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ARTICLE

The timing of epigenetic gold mineralization on the Baie Verte Peninsula, Newfoundland, Canada: new evidence from Re–Os pyrite geochronology

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Abstract The absolute timing of epigenetic mineralization, including most types of gold deposits, is difficult to resolve due to the absence of suitable minerals in veins and replacement zones. However, gold is commonly closely associated with pyrite and arsenopyrite, which may be amenable to Re–Os geochronology, providing sufficient Re and Os are present within them. This short paper outlines the use of this method to date two gold deposits in Newfoundland using pyrite. Although the Os contents of the pyrites are extremely low (≪0.1 ppb), the Os is almost exclusively radiogenic ^{187}Os, and data are amenable to model age calculations, as used in Re–Os molybdenite dating. The pyrites from these deposits correspond to low-level highly radiogenic sulphides, as defined by other studies. The Stog'er Tight and Pine Cove gold deposits yield mean Re–Os model ages of 411±7 Ma (n=4) and 420±7 Ma (n=5), respectively, which agree with isochron regression of ^{187}Os against ^{187}Re. The Re–Os age for Stog'er Tight is within uncertainty of a previous U–Pb age from 'hydrothermal' zircon (420±5 Ma) in spatially related alteration. A latest Silurian–earliest Devonian age for the mineralization is consistent with indirect age constraints from some other gold deposits in central Newfoundland and suggests a broad temporal link to the mid-Silurian Salinic Orogeny. However, the gold mineralization appears to be younger than most plutonic activity associated with this event. The results illustrate the potential value of Re–Os pyrite geochronology in understanding the temporal framework of epigenetic mineralization, especially if future improvements in analytical precision and reductions in procedural blanks allow wider application to material with similarly low Re and Os concentrations.

Keywords Gold mineralization · Geochronology · Re/Os · Newfoundland

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Introduction

Resolving the absolute timing of mineralization is important in assessing the economic potential of specific geological units or structures and in developing genetic models to guide exploration. Epigenetic deposits, including most types of gold mineralization, present a particular challenge, for they may have no genetic link to their host rocks and may be much younger. Age constraints may be obtained through geochronological studies of rocks that predate and postdate ore formation (typically dykes) or spatially related hydrothermal alteration assemblages. However, neither approach provides direct information; in the first case, constraints may be so broad as to be useless, and in the second case, interpretation depends on the assumption of a link between mineralization and alteration. Furthermore, many alteration minerals are suited only to K–Ar or Ar–Ar methods, for which ages are easily disturbed or completely reset. Gold-bearing veins occasionally contain minerals suited to U–Pb geochronology, such as zircon, rutile, titanite or monazite (e.g. Lin and Corfu 2002; Ramezani et al. 2002), but such cases are rare. The common gangue minerals associated with gold are quartz, carbonates and sulphides, which are not amenable to conventional geochronological methods.

In many gold deposits, there is a strong correlation between the abundance of sulphides (typically pyrite and arsenopyrite) and gold, to the extent that visual estimates of sulphide content are used for first-order grade control during mining. Sulphides are commonly present within discrete mineralized veins, suggesting that their formation and the introduction of gold are temporally and genetically linked. Thus, Re–Os geochronological studies of these common sulphides provide a potential method for direct dating of epigenetic gold mineralization. Re–Os studies of several gold deposits have yielded relatively precise ages, indicating that the technique holds promise. These include mesothermal-style vein deposits (e.g. Stein et al. 2000; Arne et al. 2001; Morelli et al. 2005, 2008), porphyry-type systems (e.g. Mathur et al. 2005), epithermal deposits (e.g. Mathur et al. 2003) and paleoplacer deposits such as the Witswatersrand (Kirk et al. 2001; Schaefer et al. 2010). Such work requires a high level of analytical precision and very low procedural blanks for Re and Os.

This paper documents the application of Re–Os pyrite geochronology to date two gold deposits in Newfoundland (Canada), one of which is also constrained by previous U–Pb geochronology. The Os concentrations in the samples discussed here are amongst the lowest that have thus far provided precise age determinations, and this study provides a further indication of the value of this technique in dating epigenetic hydrothermal deposits. This work is part of a wider study to establish the timing and genesis of gold mineralization in Newfoundland.

Background and principles

Re–Os geochronology (based on the decay of ^{187}Re to ^{187}Os) has long been applied to molybdenite (MoS_2), which concentrates Re at parts per million levels, but contains essentially no common (non-radiogenic) Os. As a result, molybdenite contains only radiogenic ^{187}Os (typically hundreds of parts per billion), and accurate model ages can be calculated from single samples (e.g. Stein et al. 2001). The Re–Os method has also been applied to orthomagmatic sulphide deposits, in which Re and Os are also relatively abundant; however, such use requires multiple-sample isochron methods, as common (non-radiogenic) Os is generally present (e.g. Walker et al. 1994; Lambert et al. 1999).

In contrast, sulphides (other than molybdenite) in epigenetic hydrothermal settings, such as most gold deposits, tend to be Re-depleted, typically containing a few tens of ppb of Re at most. As the half-life of ^{187}Re is some 41.2 Ga (about four times the age of the universe), their radiogenic ^{187}Os concentrations are trivial, especially if the mineralization is relatively young, and are measured in parts per trillion. Precise isotopic analysis at such concentrations is difficult, as procedural blank corrections become significant sources of uncertainty.

Some previous Re–Os studies of epigenetic gold deposits (e.g. Stein et al. 2000; Arne et al. 2001; Morelli et al. 2005) suggest that sulphides in such environments may be essentially devoid of common Os; although ^{187}Os is present at parts per trillion levels, it is almost entirely radiogenic. Such sulphides were termed 'low-level highly radiogenic' (LLHR) by Stein et al. (2000). This attribute does not diminish the analytical challenges, but the lack of common Os permits the calculation of model ages akin to those derived for molybdenite, or direct regression of daughter (^{187}Os) against parent (^{187}Re) isotopes. Although it is possible to calculate ages and initial ^{187}Os/^{188}Os ratios for LLHR sulphides using conventional isochrons, this process is complicated by the large correlated errors where samples contain very little ^{188}Os and blank corrections become significant (Stein et al. 2000). In our view, such LLHR sulphides provide the best avenue for direct dating of gold mineralization associated with pyrite and arsenopyrite.

A previous Re–Os geochronology study of gold mineralization in Canada used LLHR arsenopyrite and provided precise formation ages for two deposits in Nova Scotia (Morelli et al. 2005). Prior to this study, investigation of some Newfoundland gold deposits containing abundant arsenopyrite associated with gold (Rattling Brook, Moosehead, H-Pond and Huxter Lane; Fig. 1) indicated insufficient Re (<1 ppb) to permit precise geochronology (Kerr et al. 2006; Kerr and Selby 2010). However, two gold deposits from the Baie Verte Peninsula proved to contain LLHR pyrite, and the results and implications of these results are discussed herein.

