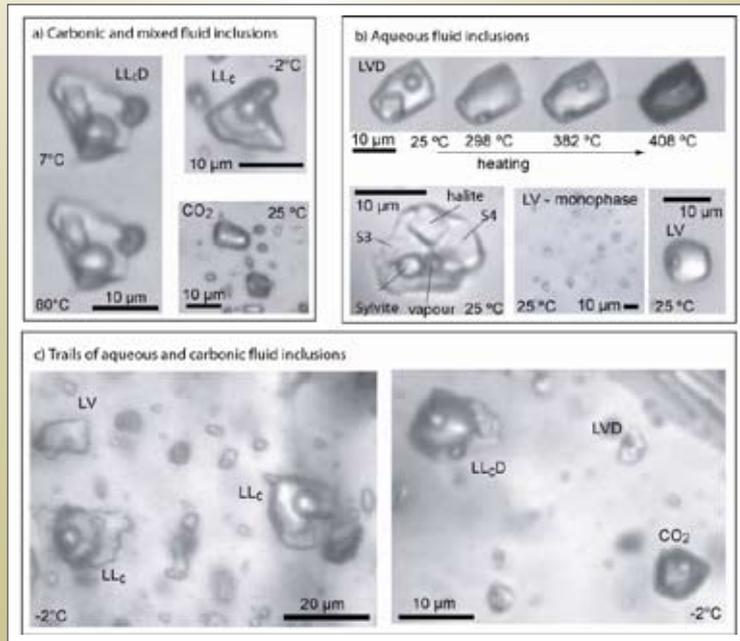
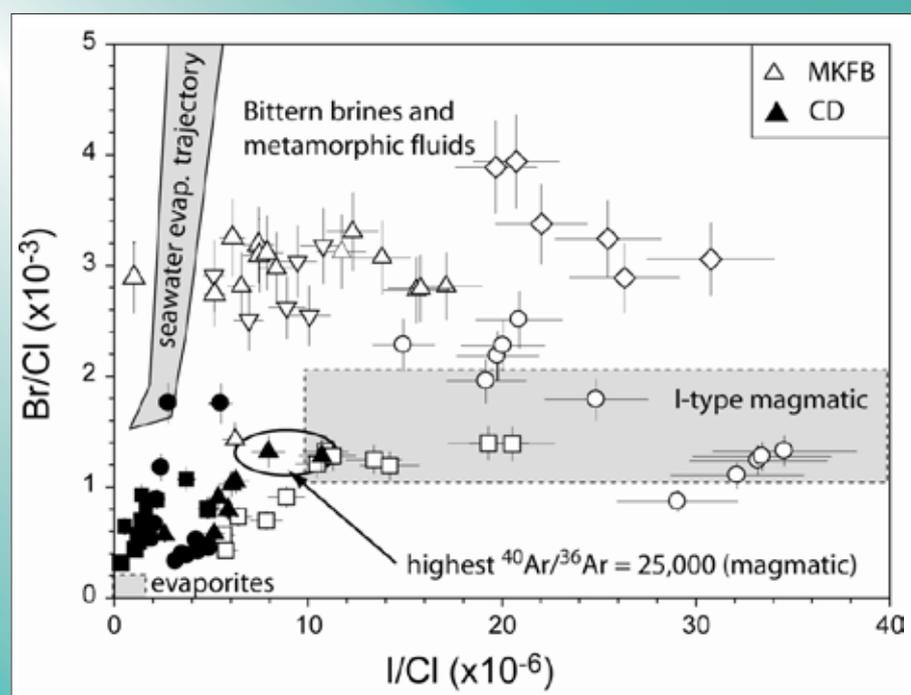


Fig 7. Quartz fluid inclusions in regional alteration include the same types seen in IOCG ore deposits: aqueous fluid inclusions with variable salinity including ultra-saline varieties with up to 4 or 5 daughter minerals, liquid CO₂ fluid inclusions and mixed aqueous-carbonic fluid inclusions. From Kendrick et al., 2008.

In the Cloncurry District, magmatic fluids with ⁴⁰Ar/³⁶Ar of ~25,000 were measured in Na-Ca alteration in the Snake Creek Anticline, which is interpreted to be related to intrusion of the nearby Saxby Granite at 1530 Ma. Elsewhere, fluids with ⁴⁰Ar/³⁶Ar of <2700 are dominated by sedimentary formation waters. These fluids have variable Br/Cl and I/Cl values consistent with fluid interaction with halite or scapolite (Fig 8).

The noble gas data suggest that Na-Ca alteration fluids in the Mary Kathleen Fold Belt were also dominated by sedimentary formation waters. However, these fluids have higher Br/Cl values than fluids in the Cloncurry District (Fig 8). The origin of CO₂ fluid inclusions, which dominate samples collected in the Knobby Quarry (up to 80%), is discussed in the light of Ne isotope data below. However, the CO₂ fluid inclusions analysed

Fig 8. Quartz fluid inclusion Br/Cl vs I/Cl for regional alteration fluid inclusions. The Cloncurry District (CD) encompasses a similar range of compositions as in Ernest Henry but is distinct to the Mary Kathleen Fold Belt (MKFB). Modified from Kendrick et al., 2008).



here had $^{40}\text{Ar}/^{36}\text{Ar}$ values of <7000. These values are lower than expected for mantle-derived CO_2 (MORB = 40,000), suggesting that, as in the Osborne IOCG deposit, the Corella Formation must have been a significant source of metamorphic CO_2 .

