Global links between gold and mantle degassing of ^{40}Ar plus methane: A 2.65 Ga case study.

M.A. Kendrick[1], J.L. Walshe[2], K.J. Petersen[3]

1 – The School of Earth Sciences, The University of Melbourne, Australia.
2 – CSIRO, ARRC, 35 Stirling Highway, Kensington, WA 6151, Australia
3 – School of Earth and Geographical Sciences, M006, The University of Western Australia, WA 6009, Australia

The processes that mobilise and transport gold through the Earth's crust have been widely debated [1-4]. Most workers emphasise the importance of CO_2-H_2O-NaCl fluids, but the nature of fluid interaction remains controversial, with either fluid mixing or unmixing considered possible triggers for gold deposition [1-9]. CH_4 fluid inclusions are also documented[2, 5, 8, 10, 11], and have a high abundance in some veins within the 2.65 Ga, St Ives Gold Camp, Australia[9, 12, 13].

Here we show CH_4 trapped in fluid inclusions at St Ives has a probable origin from the Earth's mantle. A mantle source for methane is compatible with the variable redox state of the Earth's mantle[14] and is released during serpentinisation of ultramafic rocks [15, 16]. Its presence in the continental crust confirms mantle metasomatism could contribute to the variable redox state of Archaean cratons[14]. We present a new model that links the periodicity of gold mineralisation[1, 2] to mantle depletion events recently proposed during the same time periods at ~3.3, ~2.7, ~1.9 and ~0.4 Ga [17].

A key observation in the 2.65 Ga St Ives Gold Camp[10] is that gold mineralisation is hosted by both oxidised and reduced sulphides and preferentially occupies the boundary between two km-scale alteration zones with different redox state[9, 13]: i) oxidised pyrite-magnetite-hematite-anhydrite bearing veins with δ^{34}S of 0 to -8 ‰ and albite ± phengite ± biotite ± epidote alteration are centred on intrusive complexes; flanked by ii) reduced pyrrhotite-pyrite bearing veins with higher δ^{34}S of up to +5 ‰, and muscovite ± paragonite ± chlorite ± amphibole ± biotite alteration [9, 13]. Carbonate veins in both zones have δ^{13}C values between -3 and -9 ‰ clustering around mantle values of -5 ‰ [13].

Sampling targeted drill holes in different parts of the alteration system. The selected samples contain mixed assemblages of CH_4-CO_2-H_2O-NaCl fluid inclusions, that are broadly related to the oxidation state of the veins mineralogy (Table 1). The oxidising part of the system is dominated by CO_2-H_2O-NaCl fluid inclusions (Table 1), similar to those emphasised in all previous models for gold mineralisation [1-7, 10]. Microthermometric measurements indicate CO_2 has a high purity with ice melting points in the range -56.6 to -57.8 ℃, close to the CO_2 triple point. These inclusions homogenise between +12 and +31 ℃ into either the liquid or gaseous state. The majority of aqueous fluid inclusions have salinities of 5 to <26 wt % salt (Tm = -5 to -21.9 ℃) and some have a Ca-rich composition indicated from eutectic points as low as -52 ℃. Mixed aqueous-carbonic fluid inclusions, with variable fractions of CO_2-fill, that indicate trapping in the two phase field, have clathrate melting temperatures of +3.8 to +8.2 ℃ equivalent to ~4-11 wt % NaCl eq.. Samples from the 'reduced' part of the system are dominated by non-polar fluid inclusions that are demonstrably related to sulphide

deposition and exhibit no phase change during cooling to -180 ºC (supplementary information). Laser raman indicates as many as ~80-90 % of these fluid inclusions contain pure CH_4 but some contain up to 20 mol % N_2 or 50 mol % CO_2 (Table 1 [12]).

Mineral separates (30-100 mg) of six samples were irradiated and the fluid inclusions were analysed simultaneously for Cl, Br, I and the isotopes of Ar using extended Ar-Ar methodology[18, 19]. K and Ca were determined for Ar interference corrections and all samples are corrected for minor (<2%) ingrowth of ^{40}Ar since 2.65 Ga (see supplementary information). The noble gas isotopes were extracted from fluid inclusions by sequential stepped heating or *in vacuo* crushing experiments: each sample exhibits considerable variation in age-corrected $^{40}Ar/^{36}Ar$, Br/Cl and I/Cl, indicating that different populations of fluid inclusion have been decrepitated at different stages of the experiment (Figs 1).