Geological and geochronological context

Regional geological and metallogenic setting

Newfoundland is the northeastern termination of the Appalachian Orogen of North America and includes terranes representing the Laurentian and Gondwanan continental blocks, astride the 'Central Mobile Belt' (e.g. Williams 1979; Williams et al. 1988). This central region (Dunnage and Gander Zones; Fig. 1) represents rocks formed within the early Paleozoic Iapetus Ocean, which closed sequentially between latest Precambrian and mid-Silurian times. The Baie Verte Peninsula (Fig. 1) sits at the northwestern limit of the Central Mobile Belt.

Gold occurrences in Newfoundland are hosted by rocks ranging in age from Late Precambrian to Silurian (e.g.

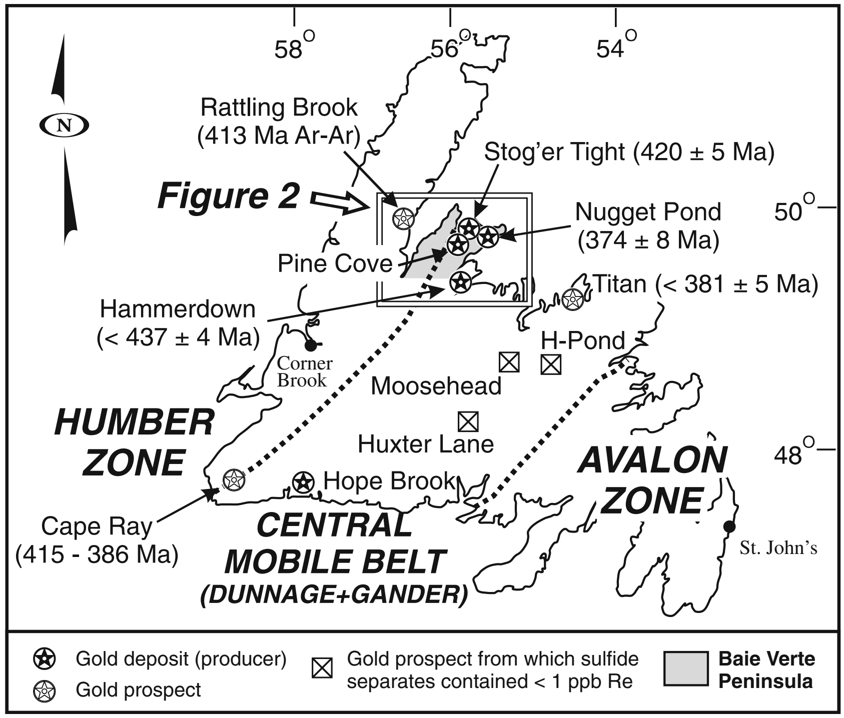

Fig. 1 Location of the Baie Verte Peninsula in Newfoundland and locations of selected gold deposits, including those for which geochronological information is available. Aside from Rattling Brook, all results indicated are U–Pb determinations, and the sources are indicated in the text. The map also shows the locations of three gold prospects from which test analyses of single sulphide separates indicated low Re contents (<1 ppb) which presently preclude dating

Wardle 2005), but the majority are in Cambrian and Ordovician volcanic and sedimentary rocks within the Dunnage Zone or Precambrian rocks of the Avalon Zone (Fig. 1). Mesothermal gold mineralization predominates in the Dunnage Zone, whereas most gold occurrences in the Avalon Zone are considered to be epithermal (after Poulsen et al. 2000). Minor epithermal gold mineralization is also known in central Newfoundland. With the exception of the epithermal varieties, all gold mineralization in Newfoundland is epigenetic, and the absolute timing of mineralization is generally poorly constrained or unknown. However, the spatial association between gold and major late-orogenic fault zones suggests that gold was mobilized and deposited during Silurian and/or Devonian orogenesis (e.g. Tuach et al. 1988; Swinden et al. 2001; Wardle 2005; Kerr et al. 2005).

Five gold deposits in Newfoundland have been exploited since 1980 (Fig. 1). The Baie Verte Peninsula and adjoining areas (Figs. 1 and 2) are the focus of much of this activity and include the only current gold producer, the Pine Cove deposit. The peninsula also contains valuable volcanogenic massive sulphide deposits, some of which have elevated gold concentrations, up to several grams per tonne locally.

Geology of the Baie Verte Peninsula

The Baie Verte Peninsula contains the boundary between the ancient continental margin of Laurentia (the Humber Zone) and the vestiges of the Iapetus Ocean (the Dunnage Zone); the two are juxtaposed along the Baie Verte Line, a long-lived fault zone marked by dismembered ophiolites (Fig. 2). The deposits examined in this study both lie within the Dunnage Zone, and the following summary of local geology is adapted from Hibbard (1983), Evans (2004) and Skulski et al. (2009, 2010).

Pre-Silurian rocks east of the Baie Verte Line fall into essentially two packages; an older sequence of ophiolitic rocks (ca. 490 Ma), in which mafic rocks have a Mg-rich 'boninitic' chemistry, overlain by a younger volcanosedimentary sequence (ca. 475 to 465 Ma) in which mafic rocks are typically island-arc tholeiites. Recent mapping and geochronology indicate that this younger 'ophiolitic cover sequence' can be correlated across the peninsula (Skulski et al. 2009, 2010). Most of the volcanogenic massive sulphide mineralization is hosted by the older ophiolitic sequence, whereas most of the epigenetic gold mineralization is hosted by the younger cover sequence. The Ordovician rocks are overlain unconformably by Silurian (ca. 440–426 Ma) bimodal volcanic rocks and associated sedimentary rocks. Granitoid rocks across the peninsula are also mostly of Lower Silurian age (ca. 440–423 Ma; Cawood and Dunning 1993; Skulski et al. 2009, 2010). The structural history of the peninsula is complex, but the dominant structures and fabrics in its eastern part are now viewed as largely of mid-Silurian (Salinic) age (Castonguay et al. 2009; Skulski et al. 2009, 2010). From the perspective of this paper, the sequence of most interest is the upper part of the Point Rousse Complex (Fig. 2), representing part of the ophiolite cover sequence. This comprises mafic to intermediate volcanic and pyroclastic rocks, volcaniclastic sedimentary rocks and synvolcanic gabbroic intrusions. This