3. Ne and He isotope applications to Proterozoic samples: Tracing the mantle component (Appendices C1 and C2)

The origin of CO_2 in the Mary Kathleen Fold Belt

Late-Isan (~1530 Ma) Na-Ca alteration in the Mary Kathleen Fold Belt is associated with H_2O and CO_2 fluid inclusions (Fig 7). Previous Ar isotope analyses suggest sedimentary formation waters are the dominant source of H_2O -dominated fluids (Appendix B4). However, stable isotope data suggest a mantle-magmatic CO_2 source (Oliver et al., 1993).

In order to investigate these different ideas and because noble gases (Ne and He) can provide definitive and independent evidence for a mantle component, combined Ne and Ar isotope analyses were targeted on two distinct fluid inclusion assemblages. Samples from the Knobby Quarry are dominated by CO_2 fluid inclusions whereas samples from Tribulation Quarry are dominated by H_2O fluid inclusions (Figs 6 and 7).

Figure 9 confirms these different fluid inclusion assemblages had different origins. H_2O -dominated

fluid inclusions define a trend between the atmosphere and a crustal component with $^{40}\text{Ar}/^{36}\text{Ar}$ of between 300 and 2000, and $^{20}\text{Ne}/^{22}\text{Ne}$ of between 9.8 and 8.4 (Fig 9). This trend is typical for sedimentary formation waters. In contrast, the $^{20}\text{Ne}/^{22}\text{Ne}$ values are positively correlated with the $^{40}\text{Ar}/^{36}\text{Ar}$ values for analyses of CO_2 -rich fluid inclusions. These fluid inclusions define a trend between a mixed crust-atmosphere end-member with $^{40}\text{Ar}/^{36}\text{Ar}$ of ~1000 and $^{20}\text{Ne}/^{22}\text{Ne}$ of 8.7, that is representative of (meta)-sedimentary rocks, and a mantle end-member with $^{40}\text{Ar}/^{36}\text{Ar}$ of 40,000 and $^{20}\text{Ne}/^{22}\text{Ne}$ of 12.5 (Fig 9).

Based on mixing between CO_2 derived from the Corella Formation (^{36}Ar concentration of 1-10 ppb; (Kendrick et al., 2008) and CO_2 derived from the mantle with a much lower ^{36}Ar concentration of 0.1-1 ppb, the highest $^{40}\text{Ar}/^{36}\text{Ar}$ value of 14,100 represents a mantle CO_2 component of ~84%. This value is in very good agreement with that obtained from stable isotopes (Oliver et al., 1993) and provides independent evidence for the involvement of mantle-derived CO_2 during the late-Isan alteration. In contrast, analyses with lower $^{40}\text{Ar}/^{36}\text{Ar}$ values indicate a greater proportion of crustally-derived CO_2 compatible with some input from the host-rocks.

The Wernecke IOCG breccia prospect analogue (Kendrick et al., in review)

The ~1595 Ma Wernecke breccias in the Yukon Territory of Canada were studied as an analogue for IOCG deposits in the Mt Isa Inlier. The Wernecke IOCG