The distinct $^{40}Ar/^{36}Ar$ values determined for samples with different alteration assemblages, and dominated by different types of fluid inclusion (Table 1), are extremely significant. Isotopes of Ar are not fractionated during phase separation [20], meaning the variation in $^{40}Ar/^{36}Ar$ (fig 1) cannot be explained by either unmixing, or variably reducing, a homogenous CO_2-H_2O parent fluid. Instead the data are consistent with three fluid end-members[13] (Figs 1 and 2; Table 1): i) H_2O-NaCl-dominated fluid inclusions with minor CO_2 have the lowest $^{40}Ar/^{36}Ar$ values of ~700-2300 and 1-10 ppb ^{36}Ar (Table 1; fig 1). These fluids are interpreted to represent 'ambient' fluids of the mid-crust that could be products of metamorphic volatilisation [3] or mixtures of metamorphic and surface-derived fluids. ii) CO_2-H_2O-NaCl fluid inclusions in oxidised veins spatially associated with intrusions imaged by seismic, or oxidised-felsic porphyrys exposed in the mine area [9, 13], have $^{40}Ar/^{36}Ar$ values of ≥17,000, a mean ^{36}Ar concentration of ~0.1-5 ppb (Figs 1; Table 1). These data are consistent with a magmatic fluid origin [18, 19] and the presence of anhydrite suggests a high SO_2 activity (Table 1). iii) CH_4 fluid inclusions in reduced veins have the highest $^{40}Ar/^{36}Ar$ values of up to ~48,000 and contain parts-per-trillion ^{36}Ar (Table 1; fig 1). The high $^{40}Ar/^{36}Ar$ values are similar to the modern day convecting mantle [21-23] and would not be acquired during reduction of CO_2 with lower $^{40}Ar/^{36}Ar$ and higher ^{36}Ar content (Table 1): wall-rock interaction would further increase the fluids ^{36}Ar content (Fig 1). An origin from natural gases in a sedimentary basin, or by cracking of higher hydrocarbons, is not favoured because CH_4 in these environments is typified by $^{40}Ar/^{36}Ar$ of <2000 and parts-per-million ^{36}Ar [24]. The most likely source of high purity CH_4 that is consistent with the Ar data (Table 1), and basement setting of gold mineralisation, is the mantle [14-16, 20]. It is now widely recognized that CH_4 is released during serpentinisation of ultramafic mantle-rocks [14-16]. The high $Cl/^{36}Ar$ values determined for the CH_4 fluid inclusions suggests they could contain HCl gas (fig 1).

Gold has a high solubility in reduced S-bearing fluids[4] and liquid hydrocarbons [27], suggesting CH_4 dominated fluids at St Ives could have been important for transporting gold. The following generic reaction illustrates a possible depositional mechanism:

$$[CH_4 + AuHS + HCl(g)]_{mantle-fluid} + [H_2O + CO_2 + SO_2]_{magmatic-fluid}$$
$$= [CO_2 + H_2O + HCl(aq)]_{fluids} + H_2S + Au \pm C \qquad (1)$$

Depending on the availability of reactants, the oxidation of bisulfide complexes and methane could result in deposition of gold, sulphide and carbon [11]. The localisation of gold in both pyrite and pyrrhotite is evidence for deposition close to the reaction front, explaining the variation in sulphur isotope signatures, and the acid solutions generated may account for the km-scale alteration haloes[9, 13].