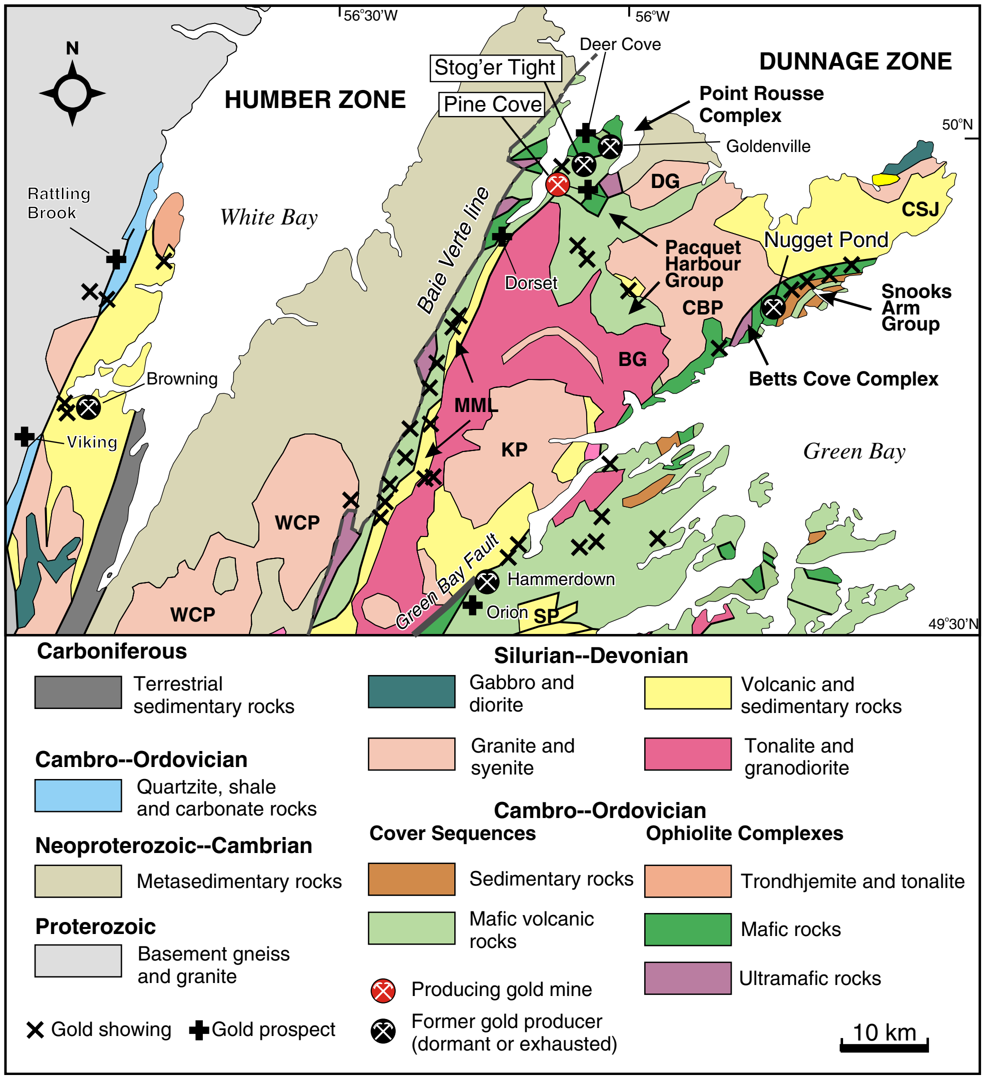

Fig. 2 Simplified geology of the Baie Verte Peninsula and adjacent areas, showing the locations of gold deposits, including present and former producers, prospects and minor showings. Silurian rock units discussed in text are indicated as follows: *WCP* Wild Cove Pond Intrusive Suite, *MML* Micmac Lake Group, *KP* Kings Point Complex, *BG* Burlington Granodiorite, *DG* Dunamagon Granite, *CBP* Cape Brule Porphyry, *CSJ* Cape St. John Group, *SP* Springdale Group. Geology after Wardle (2005) and 1:1 million scale geological map of Newfoundland

sequence hosts the closely adjacent Stog'er Tight and Pine Cove gold deposits (Fig. 2) and also several other gold prospects, including the Goldenville deposit, one of the first to be exploited in Newfoundland (Fig. 2). The age of the Point Rousse cover sequence is constrained by an imprecise U–Pb (TIMS) zircon age of 483 +9/−5 Ma from the gabbroic host rocks at the Stog'er Tight deposit (Ramezani 1992).

Gold mineralization on the Baie Verte Peninsula is diverse, ranging from replacement-style disseminated deposits to discrete auriferous quartz veins, variably associated with base metal sulphides (Evans 2004). The most significant deposits, including the two discussed herein, contain spatially associated replacement- and vein-style mineralization.

Stog'er Tight gold deposit

The Stog'er Tight gold deposit is hosted within the Point Rousse ophiolite cover sequence (Fig. 2). The deposit was discovered in the 1980s and holds a small resource of 350,000 tonnes at 4.5 g/t Au, with some local higher-grade zones (historical estimate quoted by Wardle 2005). Small-scale open-pit mining in the mid-1990s was impeded by continuity and grade-control problems, but there is now interest in reactivating the deposit, in the light of high gold prices. The following summary is drawn from Kirkwood and Dubé (1992), Ramezani (1992), Ramezani et al. (2002) and Evans (2001, 2004).

Gold mineralization at Stog'er Tight is mostly hosted by gabbroic rocks that represent three discrete sill-like intrusions within mafic volcanic and volcaniclastic rocks. The host gabbro was dated imprecisely at 483 +9/−5 Ma using U–Pb TIMS zircon methods (Ramezani 1992), and this provides a maximum age for gold mineralization. The highest-grade mineralization is associated with coarse-grained epigenetic pyrite, accompanied by red albite and abundant iron carbonate, which replace the host gabbro. These higher-grade lenses and pods sit within an envelope of chlorite–carbonate±sericite alteration, within which lower-grade mineralization is similarly associated with epigenetic pyrite. Discrete quartz veins are common within the mineralized zones, and the intensity of alteration and mineralization is the greatest where veins are abundant within metagabbro. The gold grades are strongly correlated with the amount of sulphide. Gold occurs as tiny inclusions and as microscopic veinlets (<100 mm wide) within the pyrite grains, which are closely associated with relict ilmenomagnetite, originally an igneous phase. Grades are typically <10 g/t Au, but exceed 60 g/t over narrow widths; locally, gold is visible, notably where the pyrite has weathered away (Evans 2004). The presence of both gold inclusions and microveinlets suggests that precipitation accompanied pyrite formation (Huard 1990; Evans 2004). Structural studies suggest that veining associated with gold occurred early in the deformation sequence, following the D_1 event, but preceding D_2 (Kirkwood and Dubé 1992). In contrast, Castonguay et al. (2009) suggest that gold mineralization here and elsewhere was broadly synchronous with their D_2 event, interpreted to be of Silurian age. Ramezani (1992) identified red zircon in altered mafic rocks associated with mineralization at Stog'er Tight and interpreted this to be of hydrothermal origin; two fractions of this zircon yielded $^{207}Pb/^{206}Pb$ ages of 417 and 418 Ma by TIMS methods. The age of the mineralization was interpreted as 420±5 Ma (Ramezani 1992; Ramezani et al. 2002). The iron-rich nature of the gabbro host was inferred to be an important control on gold precipitation through reduction effects caused by magnetite and ilmenomagnetite (Kirkwood and Dubé 1992; Ramezani et al. 2002).

Pine cove gold deposit

The Pine Cove gold deposit is located about 5 km from Stog'er Tight and is also hosted within the Point Rousse Complex ophiolite cover sequence (Fig. 2). It was discovered in 1988 and comprises two main zones of mineralization, collectively forming a near-surface resource of almost 3 Mt at 3 g/t Au (quoted by Wardle 2005; Anaconda Gold information). The deposit entered production as a small open-pit mine in early 2008. The following summary is derived mostly from Duncan and Graves (1992) and Evans (2004); the deposit has not to date been studied in detail through research projects.

