$^{40}Ar/^{39}Ar$ and Re-O Isotopic Ages for Hydrothermal Alteration and Related Mineralization at the Highland Valley Cu-Mo Deposit (NTS 092I), Southwestern British Columbia

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KEYWORDS: Quesnellia, Highland Valley deposit, Cu-Mo porphyry, geochronology, $^{40}Ar/^{39}Ar$, Re-Os

INTRODUCTION

The Highland Valley Cu (Mo, Ag, Au) deposit is located roughly 200 km northeast of Vancouver and 75 km southwest of Kamloops, in southern British Columbia (Fig 1). It is the largest operating base metal mine in Canada. Production began in 1962 from several separate mines, which were amalgamated in 1986 to form Highland Valley Copper, a subsidiary of Teck Cominco Limited. Recorded metal production from the Highland Valley deposit to 2005 exceeds 3.33 billion kilograms of copper (average grade of 0.43%), 44 million kilograms of molybdenum (average grade of 0.03%), 1 billion grams of silver and 7 million grams of gold.

The age of mineralization at Highland Valley has been inferred, on the basis of its syngenetic porphyry character, to be more or less coeval with the Late Triassic magmatic history of the host Guichon Creek batholith (Osatenko and Jones, 1976; Casselman *et al.*, 1995). Uranium-lead zircon dating of the batholith suggests an age within the range 213 to 207 Ma (210 ±3 Ma; Mortimer *et al*., 1990; Fig 1). However, conventional K-Ar isotopic analysis of sericite from the ore mineral assemblage has yielded ages that are significantly younger than the crystallization age of the intrusion. For example, a 202 ±8 Ma (recalculated with modern decay constants from data reported in Jones, 1975; *cf.* Breitsprecher and Mortensen, 2004) and 198 ±12 Ma (recalculated with modern decay constants from data reported in Blanchflower, 1971; *cf.* Breitsprecher and Mortensen, 2004), and 191.3 ±4 Ma (recalculated with modern decay constants from data reported in Wanless *et al.*, 1973; *cf.* Breitsprecher and Mortensen, 2004). At the lower limit of error, all three of these ages are younger than the 200 Ma base of the Jurassic epoch. At their upper limit of error, the first two analyses are both 210 Ma (Late Triassic), equivalent to the best crystallization age for the batholith (Mortimer *et al*., 1990). The Wanless *et al.* (1973) date remains Early Jurassic at its upper limit of error (195.3 Ma).

Ore mineral assemblages were resampled with the aim of subjecting them to more precise geochronological dating techniques. Samples were collected by the first author during a three-day field visit to the Valley pit in 1999. Sericite and biotite were collected for $^{40}Ar/^{39}Ar$ age determination, and molybdenite was collected for application of the Re-Os chronometer. If successful, the new dating would eliminate the ambiguity raised by the overlapping magmatic and hydrothermal ages from the deposit that existed at the time. This field examination was intended as reconnaissance for a detailed mapping project of the Highland Valley deposit. Unfortunately, the project did not proceed beyond this preliminary stage and geological relationships between the units dated were not established.

SAMPLE DESCRIPTIONS

Three distinct mineral assemblages were collected from the 1025 m level of the Valley pit (Fig 2). Sample CAS99-HV1 is molybdenite from a massive, 8 to 10 cm wide, steeply dipping vein on the southeastern corner of the pit along the bench wall. The molybdenite vein cut dark to light grey biotite-quartz diorite in which quartz is coarse grained relative to the medium-grained matrix feldspar and biotite. This unit is representative of the Bethsaida phase of the Guichon Creek batholith (McMillan, 1978).

Sample CAS99-HV2 consists of medium-grained sericite from Cu-Mo-mineralized quartz stockwork collected from a well-washed portion of the mining bench. Sericite constitutes up to several percent of the dark grey quartz vein material, but is mostly concentrated as envelopes along the vein margins. Quartz veins at this locality range from 2 to 10 mm thick and form a stockwork that makes up between 5 and 15% of the bench exposures. The plutonic hostrock in this area is mineralogically and texturally consistent with that hosting the massive molybdenite vein described above.

The third dated sample is of biotite collected from a texturally distinctive plutonic phase occurring near the centre of the pit. In contrast to the typical Bethsaida phase, this rock is much more leucocratic. It has a coarse to very coarse grained, white, quartzofeldspathic matrix with very coarse (2–4 cm), euhedral, black biotite books. It contains no observable sulphide mineralization. Contacts with the Bethsaida phase were not established.