Methane-bearing fluid inclusion assemblages have been reported for other gold deposits [2, 5, 8, 10, 11]. However, the apparent rarity of CH_4 could be because it is oxidised at the point of gold deposition producing CO_2-H_2O dominated fluid inclusions similar to those

commonly reported (reaction 1). Although unproven, a link between mantle-derived methane and mineralisation in other gold deposits maybe supported by: i) the similar timing of recently recognised mantle depletion events at ~3.3, ~2.7, ~1.9 and ~0.4 Ga [17] and the periodicity of gold mineralisation [1, 2, 28]; ii) the primitive [187]Os/[188]Os signatures determined for remobilised/placer gold in the Witwatersrand [28]; iii) the correlation between the largest gold deposits and the thinnest sub-continental lithosphere [29]; iv) the presence of mantle-derived noble gases in Asian gold deposits [5-7]; and v) the common occurrence of carbon in gold-only ore deposits[11] (reaction 1). If gold is transported by methane, the fact that gold-rich areas such as the Colorado Plateau host CO_2 gas traps with mantle-derived noble gases [21], could imply efficient oxidation of CH_4 in the mid-lower crust, where gold mineralisation is usually observed [1, 2] (Fig 2). Alternatively, if gold was transported by the SO_2-rich magmatic fluid, mantle-methane is suggested as a critical reductant. The global scale of the mineralisation processes, suggested by the proposed link to mantle-methane, can explain why it has not been possible to correlate gold-only ore deposits with a single tectonic setting [1, 2]. Furthermore, 'igneous-related', 'orogenic' and 'carlin' varieties could all have formed by similar depositional processes (Fig 3).

The ^{40}Ar/^{36}Ar value suggested for mantle-methane related to 2.65 Ga gold-mineralisation at St Ives (fig 1), is similar to the modern day mantle value of 40,000-50,000 [21-23]. This implies efficient post-Archaean subduction of Ar, which is also suggested by non-radiogenic noble gas isotope ratios of the mantle [30]. If similar CH_4-dominated samples can be located in other gold deposits, determining the isotopic composition of all the noble gases and halogens, in gold deposits of different age (~2.7, ~1.9, ~0.4 Ga and younger), will provide important constraints on mantle geochemistry. These constraints will influence our understanding of the geodynamic processes that drive planet Earth.

Table 1: Sample description and fluid inclusion $^{40}Ar/^{36}Ar$ values

No.	Drill hole/depth	Mineral	H_2O-NaCl	CO_2-H_2O-NaCl	CO_2	CO_2-CH_4	CH_4	Age-corrected $^{40}Ar/^{36}Ar$	$[^{36}Ar]$
*Oxidised veins containing magnetite-pyrite and anhydrite*									
Q1	LD7113A/329m	Quartz	60-80%	~20%	5-10%			700-2300	
Q2	LD7113A/136m	Quartz	0-5%	50-60%	30-40%			1000-11,000	
A3	LD7113A/136m	Albite	5-10%	5-10%	~90%			4000-16,000	
*Oxidised carbonate, chalcopyrite bearing vein with epidote alteration*									
C4	CD7114/141m	Carb.	80%	20%				3000-18,000	
*Reduced veins containing pyrrhotite*									
Q5	CD2949/70m	Quartz	<2%	<10%	>30%	60%		17,000-48,000	
Q6	CD2949/389m	Quartz	<2%			10%	80-90%	1500-44,000	

The drill holes are located in the Revenge (LD7113A) and Conquerer (CD2949) pits in the St Ives Gold Camp in the Yilgarn Terrane of Western Australia [9]. The age corrected $^{40}Ar/^{36}Ar$ age values are only 2% lower than the measured values (supplementary information).
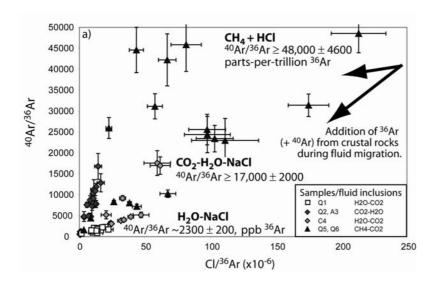
Fig 1 (Kendrick et al., 2008)

Fig 1. Fluid inclusion age-corrected $^{40}Ar/^{36}Ar$ versus $Cl/^{36}Ar$ for Au-related samples (Table 1; supplementary information). The maximum $Cl/^{36}Ar$ values determined in samples dominated by Cl-poor CH_4 fluid inclusions (Table 1) are unlikely to be explained by Cl in low salinity H_2O fluid inclusions which are very rare (< 2%) in sample Q6 (Table 1). These data are interpreted to indicate HCl is present in mantle-derived CH_4. The ^{36}Ar concentration of mantle-methane is unlikely to exceed the parts-per-trillion range because saline aqueous fluid inclusions with similar $Cl/^{36}Ar$ values contain ppb ^{36}Ar [19]. The spread in $^{40}Ar/^{36}Ar$ and $Cl/^{36}Ar$ can be explained by the addition of crustal ^{36}Ar during fluid migration.