Gold mineralization at Pine Cove is hosted by mafic volcanic rocks, volcaniclastic sedimentary rocks (typically hematitic) and gabbro. However, the exact nature of the local host rocks within the deposit is generally obscured by pervasive alteration. Duncan and Graves (1992) suggested that the highest-grade mineralization was hosted by altered gabbro and that this rock type favoured gold deposition due its iron-rich composition, as at Stog'er Tight. Gold is associated with heavily disseminated epigenetic pyrite, as seen at the Stog'er Tight deposit. Related alteration is dominated by chlorite, iron carbonate and white albite; the distinctive red albite noted at Stog'er Tight is less common. This replacement-style mineralization is associated with discrete quartz veins and quartz-carbonate breccia zones, which also contain coarse-grained disseminated auriferous pyrite. Gold occurs as inclusions and microveinlets within the pyrite, as observed also at Stog'er Tight. The gold grades of mineralization are strongly correlated with the sulphide content, to the extent that this can be used for initial grade control during mining operations; the relationship is indicated by data for gold and sulphur contents in samples collected from production drilling operations (Table 1; Fig. 3). The correlation is not exactly 1:1 because the gold is not dissolved within the pyrite, but rather physically associated with it, and there are minor quantities of other sulphide minerals. Nevertheless, this relationship provides additional evidence of the genetic and temporal association between gold deposition and pyrite formation. The structural controls on mineralization are not entirely clear, and the quartz veining has variously been considered to predate or postdate the main fabric in the host rocks (D_3 of Calon and Weicke 1990; D_2 of Castonguay et al. 2009). Other than the correlation of the host rock sequences with the equivalent units exposed in the Stog'er Tight area, there are no previous constraints on the timing of mineralization at Pine Cove.

Re–Os geochronology

Sampling, processing and analysis

Samples used in this study came from several sources. Samples from the Stog'er Tight deposit represent high-grade sulphide-rich zones within the dormant open pit, collected at closely adjacent locations. Samples from the Pine Cove deposit represent similar high-grade sulphide-rich mineralization, collected from a pre-production test pit, and the initial production pit subsequently developed at the same location. All samples contained coarse-grained pyrite. Approximate coordinates for all samples and their descriptions are given in the notes for Table 2. The pyrite separates listed in Table 2 were each derived from a discrete field sample; although the Universal Transverse Mercator coordinates listed for samples are in some cases identical, they do represent separate localities within the error of GPS measurements (typically several metres).

The samples were crushed to a grain size of ~5 mm, and sulphides were handpicked at the University of Durham. The sulphide separates consist almost exclusively of pyrite, although small quantities of silicate minerals (and gold) may occur as inclusions. The Re–Os analyses were undertaken at the TOTAL laboratory for source rock

Table 1 Gold (ppm) and sulphur (weight percent) data from recent 2010 production drilling at the Pine Cove gold mine; these samples were selected to cover a wide range of gold values typical of the ore

Number	Au (ppm)	S (wt.%)	Number	Au (ppm)	S (wt.%)
9623	1.000	0.27	9762	1.413	0.65
9636	3.125	0.63	9774	15.698	4.03
9647	1.924	0.33	9776	13.643	4.25
9649	0.913	0.15	9777	10.155	3.07
9651	0.290	0.53	9782	3.101	0.88
9654	2.424	0.27	9784	2.496	0.83
9699	8.920	1.50	9785	3.595	0.97
9749	6.109	0.56	9788	0.048	0.17
9751	4.249	2.12	9796	5.324	1.39
9754	0.169	0.20	9801	0.053	0.22

Gold was analysed at Atlantic Analytical Laboratories in Springdale, NL, Canada (data provided by Anaconda Gold). Sulphur was analysed by Actlabs in Ancaster, ON, Canada, using the Leco Furnace method. Gold assays provided by Anaconda Gold, completed by Atlantic Analytical Laboratories. Laboratories in Springdale, NL, Canada. Sulphur analyses by Leco Furnace method, Actlabs, Ancaster, ON, Canada

geochronology and chemistry in the Northern Centre for Isotope and Element Tracing (NCEIT) at Durham University. The methods of digestion and analysis follow that described by Selby et al. (2009) and references therein. In brief, the separates were weighed accurately and loaded into a Carius Tube with a known amount of a mixed Re–Os tracer solution containing ^{185}Re and ^{190}Os and placed in an oven at 220°C for 48 h. Osmium and Re were isolated

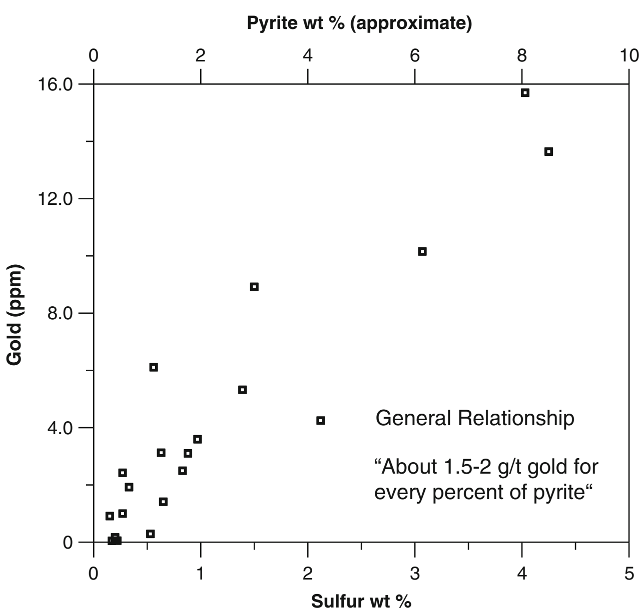

Fig. 3 Scatter diagram showing the relationship between gold grade (parts per million) and sulphide (weight percent) in 20 samples from 2010 production drilling at Pine Cove. Assuming that other sulphides are of trivial abundance and that pyrite contains ~50 wt.% S, results suggest that every percent of sulphide accounts for 1.5 to 2.0 g/t Au. Gold assay data provided by Anaconda Gold; for details of analyses, see the notes for Table 1

using solvent extraction (in $CHCl_3$) and microdistillation, followed by anion column and single-bead chromatography methods, respectively. The Re and Os solutions were loaded onto Ni and Pt filaments, respectively, and analysed using negative-ion mass spectrometry on a Thermo Electron TRITON mass spectrometer at the University of Durham. Procedural blanks during the course of this study were 3.5± 0.6 pg/g (Re) and 0.16±0.05 pg/g (Os), with ^{187}Os/^{188}Os ratio of 0.216±0.028 (n=3). Uncertainty estimates for the data are derived by propagation of uncertainties in the mass spectrometer measurements, blank abundances, isotopic compositions, spike calibrations and the results from analyses of a Re–Os standard (Table 2). The Re–Os isotopic data are used to determine dates in two ways: the regression of the ^{187}Re/^{188}Os and ^{187}Os/^{188}Os values, including the 2σ calculated uncertainties and the associated error correlation function (rho), and the regression of ^{187}Re and ^{187}Os^R. In both cases, Re–Os dates were determined using Isoplot V. 3.0 with the ^{187}Re decay constant (λ) of 1.666×10^{-11} year^{-1} (Smoliar et al. 1996; Ludwig 2003).