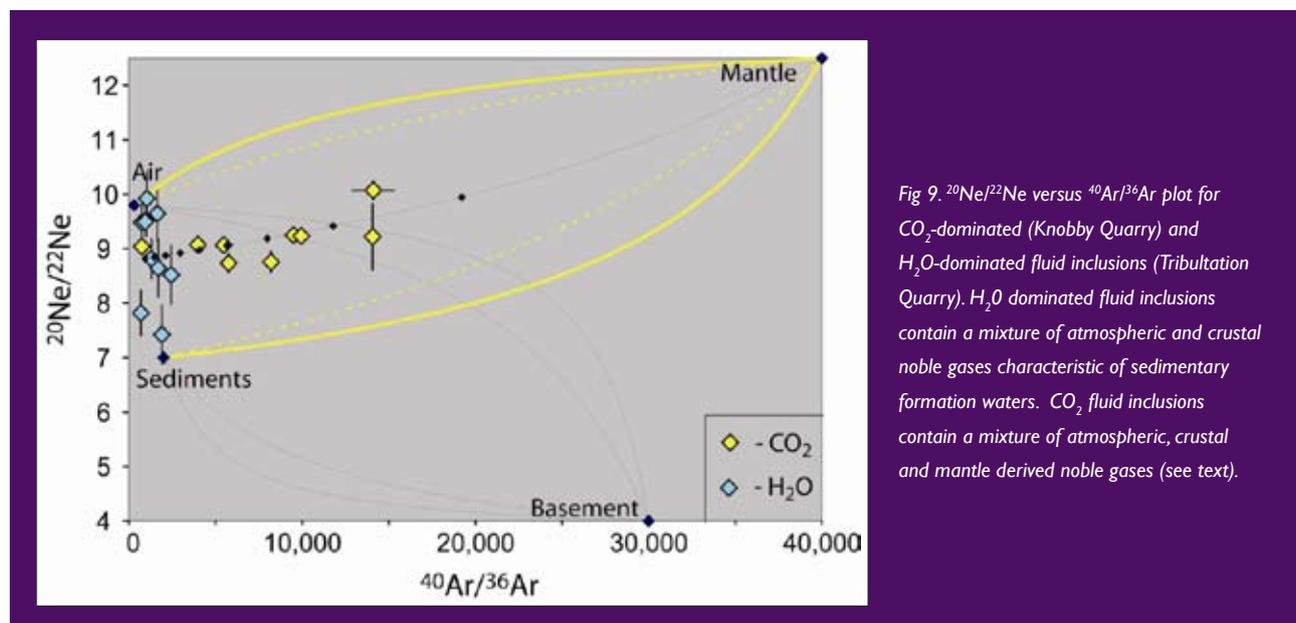


Fig 9. $^{20}\text{Ne}/^{22}\text{Ne}$ versus $^{40}\text{Ar}/^{36}\text{Ar}$ plot for CO_2 -dominated (Knobby Quarry) and H_2O -dominated fluid inclusions (Tribulation Quarry). H_2O dominated fluid inclusions contain a mixture of atmospheric and crustal noble gases characteristic of sedimentary formation waters. CO_2 fluid inclusions contain a mixture of atmospheric, crustal and mantle derived noble gases (see text).

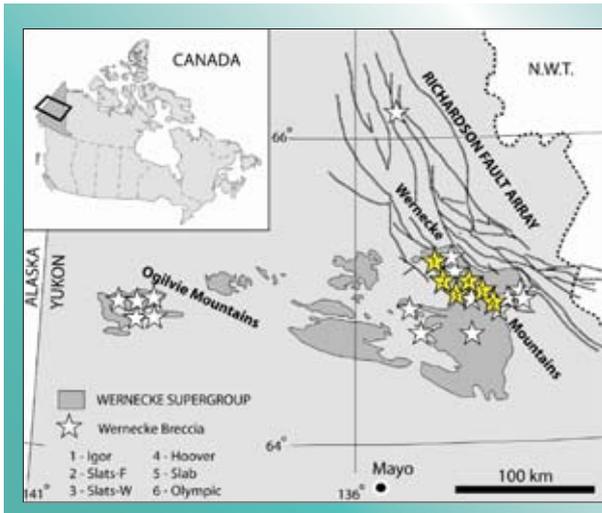


Fig 10. Map of the Yukon Territory showing the Wernecke Breccia Prospects close to the Richardson Fault Array.

deposits are hosted by greenschist facies rocks and are not associated with granitic intrusions (Fig 10).

Initial work with Ar, Kr, Xe, Cl, Br and I demonstrated a very similar range of compositions as seen in the Mt Isa

IOCG deposits. Fractionated halogen signatures favour fluid interaction with halite (Fig 11), compatible with the preservation of meta-evaporitic scapolite in strata close to the largest prospect with the highest salinity fluid inclusions.

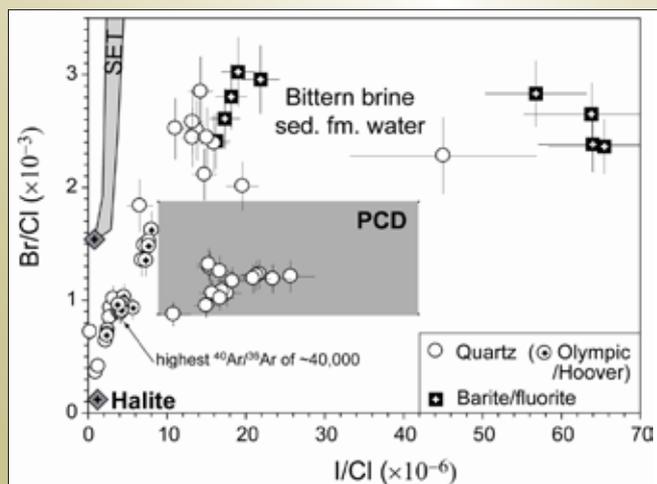


Fig 11. Quartz, barite and fluorite fluid inclusion Br/Cl vs I/Cl for Wernecke IOCG prospects. The correlation between Br and I can be explained by fluid interaction with halite.