Fig 2 (Kendrick et al., 2008)

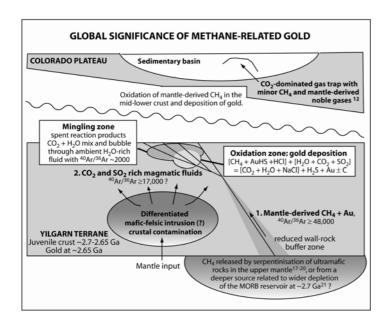**GLOBAL SIGNIFICANCE OF METHANE-RELATED GOLD**

Fig 3. Schematic model through the earths crust and upper mantle illustrating how gold mineralisation might relate to, poorly understood, but emerging mantle depletion events that operate on a global scale[17]. Alternatively mantle CH_4 could be sourced from above a subducting slab. See refs [1, 2] for geochronology.

[1]   R.J. Goldfarb, D.I. Groves, S. Gardoll, *Orogenic gold and geologic time: a global synthesis, Ore Geology Reviews 18(2001) 1-75.*

[2]   D.I. Groves, R.J. Goldfarb, F. Robert, C.J.R. Hart, *Gold deposits in metamorphic belts: Overview of current understanding, outstanding problems, future research and exploration significance, Economic Geology 98(2003) 1-29.*

[3]   R. Powell, T.M. Will, G.N. Phillips, *Metamorphism in Archean Greenstone Belts - Calculated Fluid Compositions and Implications for Gold Mineralization, Journal of Metamorphic Geology 9(1991) 141-150.*

[4]   G.N. Phillips, K.A. Evans, *Role of CO2 in the formation of gold deposits, Nature 429(2004) 860-863.*

[5]   T. Graupner, S. Niedermann, U. Kempe, R. Klemd, A. Bechtel, *Origin of ore fluids in the Muruntau gold system: Constraints from noble gas, carbon isotope and halogen data, Geochimica et Cosmochimica Acta 70(2006) 5356-5370.*

[6]   J. Mao, Y. Li, R.J. Goldfarb, Y. He, K. Zaw, *Fluid inclusion and noble gas studies of the Dongping Gold Deposit, Hebei Province, China: A mantle connection for mineralisation?, Economic Geology 98(2003) 517-534.*

[7]   X. Li, J. Mao, C. Wang, Y. Watanabe, *The Dabuhe gold field at the eastern margin of the Tibetan Plateau: He, Ar, S, O and H isotopic data and their metallogenic implications, Ore Geology Reviews(2006).*

[8]   T.P. Mernagh, A.S. Wygralak, *Gold ore-forming fluids of the Tanami region, Northern Australia, Mineralium Deposita 42(2007) 145-173.*

[9]   P. Neumayr, J. Walshe, S. Hagemann, K. Petersen, T. Roache, P. Frikken, L. Horn, S. Halley, *Oxidized and reduced mineral assemblages in greenstone belt rocks of the St. Ives gold camp, Western Australia: vectors to high-grade ore bodies in Archaean gold deposits?, Mineralium Deposita in press(2007).*

[10]   P. Duuring, K.F. Cassidy, S.G. Hagemann, *Granitoid-associated orogenic, intrusion-related, and porphyry style metal deposits in the Archean Yilgarn Craton, Western Australia, Ore Geology Reviews 32(2007) 157-186.*

[11]   D.I. Norman, N. Blamey, *Methane in Carlin-type gold deposit fluid inclusions, Geochimica et Cosmochimica Acta Supplement 69(2005) A124.*