To ensure and monitor long-term mass spectrometry reproducibility, in-house standard solutions of Re and Os (AB-1) are repeatedly analysed at the NCEIT. The Re standard analysed during the course of this study is made from 99.999% zone-refined Re ribbon and is considered to be identical to that of AB-1 (Creaser et al. 2002). The NCIET Re standard yields an average ^{185}Re/^{187}Re ratio of 0.598020±0.00165 (1σ, n=85). The Os standard (AB-2), made from ammonium hexachloro-osmate, yields a ^{187}Os/^{188}Os ratio of 0.10681±0.00016 (1σ, n=80). In addition to monitoring the AB-2 standard, this paper details further use of the Durham Romil Osmium Standard (DROsS) for monitoring the mass spectrometry reproducibility of osmium isotope compositions. The DROsS values

Table 2 Re/Os concentration and isotopic data for the Stog'er Tight and Pine Cove gold deposits, Baie Verte Peninsula, Newfoundland

Sample number	Analysis number	Total Re (ppt)	Uncertainty (2 SD)	Total Os (ppt)	Uncertainty (2 SD)	^{187}Re (ppt)	Uncertainty (2 SD)	^{187}Os (ppt)	Uncertainty (2 SD)
Part 1: concentration data									
Stog'er Tight gold deposit									
Stog-1	121-1	705	10	3.2	12.8	443	6	3.1	0.1
Stog-2	121-2	2,811	15	20.6	0.6	1,767	6	12.9	4.8
AK08-028	150-2	1,895	12	9.2	1.9	1,191	8	7.8	0.9
AK08-027B	149-1	2,932	15	12.8	11.5	1,843	9	12.5	0.3
Pine Cove gold deposit									
Pine Cove 1	121-3	17,697	70	81.4	23.9	11,122	44	77.4	3.3
Pine Cove 2	121-4	25,995	99	115.3	136.4	16,339	62	114.4	2.0
AK07-015	121-5	7,110	29	33.8	10.8	4,469	18	30.2	2.9
AK08-025A	149-4	7,313	29	35.4	16.5	4,597	18	30.2	2.0
AK08-025C	149-5	1,997	12	10.3	16.1	1,255	8	9.6	0.8
Part 2: isotopic ratios and model ages									
Sample	Analysis	^{187}Re/^{188}Os	Uncertainty (2 SD)	^{187}Os/^{188}Os	Uncertainty (2 SD)	rho	Os^{rad} %	Model age (Ma)	Uncertainty (2 SD)
Stog'er Tight gold deposit									
Stog-1	121-1	43,067	125,568	302	880	1.00	99.5	419.1	10.5
Stog-2	121-2	1,751	58	13	0	0.97	99.1	437.5	164.0
AK08-028	150-2	6,492	1,131	43	7	0.99	99.6	391.0	45.2
AK08-027B	149-1	37,959	24,828	257	168	1.00	99.9	404.3	10.2
Pine Cove gold deposit									
Pine Cove 1	121-3	72,439	15,276	522	110	1.00	96.5	416.5	18.0
Pine Cove 2	121-4	426,576	357,540	3,004	2,518	1.00	99.4	418.6	7.5
AK07-015	121-5	31,510	7,350	231	54	1.00	92.2	403.6	39.1
AK08-025A	149-4	48,416	16,224	366	123	1.00	95.0	429.5	26.5
AK08-025C	149-5	45,005	50,781	361	408	1.00	94.9	456.0	38.9
Part 3: sample locations and weights									
Stog'er Tight deposit						Pine Cove deposit			
Sample	UTM (E)	UTM (N)	Mass (g)			Sample	UTM (E)	UTM (N)	Mass (g)
Stog-1	566150	5535050	0.43			Pine Cove 1	562350	5534400	0.40
Stog-2	566150	5535050	0.40			Pine Cove 2	562350	5534400	0.40
AK08-028	566100	5534975	0.41			AK07-015	562360	5534425	0.39
AK08-027B	566200	5534970	0.41			AK08-025A	562385	5534420	0.40
						AK08-025C	562385	5534420	0.41

Coordinates are UTM, Zone 21, NAD1927 Canada Datum; NTS Map Sheet 12H/16; 1:50,000 scale

UTM Universal Transverse Mercator

recorded during this study yield an $^{187}Os/^{188}Os$ ratio of 0.160989±0.000404 (2σ, n=10). These in-house standard measurements were conducted during the same sample period as the study by Rooney et al. (2010) and are thus identical and are in excellent agreement with previous determinations (Rooney et al. 2010 and references therein).

Summary of analytical data

Eight of the nine samples have Re abundances ranging from <1 to about 26 ppb (Table 2); sample Stog-1 contains only 0.7 ppb (700 ppt) Re. There are wide variations in Re contents amongst the separates from individual deposits. Stog'er Tight pyrite samples contain from 0.7 to 2.9 ppb Re and 3 to 20 ppt Os; Pine Cove pyrite samples contain from 2 to 26 ppb Re and 10 to 115 ppt Os. These extremely low Os contents are well-correlated with the Re concentrations (Table 2). All samples have extremely high $^{187}Re/^{188}Os$ (up to 4.3×10^5) and $^{187}Os/^{188}Os$ ratios (up to 3,000); these extreme values have similarly large uncertainties (Table 2). Such results indicate that the pyrite separates essentially lack common Os, and the large uncertainties reported for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ essentially represent propagated blank uncertainties. These uncertainties are almost perfectly correlated, as expressed by the parameter rho, which approaches 1 for most analyses (Table 2; calculation of rho using Ludwig 2003). In summary, results indicate that virtually all of the Os detected is ^{187}Os of radiogenic origin ($^{187}Os^R$), with a minimum value of 92% $^{187}Os^R$ in sample AK07-015 from Pine Cove. All of the Stog'er Tight separates contain >99% $^{187}Os^R$, and all remaining samples from Pine Cove have >95% $^{187}Os^R$. The dominance of radiogenic Os and the high $^{187}Re/^{188}Os$ ratios are diagnostic of LLHR sulphides (Stein et al. 2000; Morelli et al. 2005), in which the initial $^{187}Os/^{188}Os$ ratio approaches zero. It is possible to perform a conventional isochron regression of $^{187}Re/^{188}Os$ against $^{187}Os/^{188}Os$ with data of this type, even with such large uncertainties, because the latter are highly correlated (e.g. Stein et al. 2000; Morelli et al. 2005, 2008; Selby et al. 2009). However, given the virtual absence of common Os, the preferred method for age calculation uses model ages (as in Re–Os molybdenite geochronology), or direct regression of parent isotope (^{187}Re) against daughter isotope (^{187}Os). This approach is consistent with that used in other studies of LLHR sulphides cited above, but the Os concentrations in some pyrite separates from the Baie Verte samples are lower than recorded in these previous examples.