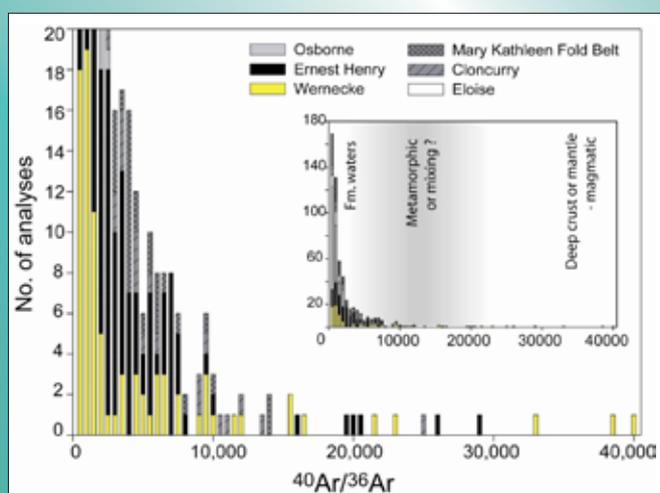


Fig 12. Quartz fluid inclusion $^{40}\text{Ar}/^{36}\text{Ar}$ data for Wernecke and Isan IOCG deposits are extremely variable suggesting the involvement of sedimentary formation water and magmatic fluids.

The Ar data favour mixed fluid origins from sedimentary formation waters and basement-fluids of either metamorphic or magmatic origin. The basement fluids are characterised by maximum $^{40}\text{Ar}/^{36}\text{Ar}$ values of 40,000 (Fig 12).

Unlike the Mt Isa Inlier a source for magmatic fluids is unknown in the Wernecke Mountains (Fig 10). Therefore, He and Ne isotope analyses were undertaken to test if a mantle component related to juvenile magmatism was present. The fluid inclusion $^3\text{He}/^4\text{He}$ values of <0.02 are close to production ratios in the lower crust (Table 1) and fluid inclusion $^{20}\text{Ne}/^{22}\text{Ne}$ values are less than the atmospheric value of 9.8 (Fig 13). These data suggest a crustal origin for the breccia fluids.

However, IOCG deposits are U-rich meaning radiogenic ingrowth of $^4\text{He}^*$ or nucleogenic ingrowth of $^{22}\text{Ne}^*$ could have altered the initial $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ values. In order to test the robustness of our conclusion based on the measured $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ values, we investigated the U concentration of the samples studied and the release of noble gases from a mineral matrices during in vacuo crushing (see section 4 on scapolite). We demonstrated that neither the $^3\text{He}/^4\text{He}$ nor $^{20}\text{Ne}/^{22}\text{Ne}$ value is correlated with the U concentration in the Wernecke samples, and we quantified the slow release of noble gas from a mineral matrix during in vacuo crushing. This enabled a contribution from matrix derived noble gases to be ruled out and as a result, the noble gas compositions measured by in vacuo crushing are shown to be close to the initial values of the fluid inclusions.

The Wernecke study has had two major outcomes:

- i) it has shown that combined He and Ne isotope analysis can be successfully applied to Proterozoic sulphide samples; and
- ii) together with the Isan data, it has provided an unprecedented understanding of IOCG related fluids.

The fluids involved in IOCG mineralisation in the Wernecke Mountains appear very similar to those in the Ernest Henry ore deposit, interaction with scapolite (or halite) has been an important source of salinity. However, an unexpected finding, considering the lack of exposed intrusions (Fig 10), is that a magmatic component is probably also present.

Summary of IOCG fluid sources: Isa and Wernecke

The new information on IOCG fluid sources, obtained from noble gas and halogen studies in Mt Isa's Eastern Fold Belt and the Wernecke Mountains, confirm that fluid interaction with evaporites has been a major process (Barton and Johnson, 1996). Magmatic fluids are present in some of the ore deposits and in some areas of barren alteration within the Eastern Fold Belt. This suggests magmatic fluids are not a critical ingredient for mineralisation: they are not always present and when they are mineralisation does not always follow. Osborne is the best example of an IOCG deposit in which both the age and noble gas data favour a 'non-magmatic' metamorphic origin.

Fluids with a sedimentary formation water origin are

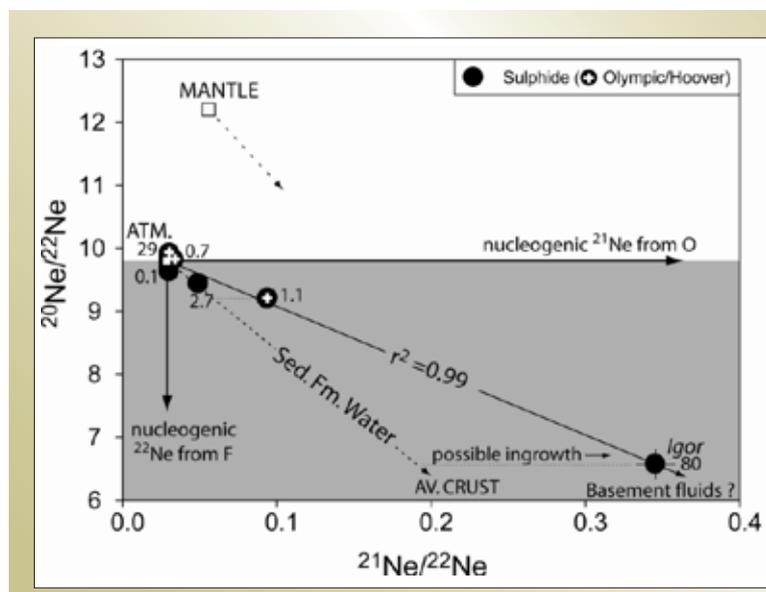


Fig 13. Ne isotope plot for sulphide fluid inclusions, Wernecke, Canada. The data define a trend for basement-fluids.

dominant throughout the Eastern Fold Belt and are present in the Wernecke Mountains. Therefore, the similar timing of many ore deposits and magmatism in the Eastern Fold Belt (and Wernecke?) probably reflects the initiation of regional fluid convection driven by batholithic heat. Magmatic fluids became entrained in these convective cells and are preserved in places. CO₂ was derived from both mafic intrusions (e.g. Knobby and Eloise?) and devolatilisation of the host rocks and/or underlying strata (e.g. Osborne).