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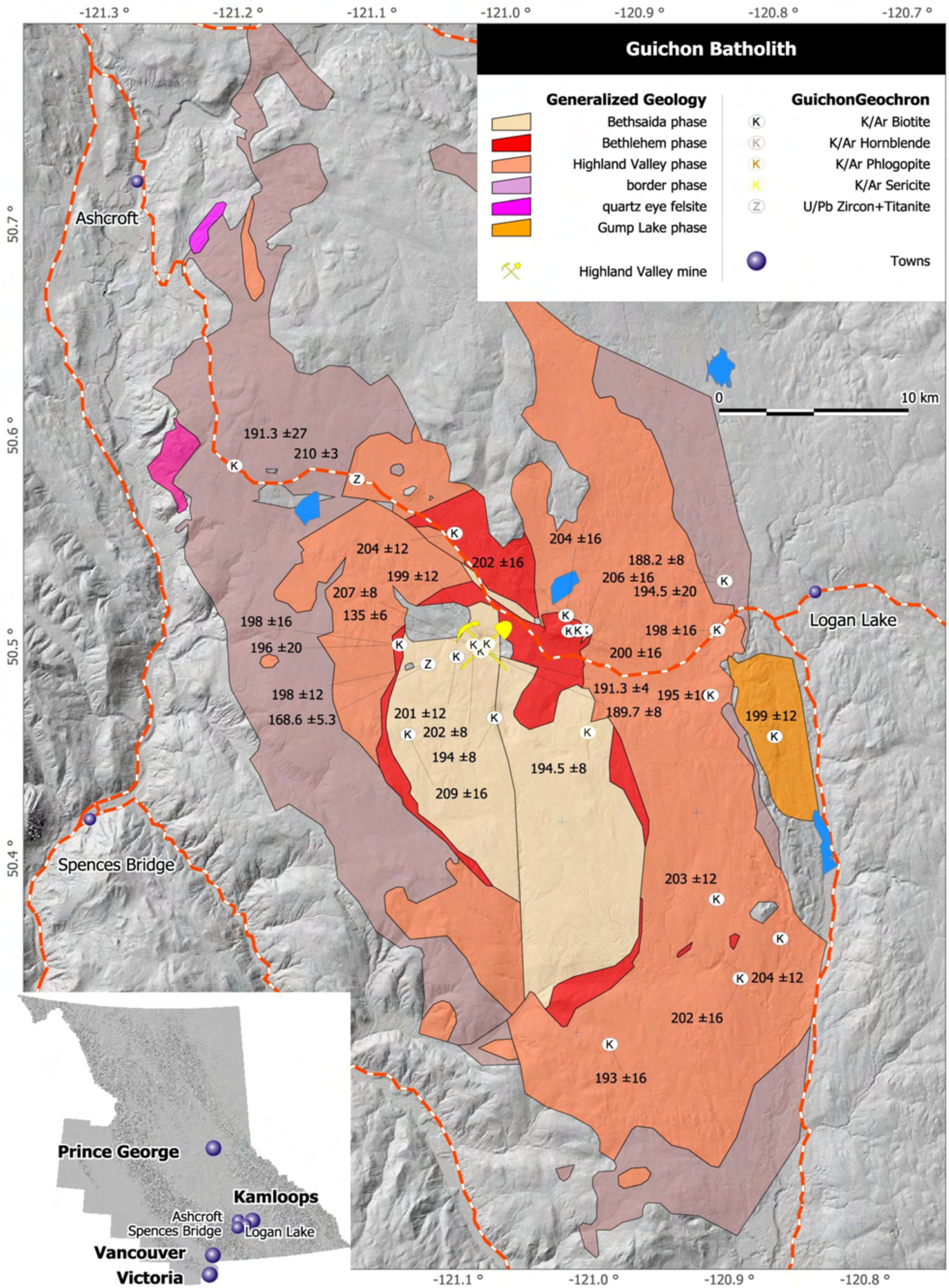

Figure 1. Location and generalized geology of the Guichon batholith. Also shown is the distribution of geochronological data from the batholith and the location of the Highland Valley mine, the collection site of the samples analyzed for this study. Major units and geological contacts are from the compilation of Massey *et al.* (2005); geochronological data are from the compilation of Breitsprecher and Mortensen (2004; 'unreliable' data omitted).