Age of the Stog'er Tight gold deposit

The four pyrite separates from the Stog'er Tight deposit have low but variable Re contents (0.7 to 2.9 ppb) and extremely low Os contents (3.2 to 20.6 ppt); the detected Os is in all cases >99% radiogenic (Table 2). The causes of Re abundance variation amongst the pyrite separates remain unknown, but have important implications for determining the feasibility of dating through test analyses (see later discussion). The Re–Os model ages range from 391 to 437 Ma, but the most precise amongst these indicate ages of 404.3±10.3 and 419.1±10.5 Ma, respectively (Table 2). Sample Stog-2 has a large uncertainty; no material remains from this for further repeats. The weighted average of all four model ages is 411.0±7.2 Ma (Fig. 4a), with a MSWD of 1.7, with a probability of fit of 17%. A direct regression of ^{187}Re against ^{187}Os yields a slightly younger and less precise age of 399±13 Ma (MSWD=0.33), with an initial ^{187}Os content of 0.15±0.14 ppt (Fig. 5a). Both ages are the same within uncertainty, but the more precise estimate from the model ages is our preferred solution. The age is within uncertainty of (but younger than) the 420±5-Ma U–Pb age obtained from proposed hydrothermal zircon by Ramezani et al. (2002).

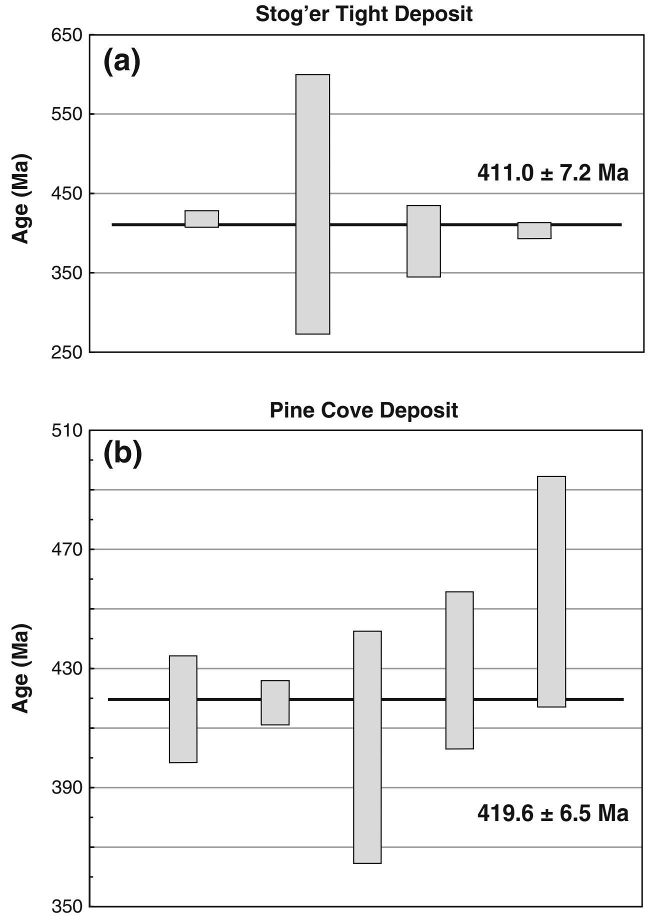

Fig. 4 Re–Os model ages, showing 2 sigma uncertainties and solutions. **a** Stog'er Tight deposit. **b** Pine Cove deposit. Note that there is a significant difference in the vertical scale between **a** and **b**. See text for discussion and additional information

Age of the pine cove gold deposit

The five separates from the Pine Cove gold deposit have a very wide range in Re contents, from about 2 to 26 ppb Re, but most contain >7 ppb Re, in contrast to the Re-poor material from Stog'er Tight. As for Stog'er Tight, the causes of such Re abundance variation remain unknown. Total Os contents range from 10 to 115 ppt (Table 2). As in the case of Stog'er Tight, the Os is overwhelmingly radiogenic (92.2% to 99.4%), and the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios have large correlated uncertainties due to propagation of the procedural blank. Re–Os model ages range from 416.5 to 456.0 Ma, and the weighted average of the five analyses is 419.6±6.5 Ma (Fig. 4b), with a MSWD of 1.2 and a probability of fit of 30%. Regression of ^{187}Re against ^{187}Os yields an identical but less precise age of 420±19 Ma (MSWD=2.2) and an initial ^{187}Os content of −0.7±3 ppt (Fig. 5b). As in the case of Stog'er Tight, the weighted average of the model ages represents our preferred solution.

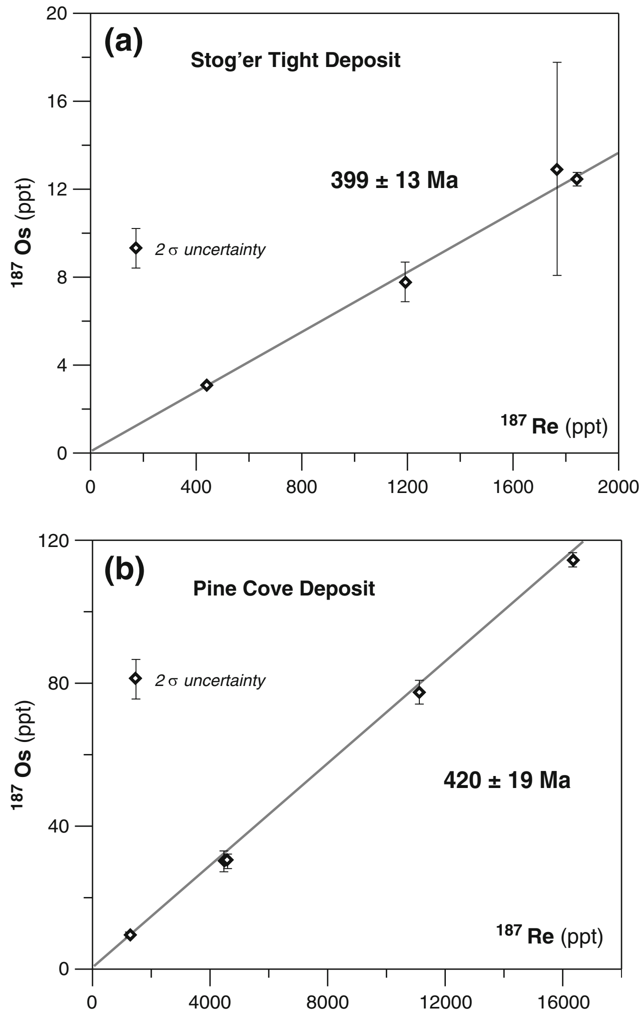

Fig. 5 ^{187}Re–^{187}Os (parent–daughter) isochron ages, showing 2 sigma uncertainties and solutions. **a** Stog'er Tight deposit. **b** Pine Cove deposit. See text for discussion