The mixed fluid origins and demonstrated importance of wall-rock interaction suggest that Cu and other ore constituents were acquired by wall-rock leaching. This is compatible with the spatial association of mafic intrusions and ore deposits in the Mt Isa Inlier (Oliver et al., 2008), Sm-Nd evidence for metal sources in the Olympic Dam deposit (Johnson and McCulloch, 1995), and the world-wide correlation of wall-rock plus deposit U concentration (Hitzman and Valenta, 2005).

This work suggests that the major exploration vectors are:

- i) regional permeability enhancing structures (e.g. the Cloncurry Fault);
- ii) the presence of mafic intrusions (e.g. leachable source rocks); and
- iii) the presence of meta-evaporites which enhance salinity, increasing the transport capacity of regional fluids. Outcropping granites (or mantle CO₂) provide evidence for a heat engine to drive fluid convection, but mineralisation can occur without them, e.g. Osborne.

4. Investigations of scapolite as a halogen monitor and its influence on halogen fractionation in the mid-crust (Appendix C3)

Scapolite is an abundant mineral in the Eastern Fold Belt of the Mt Isa Inlier where it replaced evaporite minerals in the meta-evaporitic Corella Formation and also formed during metasomatic alteration. Scapolite can contain up to 3.8 wt % Cl and is suggested to have a Br/Cl partition coefficient of one (Pan and Dong, 2003).

The Br/Cl and I/Cl composition of scapolite is of interest for several reasons. Firstly, if gem quality scapolites have uniform Br/Cl and I/Cl compositions they could be used to refine our measurements. Secondly, if scapolite preserves the low Br/Cl and I/Cl values of halite, it is possible the fractionated Br/Cl and I/Cl values reported for all the IOCG deposits studied above (Figs 4, 5, 8 and 10), could have arisen by scapolite breakdown, rather than halite dissolution. Thirdly, measuring the extent of Br/Cl and I/Cl variation in scapolite provides a means to determine the extent of Br/Cl and I/Cl fractionation in metamorphic fluids and during metamorphic processes.

Analysis of scapolite

Work was undertaken to test if the extended Ar-Ar methodology could be applied to measure the Br/Cl and I/Cl values of the scapolite matrix. Initially this was attempted by step-heating; however, two major problems were encountered: firstly scapolite is so rich in Cl that it was difficult to obtain crystals small enough that

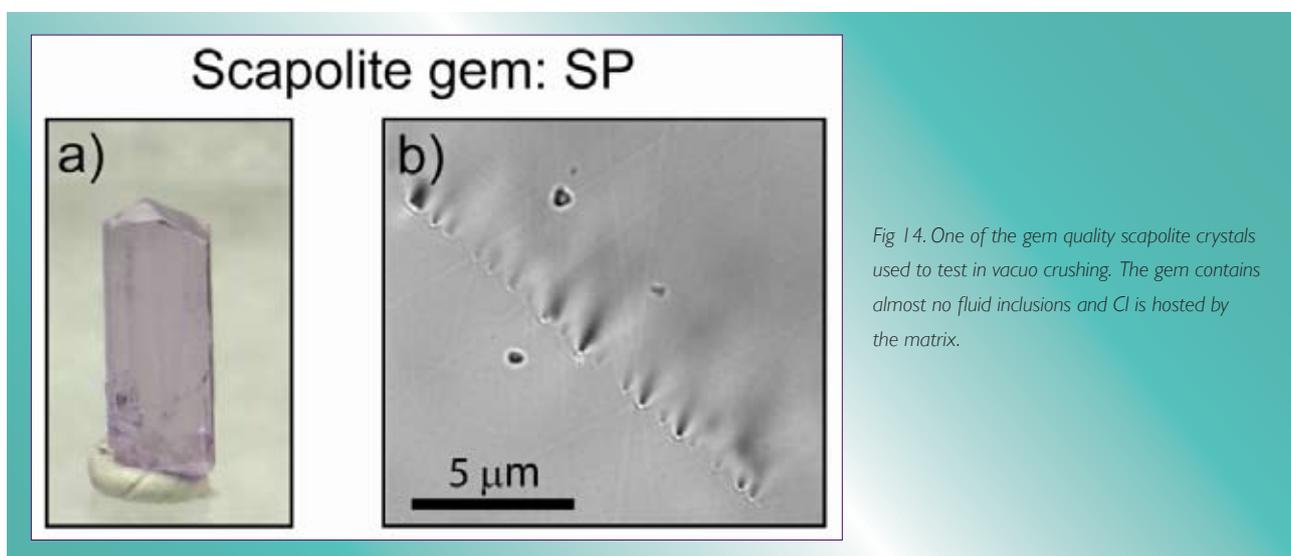


Fig 14. One of the gem quality scapolite crystals used to test *in vacuo* crushing. The gem contains almost no fluid inclusions and Cl is hosted by the matrix.