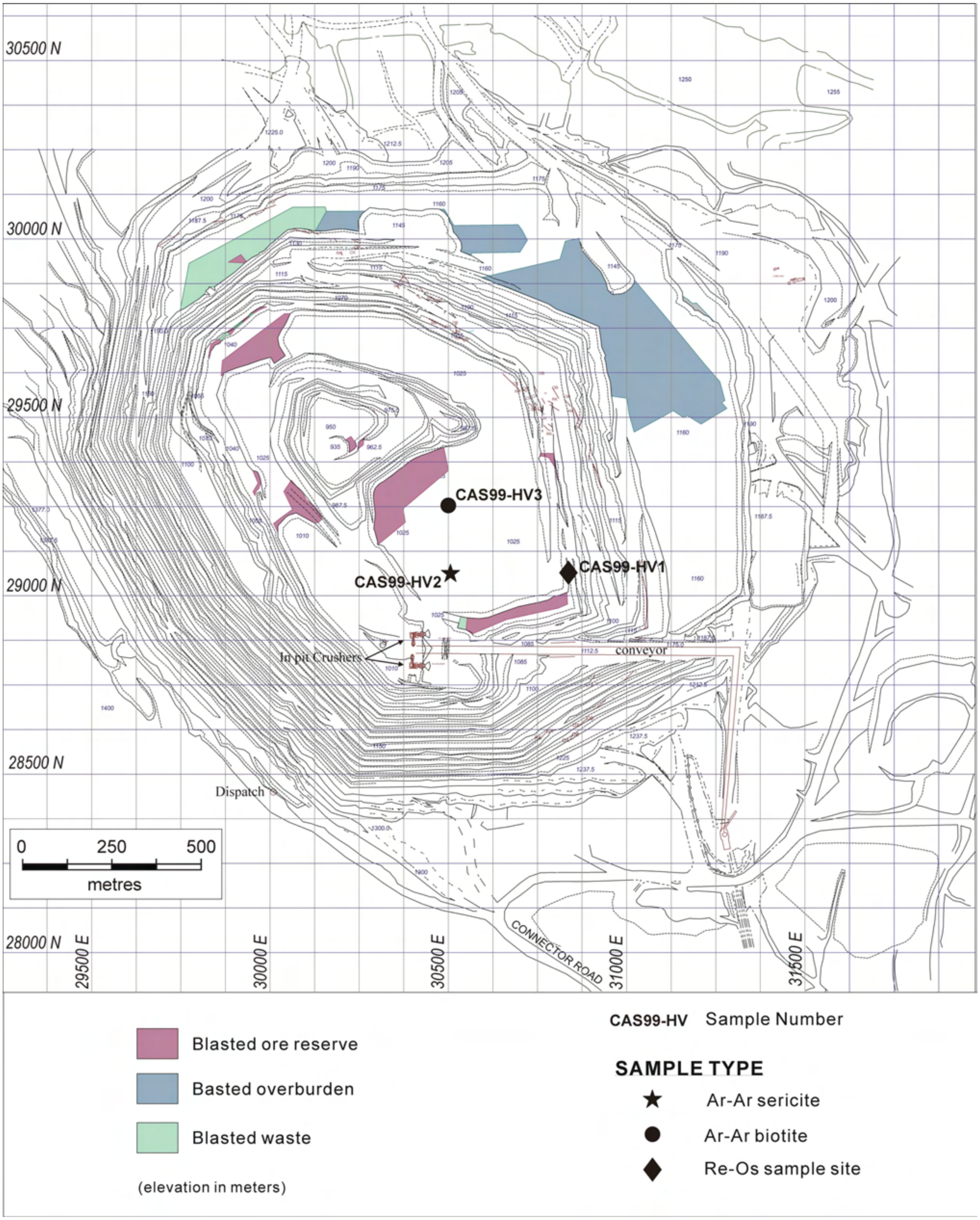

Figure 2. Valley pit, indicating locations of the individual samples dated.

TABLE 1. RE-OS ISOTOPIC DATA FOR AGES FOR MOLYBDENITE, VALLEY PIT, HIGHLAND VALLEY CU-MO DEPOSIT.