[12]   K. Petersen, S.G. Hagemann, P. Neumayr, J.L. Walshe, *Multiple hydrothermal fluid pulses through time at the Kambalda gold deposits, Yilgarn Craton, Western Australia, in: C.J. Andrew, e. al., (Eds), Proceedings of the ninth biennial meeting of the society for geology applied to mineral deposits: Digging Deeper 1, Irish Association for Economic Geology, Dublin, 2007, pp. 675-678.*

[13]   J.L. Walshe, P. Neumayr, K. Petersen, S. Halley, A. Roache, C. Young, *Scale-integrated, architectural and geodynamic controls on alteration and geochemistry of gold systems in the Eastern Goldfields Province, Yilgarn Craton, Project M358., Minerals and Energy Research Institute of Western Australia, Perth, 2006, p. 200.*

[14]   E. Thomassot, P. Cartigny, J.W. Harris, K.S. Viljoen, *Methane-related diamond crystallization in the Earth's mantle: Stable isotope evidences from a single diamond-bearing xenolith, Earth and Planetary Science Letters 257(2007) 362-371.*

[15]   H.K. Sachan, B.K. Mukherjee, R.J. Bodnar, *Preservation of methane generated during serpentinization of upper mantle rocks: Evidence from fluid inclusions in the Nidar ophiolite, Indus Suture Zone, Ladakh (India), Earth and Planetary Science Letters 257(2007) 47-59.*

[16]   K. Schmidt, A. Koschinsky, D. Garbe-Schonberg, L.M. de Carvalho, R. Seifert, *Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev*

hydrothermal field, 15[degree sign]N on the Mid-Atlantic Ridge: Temporal and spatial investigation, Chemical Geology 242(2007) 1-21.

[17] S.W. Parman, Helium isotopic evidence for episodic mantle melting and crustal growth, Nature 446(2007) 900-903.

[18] J.K. Böhlke, J.J. Irwin, Laserprobe analyses of Cl, Br, I, and K in fluid inclusions: Implications for the sources of salinity in some ancient hydrothermal fluids., Geochimica et Cosmochimica Acta 56(1992) 203-225.

[19] M.A. Kendrick, J.M. Miller, D. Phillips, 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(2006) 2540-2561.

[20] M. Ozima, F.A. Podosek, Noble Gas Geochemistry, Cambridge University Press, 2002.

[21] C.J. Ballentine, B. Marty, B.S. Lollar, Neon isotopes constrain convection and volatile origin in the Earth's mantle, Nature 433(2005) 33-38.

[22] P. Burnard, D. Graham, G. Turner, Vesicle-specific noble gas analyses of "popping rock"; implications for primordial noble gases in the Earth., Science 276(1997) 568-571.

[23] B. Marty, F. Humbert, Nitogen and argon isotopes in oceanic basalts, Earth and Planetary Science Letters 152(1997) 101-112.

[24] R.K. O'Nions, C.J. Ballentine, Rare gas studies of basin scale fluid movement, Phil. trans. Roy. Soc. Lon. A 344(1993) 141-156.

[25] R. Burgess, E. Layzelle, G. Turner, J.W. Harris, Constraints on the age and halogen composition of mantle fluids in Siberian coated diamonds, Earth and Planetary Science Letters 197(2002) 193-203.

[26] J.G. Schilling, C.K. Unni, M.L. Bender, Origin of chlorine and bromine in the oceans., Nature 273(1978) 631-635.

[27] A.E. Williams-Jones, A.A. Migdisov, The solubility of gold in crude oil: implications for ore genesis, in: C.J. Andrew, et.al., (Eds), Digging Deeper 1, Irish Association for Economic Geology, Dublin, 2007, pp. 765-768.

[28] J. Kirk, J. Ruiz, J. Chesley, S. Titley, J. Walshe, A detrital model for the origin of gold and sulfides in the Witwatersrand basin based on Re-Os isotopes, Geochimica et Cosmochimica Acta 65(2001) 2149-2159.

[29] F.P. Bierlein, D.I. Groves, R.J. Goldfarb, B. Dube, Lithospheric controls on the formation of provinces hosting giant orogenic gold deposits, Mineralium Deposita 40(2006) 874-886.

[30] G. Holland, C.J. Ballentine, Seawater subduction controls the heavy noble gas composition of the mantle, Nature 441(2006) 186-170.