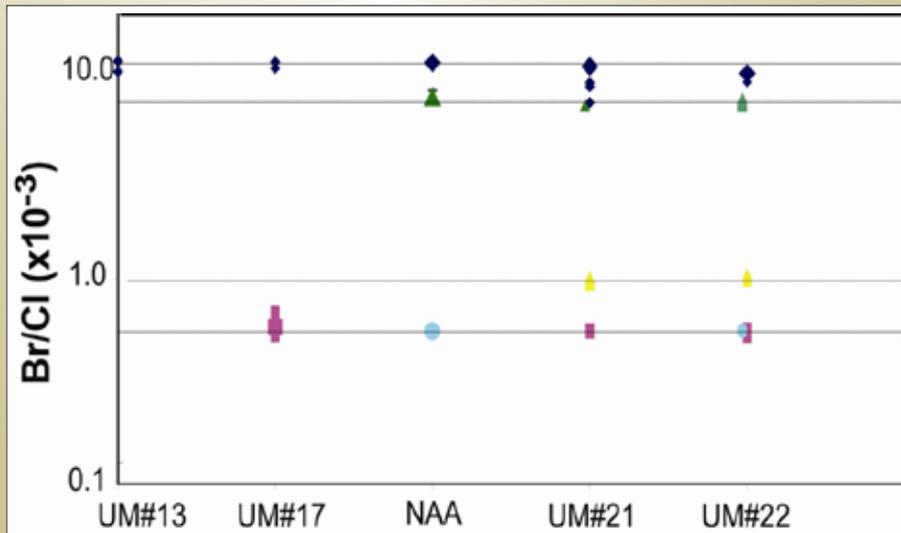


Fig 15. The Br/Cl values of four scapolite crystals (SY – blue diamonds; BB1 – green triangles; BB2 – blue circles; SP – pink squares) determined in four irradiations are within uncertainty of each other and independent analyses by neutron activation analysis (NAA).

measurements remained on scale; and secondly, it was found that scapolite is unstable during step-heating and melts completely at temperatures of <1200 °C. Fractionation of the noble gas proxies within molten scapolite, made Br/Cl and I/Cl determination impossible by step-heating.

In order to overcome these problems an attempt was made to extract noble gases from the scapolite matrix by in vacuo crushing. This was undertaken using the air actuated in vacuo crushing device used in He and Ne isotope analysis. This experiment demonstrated that prolonged in vacuo crushing can quantitatively extract noble gases from the mineral matrix but gases are extracted very gradually.

Two important implications of this finding are: in vacuo crushing can be used to analyse scapolite Br/Cl and I/Cl values; and, by quantifying the rate of noble gas extraction, we can preclude the involvement of matrix derived noble gases when a fluid inclusion bearing sample is crushed fewer than 1000 times. Deconvolution of fluid inclusion and matrix derived Ne proved essential in interpretation of the Wernecke data (Section 3).

Scapolite as a Br/Cl and I/Cl standard

Four gem quality crystals of scapolite were examined in detail by microscopy, electron microprobe and combined noble gas plus halogen analysis. The scapolite crystals were broken up and 3-50 mg of the different crystals were included in four independent irradiations. The irradiations

were carefully monitored with two meteorite standards allowing precise determination of halogen ratios and propagation of uncertainty.

In addition, 800-1000 mg of the same crystals were analysed by instrumental neutron activation analysis (NAA). This was undertaken to provide an independent measurement of Br/Cl and test the reproducibility of halogen values in several irradiations. The results show Br/Cl values determined by the two techniques are in good agreement (Fig 15) and that scapolite gems have reproducible Br/Cl values.

Based on the best measurements for each sample, the scapolites have Br/Cl values that are reproducible to 4 % (2σ). Therefore scapolite crystals can be used as monitors and because they are easier to analyse than the meteorite standards, they will enable improved accuracy in Br/Cl and I/Cl measurements.

Br/Cl and I/Cl fractionation in the mid-crust

In addition to the four scapolite gems developed as irradiation monitors (above) a further eight scapolite crystals were obtained from museum collections and field locations in the Mt Isa Inlier to enable the composition of scapolite to be investigated in a broad range of metamorphic environments including the Grenville Province of Canada, Norway, Pakistan, Tanzania and the Mt Isa Inlier.

Scapolite is shown to have an extremely variable Br/Cl and I/Cl composition (Fig 16). The lowest Br/Cl and I/Cl values of $\sim 0.5 \times 10^{-3}$ and 2×10^{-6} , respectively, are close to but slightly above those of halite (or halite dissolution water fluid inclusions; Figs 16). The highest Br/Cl and I/Cl values were determined in a Cl-poor Grenville scapolite.