Sample	Re (ppm)	^{187}Re (ppm)	^{187}Os (ppb)	Age, with 2σ uncertainty (Ma)
CAS99-HV1a	112.5	70.708	243.92	206.7 ± 1.5
CAS99-HV1b	155.81	97.932	336.36	205.8 ± 1.5

Uncertainty is 2σ (95% confidence). All known sources of uncertainty which affect the age have been fully propagated to calculate the uncertainty estimates, which includes a value of ±0.31% uncertainty for the half-life of ^{187}Re. Age calculated using the decay constant $\lambda^{187}Re = 1.666 \times 10^{-11}$ y^{-1} (Smoliar et al., 1996).

TABLE 2. ^{40}AR-^{39}AR ANALYTICAL DATA FOR MICAS, VALLEY PIT, HIGHLAND VALLEY CU-MO DEPOSIT.

T°C	mV 39	39%	Age (Ma) ±1σ	% ATM	37/39	36/40	39/40	% IIC
600	40.7	2.5	140.9 ± 1.9	23.8	0.04	0.000806	0.023733	0.01
650	78.3	5.0	200 ± 1.4	9.3	0.01	0.000318	0.01956	0
700	12.2	0.7	206.5 ± 4.5	3.1	0.01	0.000106	0.020226	0
750	4.9	0.3	203.4 ± 6.9	2.3	0.01	0.000079	0.020739	0
800	70.5	4.5	205.8 ± 1.2	0.3	0	0.000012	0.020868	0
850	69.0	4.4	206.9 ± 1.2	0.6	0	0.000021	0.020693	0
900	67.0	4.2	207.9 ± 1.2	0.8	0	0.000027	0.020552	0
950	104.6	6.6	210.9 ± 1.1	0.5	0	0.000019	0.020288	0
1000	269.7	17.2	208.3 ± 1	0.3	0	0.000012	0.0206	0
1050	369.7	23.6	206.5 ± 1	0.3	0	0.000013	0.020793	0
1100	306.2	19.5	205.7 ± 1	0.6	0.01	0.000023	0.020805	0
1250	160.4	10.2	206 ± 1	2.8	0.06	0.000096	0.020334	0.01
1450	11.9	0.7	201.7 ± 7.6	49.5	0.33	0.001675	0.010807	0.07

Mean age (800°C - 1450°C) = 206.9 ±2.1 Ma (2σ uncertainty, including error in J)
J = 0.002532 ±0.000025 (0.9 %)
37/39,36/40 and 39/40 Ar ratios are corrected for mass spectrometer discrimination, interfering isotopes and system blanks
% IIC, interfering isotopes correction

T°C	mV 39	39%	Age (Ma) ±1σ	% ATM	37/39	36/40	39/40	% IIC
550	1.5	0	129 ± 29.5	9.9	0.22	0.00034	0.030773	0.07
575	3.1	0.1	144.8 ± 13.1	10.7	0.18	0.000366	0.027037	0.05
600	6.9	0.2	178.2 ± 7.1	6.0	0.35	0.000207	0.022902	0.08
625	12.3	0.4	198.5 ± 4.9	4.5	0.68	0.000155	0.020767	0.15
650	19.4	0.6	197 ± 2.7	3.1	0.66	0.000108	0.021234	0.15
675	30	1	196 ± 1.9	3.3	0.25	0.000114	0.021311	0.05
700	36.5	1.2	197.5 ± 1.7	5.4	0.02	0.000185	0.020685	0
725	47.9	1.6	201.2 ± 1.5	3.9	0	0.000133	0.020607	0
750	62.6	2.1	203 ± 1.3	1.8	0	0.000062	0.020859	0
800	243.6	8.5	204.1 ± 1	2.3	0	0.00008	0.020629	0
850	716.5	25.1	204.3 ± .9	0.6	0	0.000021	0.020978	0
875	406	14.2	204.4 ± .9	0.5	0	0.000017	0.020989	0
900	277.4	9.7	203.9 ± 1	0.6	0	0.000022	0.021008	0
925	189.1	6.6	203.9 ± 1	0.9	0	0.000032	0.020951	0
950	139.1	4.8	204.1 ± 1	0.8	0	0.000029	0.020945	0
975	118.9	4.1	204 ± 1	0.8	0	0.000027	0.020969	0
1000	114.6	4	204.2 ± 1	0.7	0	0.000025	0.020957	0
1050	191.5	6.7	205.6 ± 1	0.5	0	0.000017	0.020853	0
1100	188.3	6.6	205.9 ± 1	0.0	0	0.000003	0.020914	0
1250	37.9	1.3	209.5 ± 1.8	9.6	0.01	0.000325	0.01858	0
1450	2.2	0	346.6 ± 70.4	66.7	0.1	0.002258	0.00398	0.01