Discussion

The timing of gold mineralization

Pyrites from the Stog'er Tight and Pine Cove gold deposits are LLHR sulphides (i.e. ^{187}Re/^{188}Os >5,000 and >80% ^{187}Os^{R}; Stein et al. 2000). Only sample Stog-2 fails to meet this precise definition, but it still has extremely high ^{187}Re/^{188}Os (~3,000) and over 99% ^{187}Os^{R} and can be treated in the same way. In view of these attributes, the weighted averages of the Re–Os model ages are considered to give the best estimate of the time of pyrite formation and related gold mineralization. These results indicate ages of 411±7 Ma for Stog'er Tight and 420±7 Ma for Pine Cove, which overlap within their respective uncertainties. The mean model ages also overlap the less precise estimates obtained through regression of ^{187}Re against ^{187}Os (399±13 and 420±19 Ma, respectively). These results are within uncertainty and suggest that these two gold deposits formed within the same narrow time interval, consistent with the many geological similarities between them. The age for Stog'er Tight is also within uncertainty of the 420±5 Ma U–Pb age obtained from 'hydrothermal' zircon in quartz-albite alteration zones (Ramezani et al. 2002). The similarity in the ages obtained through these two independent methods supports our interpretation of the Re–Os data and also the interpretation of the zircon as hydrothermal in origin. The Re–Os results from the Pine Cove deposit provide the first geochronological constraints on the timing of the gold mineralization. The uncertainties on the ages bracket the Silurian–Devonian boundary (ca. 416 Ma), suggesting that both gold deposits formed in latest Silurian or earliest Devonian times.

Implications for wider application of Re–Os pyrite geochronology to gold mineralization

These results add to a small number of relatively precise Re–Os dates obtained from LLHR pyrite and/or arsenopyrite associated with epigenetic gold mineralization (e.g. Stein et al. 2000; Arne et al. 2001; Morelli et al. 2005, 2008; Mathur et al. 2003, 2005; Schaefer et al. 2010). These previous studies also dealt with Re- and Os-depleted material, but the pyrites from the Baie Verte deposits have some of the lowest Os contents that have yet proved amenable to age determination. If material with such low levels of Os can routinely be dated in this manner, Re–Os pyrite geochronology could in time prove to be a vital tool in establishing the timing of epigenetic gold mineralization in a variety of settings. In this context, it should be noted that the Re contents of these pyrite separates from the individual gold deposits vary by about one order of magnitude. The feasibility of direct Re–Os dating is commonly tested at the outset by determining the Re content of a single sample, but the results suggest that this method may not give a definitive answer.

However, it is important to note that the two deposits examined in this study were developed in host rocks that lacked primary (syngenetic) sulphides and that the mineralized rocks appear to contain only a single generation of epigenetic pyrite, associated with the gold, and developed through replacement of primary magnetite and ilmenomagnetite (Huard 1990; Ramezani et al. 2002). This is in many respects an ideal situation, as the danger of mixed results including radiogenic Os retained from earlier syngenetic sulphides is minimized. However, in a wider context, many types of epigenetic mineral deposits (including but not limited to hydrothermal gold mineralization) are thought to be controlled by interactions between mineralizing fluids and pre-existing sulphides that act as reducing agents. Further consideration of the potential effects of two or more generations of sulphides within deposits upon Re–Os systematics is an important avenue for future research. Mixing of more than one generation of Re-bearing sulphides has the potential to significantly complicate interpretation of low-level Re–Os data.

Correlations with rock units and events on the Baie Verte Peninsula

The ages from this study and other relevant local geochronological data are summarized in a time correlation chart (Fig. 6). Several important rock units in the area, including plutonic suites and felsic volcanic rocks, yield Silurian U–Pb ages. Major plutonic suites in the area, including the Burlington granodiorite, the Dunamagon granite and the Cape Brule porphyry (see also Fig. 2), are dated at ca. 446 to ca. 423 Ma (Cawood and Dunning 1993; Skulski et al. 2010). Felsic volcanic rocks of the Cape St. John Group, MicMac Lake Group, Kings Point Complex and Springdale Group (see also Fig. 2) have ages of ca. 441 to ca. 426 Ma (Chandler et al. 1987; Coyle 1989; Cawood and Dunning 1993; Skulski et al. 2010). In the context of recent ages (quoted by Skulski et al. 2010), the uncertainties are not yet published, but are understood to be small (<±3 Ma; V. McNicoll, personal communication, 2009). The Re–Os ages obtained for the gold mineralization at Stog'er Tight and Pine Cove do overlap some of these results but are mostly resolvably younger, suggesting that there may be no *direct* connection between this plutonism and volcanism and gold-bearing hydrothermal fluids. Rather, the gold mineralization at these deposits appears to postdate these important local plutonic and volcanic events. Ramezani et al. (2002) concluded that gold mineralization at Stog'er Tight was associated with the 'waning stages' of Silurian orogenesis, and our results agree broadly with this interpretation. However, the gap between plutonism, volcanism and ore formation appears to be slightly longer on the basis of the new U–Pb and Re–Os data.