The spread in scapolite Br/Cl and I/Cl is even greater than that observed in crustal fluids formed by the evaporation of seawater or dissolution of halite (Fig 16). The high Br/Cl and I/Cl values determined for Mt Isa scapolite indicate that scapolite could not have been the source of salinity for fluids with low Br/Cl and I/Cl values, if scapolite has a Br/Cl partition coefficient of one (Pan and Dong, 2003). However, the highest Br/Cl value measured in Cl-poor scapolite is not representative of a typical crustal fluid, suggesting Br could have a higher affinity for scapolite than Cl (cf. Pan and Dong, 2003). If this is the case fluid interaction with Mt Isa scapolite could yield a high salinity fluid with low Br/Cl, as observed (Fig 16). Further work is required to test if the Br/Cl partition coefficient is related to the composition of scapolite.

5. Application of combined Ar, Kr, Xe, Cl, Br, I and He-Ne isotope analysis to Archaean orogenic gold deposits (Appendix C4)

The St Ives Gold Camp, WA

Six quartz, albite and carbonate samples were selected to encompass oxidised (pyrite) and reduced (pyrrhotite) styles of alteration in the St Ives Gold Camp. Work by Klaus Petersen has demonstrated that pyrrhotite-bearing quartz is dominated by high-purity methane fluid inclusions, whereas CO₂ and H₂O fluid inclusions are associated with pyrite-bearing veins (Petersen et al., 2007). These different fluid inclusion assemblages were analysed for noble gases to test the 'Walshe Model' for gold mineralisation outlined by Neumayr et al. (2007). In this model CH₄ fluid inclusions are predicted to have a mantle-origin and noble gas signature (see the Y4 report for model details).

Combined Ar and Cl analyses indicate that CH₄ fluid inclusions have high Cl/³⁶Ar values compatible with the presence of HCl gas (Fig 17). Furthermore, the highest ⁴⁰Ar/³⁶Ar value of $\sim 48,000$ (Fig 17) is compatible with a mantle origin for CH₄ if noble gases have been recycled into the mantle since the Archaean (Holland and Ballentine, 2006).

The noble gas composition of the CH₄ cannot be easily explained by the localised reduction of CO₂; however, the high ⁴⁰Ar/³⁶Ar values could reflect a deep-crustal rather than mantle CH₄ source. Importantly, CH₄ is inferred to have had an independent origin to CO₂ in either the mantle or deep-crust. Two factors favour the mantle:

- i) deeply-derived CH₄ is produced during the serpentinisation of ultramafic rocks (Sachan et al., 2007), and
- ii) from a global perspective noble gases provide evidence for the involvement of mantle-volatiles in gold mineralisation (Graupner et al., 2006; Mao et al., 2003).

Definitive evidence?

Helium and Ne isotope analyses have been undertaken on sulphide samples associated with Au mineralisation from the Finiston Lodes and Revenge mines, in the Eastern Goldfields, to further test the deep-crust versus mantle CH₄ source.

To date He isotope analyses suggest a crustal source. However, the preliminary Ne isotope analyses (3 samples) are compatible with a small mantle component. The discrepancy between He and Ne isotopes could be explained by the very small atomic size of He that could have preferentially leaked from (or into) the fluid inclusions over time. Alternatively, the Ne isotope analyses were affected by an unusually large blank component and may have been unrepresentative of the fluid composition. Subsequent analyses on a different set of three larger sulphide samples, in which the blank component was minimised, indicate a purely crustal origin. However, because it is not possible to see fluid inclusions in sulphide minerals using conventional microscopy it is not known if the fluid inclusions analysed contained significant CH₄.

In order to fully evaluate the source of methane it will be necessary to measure the noble gas composition of pure CH₄ fluid inclusions. Suitable samples are available and have already been analysed for Ar (Fig 17). However, He and Ne analyses have been limited by the low retentivity of He in quartz fluid inclusions, and the difficulty of 'cleaning' CH₄ samples to a high enough purity for Ne isotope analysis. Ne isotope analysis has proven more demanding than Ar isotope analysis,