Mean age (800°C - 1100°C) = 204.4 ± 2 Ma (2σ uncertainty, including error in J)
J = 0.002532 ± 0.000025 (0 .9 %)
37/39,36/40 and 39/40 Ar ratios are corrected for mass spectrometer discrimination, interfering isotopes and system blanks
% IIC, Interfering isotopes correction

RE-OS DATING OF MOLYBDENITE

Two separate fractions of the Valley pit molybdenite sample (CAS99-HV1a and b) were analyzed at the University of Alberta Radiogenic Isotope Facility in Edmonton, under the supervision of R.A. Creaser. Methods used for molybdenite analysis are described in detail by Selby and Creaser (2001a). The ^{187}Re and ^{187}Os concentrations in molybdenite were determined by isotope dilution mass spectrometry using Carius-tube, solvent extraction, anion chromatography and negative thermal ionization mass spectrometry techniques. Isotopic analysis was made using a Micromass Sector 54 mass spectrometer by Faraday collector. Total procedural blanks for Re and Os are less than 15 and 2 pg (<25 fg ^{187}Os), respectively. These procedural blanks are insignificant in comparison to the Re and Os concentrations in molybdenite. The Chinese molybdenite powder HLP-5 (Markey *et al.*, 1998), which is used as an in-house 'control sample' by AIRIE, Colorado State University, is also routinely analyzed at the University of Alberta. This 'control sample' yielded an average Re-Os date of 220.5 ±0.5 Ma (±0.45% at the 2σ level, n = 17). This Re-Os age is identical to a 221.0 ±1 Ma (±0.4 % at the 1σ level, n = 19) age determined by alkaline fusion (Markey *et al.*, 1998) and two Carius-tube ages of 219.8 ±0.7 and 221.0 ±0.8 Ma (H. Stein, pers comm, 2000).

Re-Os Results

The analytical data and calculated ages for both the initial and repeat analyses of molybdenite sample CAS99-HV1 (a and b) are shown in Table 1. Sample CAS99-HV1a yielded an initial calculated age of 206.7 ±1.5 Ma. This is slightly older than the repeat analysis age of 205.8 ±1.5 Ma, but is equivalent within the stated limits of error.

AR-AR DATING OF MICAS

Two different mica samples, one of sericite (CAS99-HV2) from Cu-Mo-bearing quartz stockwork and a second of coarse, euhedral magmatic biotite (CAS99-HV3), were analyzed at Dalhousie University by the conventional ^{40}Ar/^{39}Ar step-heating method under the supervision of P.H. Reynolds.

Individual grains were hand-picked from each of the samples. These grains were wrapped in aluminum foil and interspersed with three to five aliquots of the flux monitor (the hornblende standard MMhb-1, with an assumed age of 520 ±2 Ma; Samson and Alexander, 1987). The entire package was irradiated in the McMaster University nuclear reactor.

An internal tantalum resistance furnace of the double-vacuum type was used to carry out the step-heating. All isotopic analyses were made in a VG 3600 mass spectrometer.

Ar/Ar Results

The results of the sericite (CAS99-HV2) and magmatic biotite (CAS99-HV3) analyses are given in Tables 2a and b. The sericite sample produced a uniform release spectrum, as shown in Figure 3a. A plateau age of 204 ±2 Ma is defined by 10 steps representing approximately 90% of the total gas released (age uncertainty given is at the 95% confidence limit and includes the uncertainty in the irradiation parameter, J).

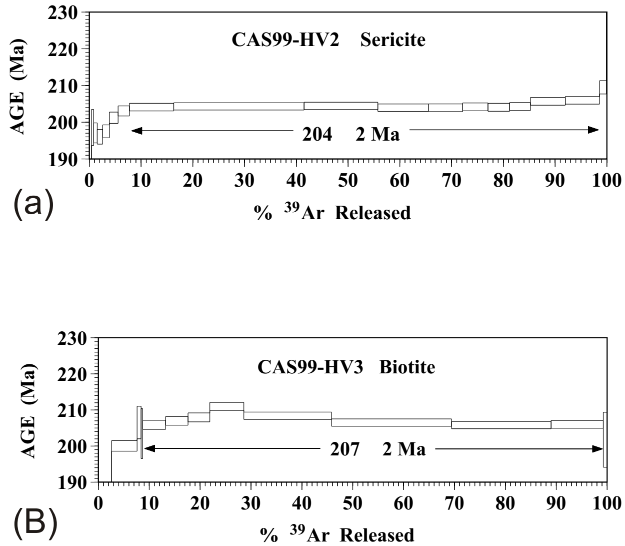

Figure 3. ^{40}Ar/^{39}Ar age spectra plots for a) hydrothermal sericite from Cu-Mo-mineralized quartz stockwork (CAS99-HV1), and b) very coarse grained euhedral biotite from leucocratic quartz diorite of the Guichon Creek batholith (CAS99-HV2).