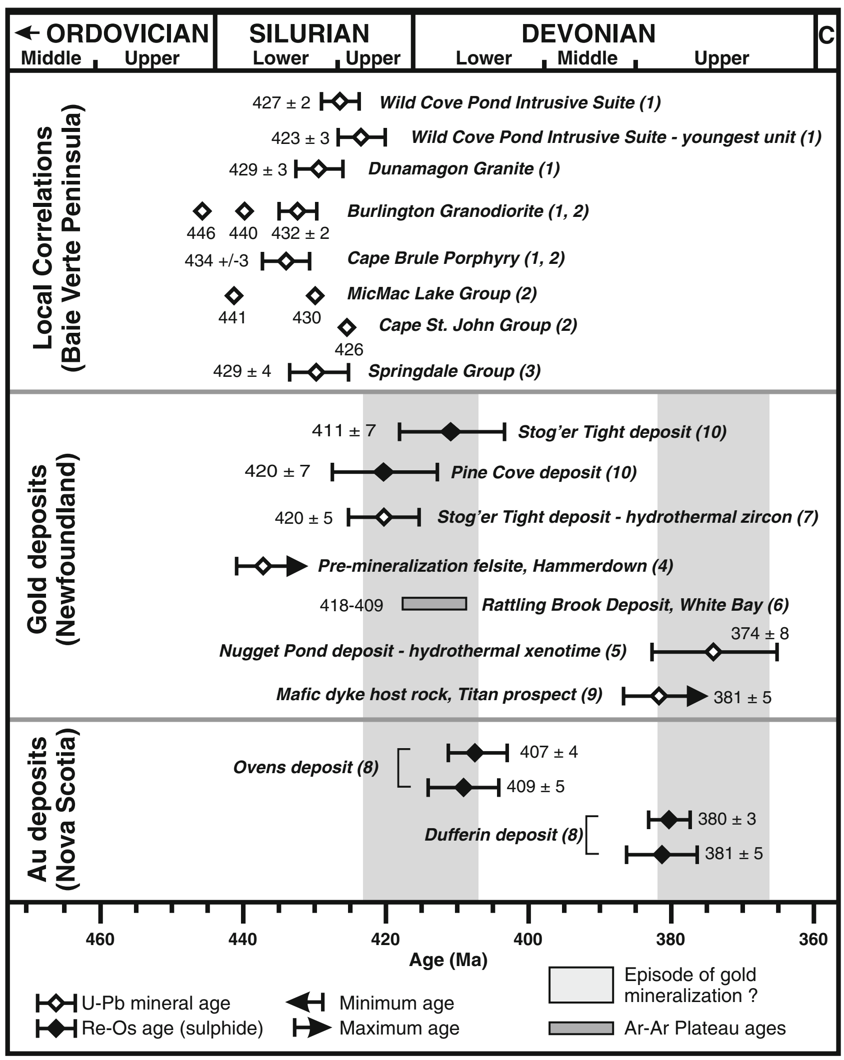

Fig. 6 Time–space correlation chart showing the results obtained from this study in the context of U–Pb age determinations from local rock units on the Baie Verte Peninsula and ages obtained by various methods for gold deposits in Newfoundland and Nova Scotia. References for data sources: (*1*) Cawood and Dunning (1993), (*2*) Skulski et al. (2009, 2010), (*3*) Chandler et al. (1987), (*4*) Ritcey et al. (1995), (*5*) Sangster et al. (2008), (*6*) Kerr and van Breemen (2007), (*7*) Ramezani et al. (2002), (*8*) Morelli et al. (2005), (*9*) McNicoll et al. 2006 and (*10*) this study

Regional structural syntheses (e.g. Castonguay et al. 2009; Skulski et al. 2009) suggest that faults spatially associated with gold mineralization, including these deposits, are D_2 structures, attributed to the Silurian Salinic Orogeny. These D_2 structures affect many of the Silurian rocks listed above but are generally easier to discern in volcanic sequences than in massive plutonic rocks. The Salinic Orogeny is a widely recognized event across Newfoundland and is generally considered to be of mid-Silurian age (Dunning et al. 1990). Assuming that structural correlations are valid, the Re–Os ages for the Stog'er Tight and Pine Cove deposits now provide a minimum age constraint on the timing of this important event. The onset of the Salinic Orogeny (at least on the Baie Verte Peninsula) is now bracketed between the 426-Ma U–Pb age (Skulski et al. 2010) of the Cape St. John Group (which it affects) and the 420-Ma Re–Os age from the Pine Cove gold deposit (which is controlled by or exploits these D_2 structures).

Finally, these results may have significance for mineral exploration in that they show that this gold mineralization postdates the intrusion or deposition of important Silurian rock units (Fig. 6). This implies that such rocks are potential hosts to similar gold mineralization, assuming that other conditions conducive to gold deposition were met. The Silurian rocks of the Baie Verte Peninsula are not known to be widely mineralized but neither have they been explored extensively for gold, in part because the exact temporal relationship between gold mineralization and their formation remained undefined.

Correlations with other dated gold deposits

The results from Stog'er Tight and Pine Cove are also of interest in the context of other data relevant to the timing of gold mineralization in Newfoundland (Figs. 1 and 6). The results from the Baie Verte area fit well with constraints from the Rattling Brook gold deposit in White Bay (Figs. 1 and 2), dated at 418 to 409 Ma using $^{40}Ar/^{39}Ar$ data from pre- and post-mineralization dykes (Kerr and van Breemen 2007). Unfortunately, a previous attempt to use the Re–Os technique on pyrite and arsenopyrite from Rattling Brook failed due to very low Re contents (<1 ppb) and limited variation in Re/Os; these sulphides were not of the LLHR type (Kerr et al. 2006; Kerr and Selby 2010). The Rattling Brook deposit is a very different style of disseminated gold mineralization, associated with arsenopyrite and pyrite hosted in altered Precambrian granite and Cambrian–Ordovician sedimentary rocks (Kerr 2005). Nevertheless, it apparently formed in the very same time interval as Stog'er Tight and Pine Cove. The results are also consistent with a U–Pb age from felsitic dykes that share the same trend as (and are locally cut by) gold-bearing quartz veins at the Hammerdown deposit near Springdale, Green Bay (Figs. 1 and 2). However, this age of 437±4 Ma provides only a maximum age for the mineralization (Ritcey et al. 1995).

There remains some evidence for a younger (Devonian) episode of gold mineralization in the form of the U–Pb xenotime age of 374±8 Ma reported from a cross-cutting Au-bearing vein at the Nugget Pond deposit (Sangster et al. 2008). Re–Os results from the Nugget Pond deposit did not yield data that could confirm or refute this conclusion, as imprecise model ages from LLHR sulphides fall within the Ordovician, perhaps recording the presence of Re-enriched syngenetic sulphides (Kerr and Selby 2010; see discussion above). Evidence for Devonian gold mineralization is also provided by a 381±5-Ma U–Pb SHRIMP age from altered gabbroic host rocks at the Titan Prospect near Gander (McNicoll et al. 2006; located in Fig. 1). Thus, there remains evidence of at least two periods of gold mineralization in Newfoundland. Confirmation of the younger episode through direct Re–Os dating is an important priority for future research.

Finally, the results from Stog'er Tight and Pine Cove are also very similar (but not identical) to some of the Re–Os arsenopyrite ages reported from turbidite-hosted lode gold deposits in the Meguma Group of Nova Scotia (Morelli et al. 2005). The two ages reported by these workers from the Ovens gold deposit (409±5 Ma; 407±4 Ma) are within uncertainty of our results from Stog'er Tight, but younger than the Pine Cove result. Interestingly, Morelli et al. (2005) reported Devonian ages (380±3 Ma; 381±5 Ma) from the nearby Dufferin gold deposit, which also resemble those noted above from Newfoundland. This coincidence of this pattern from two widely separated regions of the northern Appalachians is intriguing, but it remains poorly defined. The results reported here underline the potential of Re–Os pyrite geochronology to generate additional data from deposits across the region and perhaps better understand the temporal relationship between gold mineralization and these mid-Paleozoic orogenic events within the northern Appalachian Orogen.

Conclusions

This study demonstrates that Re–Os geochronological studies of pyrites associated with epigenetic gold mineralization at two deposits on the Baie Verte Peninsula of Newfoundland can yield useful and precise age information, despite very low Re and Os contents. The pyrites are LLHR sulphides that lack common Os and are amenable to model age calculations akin to those employed in molybdenite dating. However, the high degree of precision obtained from Re–Os dating of molybdenites that have parts per million-level Re contents (±1 to 2 Ma in Paleozoic samples) is not presently possible at such low Re and Os contents. It is suggested that LLHR sulphides of this type provide the best potential route for geochronological studies of epigenetic gold deposits, especially if future reductions in procedural blanks can reduce the age uncertainties and facilitate analysis of material with even lower Re contents. The consistency between our results and an earlier U–Pb determination on ‘hydrothermal’ zircon provides a further indication of the utility of the method for such purposes. Pyrite geochronology has the potential to provide useful information on the relationships between gold mineralization and tectonic and magmatic events. The wide range of Re and Os contents shown by pyrite separates from these individual deposits implies that ‘feasibility screening’ using single-sample analyses of Re content may not always be effective and that even deposits that apparently lack sufficient Re upon testing might eventually yield dateable sulphides.

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