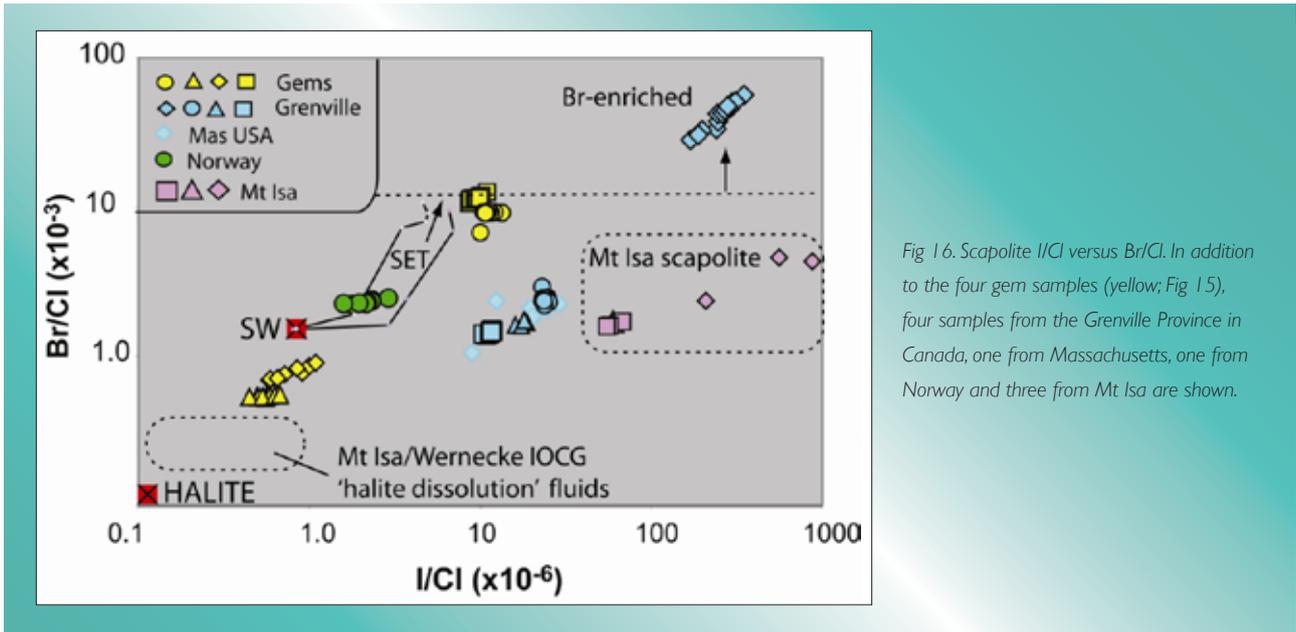


Fig 16. Scapolite I/Cl versus Br/Cl. In addition to the four gem samples (yellow; Fig 15), four samples from the Grenville Province in Canada, one from Massachusetts, one from Norway and three from Mt Isa are shown.

meaning modifications to the extraction line are required to enhance the purification process. At such a time that line up grades have been completed, the analyses of CH₄ bearing samples will be extended to other gold

fields including the 1.8 Ga Tanami Goldfields, for which CH₄-dominated samples are also available. These analyses will ultimately provide a definitive test for the CH₄-related 'Walshe model' of gold mineralisation.

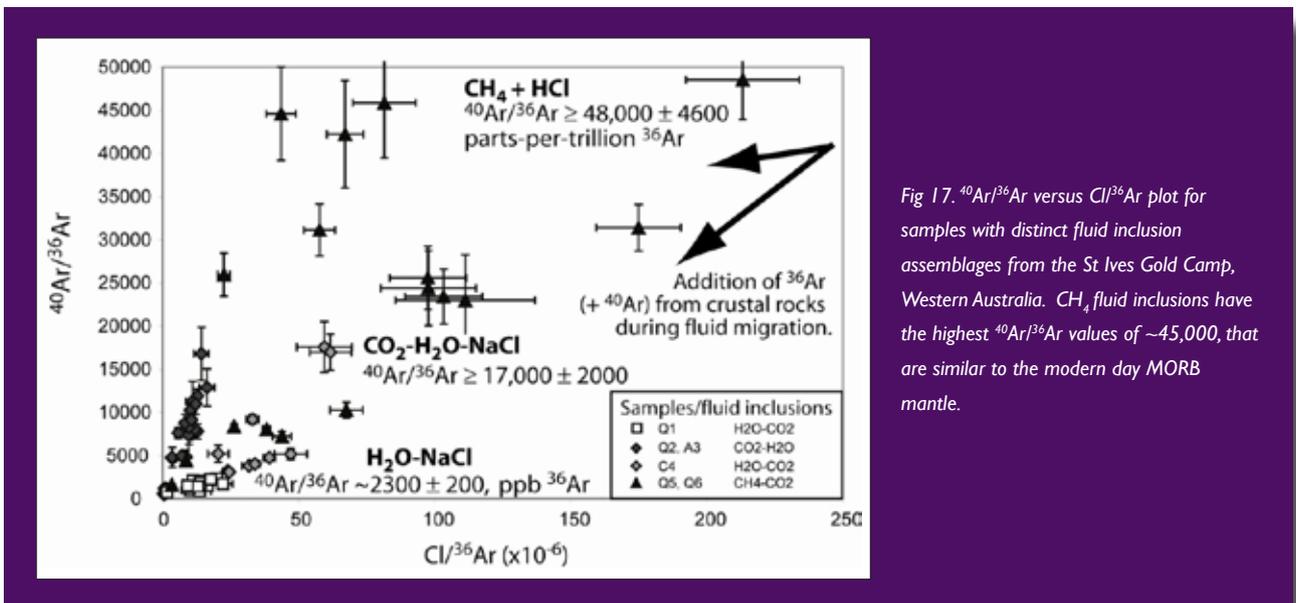


Fig 17. ⁴⁰Ar/³⁶Ar versus Cl/³⁶Ar plot for samples with distinct fluid inclusion assemblages from the St Ives Gold Camp, Western Australia. CH₄ fluid inclusions have the highest ⁴⁰Ar/³⁶Ar values of ~45,000, that are similar to the modern day MORB mantle.

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