The spectral plot for the biotite sample is shown in Figure 3b. A plateau age of 207 ±2 Ma is defined by eight steps representing approximately 90% of the total gas released (age uncertainty given is at the 95% confidence limit and includes the uncertainty in the irradiation parameter, J).

DISCUSSION

Rhenium-osmium dating laboratories continue to demonstrate the remarkable robustness of the Re-Os geochronometer. Not only can it withstand post-ore hydrothermal metamorphism (Selby and Creaser, 2001b), but also granulite-facies temperatures (Bingen and Stein, 2002). Therefore, the Re-Os isotopic age determined from the molybdenite veins should record their age of formation, not the age of some later disturbance. The age for molybdenum mineralization at the Highland Valley deposit is indistinguishable from the magmatic crystallization age based

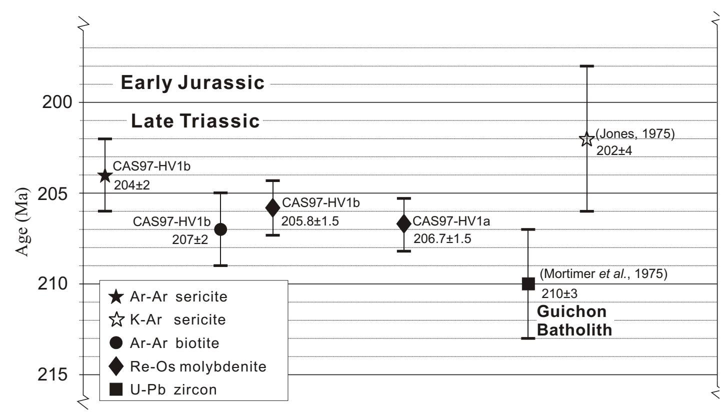

Figure 4. Summary of selected isotopic ages reported for the Highland Valley Cu-Mo deposit. Error bars indicate 2σ uncertainty.

upon the U-Pb zircon data of Mortimer *et al*. (1990; 210 ±3 Ma). Both are Late Triassic, with error envelopes overlapping between 207 and 207.2 Ma (Fig 4). However, at the outer error limits, molybdenite mineralization could be as much as 8.7 m.y. younger than the crystallization age. The age at which the crystallized body cooled through the biotite closure temperature (~350°C for a rapidly cooling body; Harrison *et al.*, 1985) is recorded by the magmatic biotite sample as 207 ±2 Ma. Error limits permit a range of interpretations of the time required to cool through the biotite closure temperature: from instantaneous to approximately 8 m.y. Clearly, more precise geochronometric analyses are required before a definitive history of magmatic crystallization and mineralization can be constructed. In particular, a precise crystallization age for the Bethsaida phase, which hosts the Highland Valley deposit, needs to be determined. It is the youngest of four major intrusive pulses, whereas the crystallization age determination of Mortimer *et al.* (1990) is from a sample of the Highland Valley phase, the second oldest major phase within the Guichon Creek batholith.

When considered in isolation, these new age data constrain the timing of mineralization within the Valley pit to within 3 m.y., between 205 and 207 Ma (age range increases to 6.2 m.y. at the outer limits of the error envelopes). The calculated ages for each of the newly dated minerals appear to follow a sequence that is consistent with the observed textural and crosscutting relationships. Magmatic biotite gives the oldest calculated cooling age (207 ±2 Ma). Molybdenite from veins that crosscut the plutonic host is next in the sequence (206.7 ±1.5 Ma, 205.8 ±1.5 Ma). Sericite is inferred to have formed latest in the magmatic history of the batholith, and returned the youngest age determination (204 ±2 Ma).

Mineralization at the Highland Valley mine, herein dated as between *ca.* 204 and *ca.* 207 Ma, can now be considered as nearly contemporaneous with the *ca.* 204 Ma mineralization in the Iron Mask batholith (60 km to the east), as reported by Logan *et al.* (2007).

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