

Heritage Stone 8. Formation of Pinolitic Magnesite at Quartz Creek, British Columbia, Canada: Inferences from Preliminary Petrographic, Geochemical and Geochronological Studies

Alexandria Littlejohn-Regular, John D. Greenough and Kyle Larson

*Department of Earth Environmental and Geographic Sciences, University of British Columbia Okanagan
3333 University Way, Kelowna, British Columbia, V1V 1V7, Canada
E-mail: john.greenough@ubc.ca*

Appendix A: Detailed Analytical Methods (for on-line repository)

Tables 1 and 4, cited below, can be viewed by accessing the Littlejohn-Regular et al. 2021 paper in Geoscience Canada.

Specimens

Thin sections and rock powders were prepared by cutting specimens on a rock saw and grinding on a diamond lap to remove cut, weathered and altered surfaces. Specimens were then washed in tap water, rinsed in double distilled and deionized water and sent for thin sectioning at U.

Western Ontario.

Whole Rock Analyses

Analyses of specimens PIN 1 through 5 were performed at ACME Analytical Laboratories, Vancouver. Specimens, all of which weighed > 200 g, were crushed with > 70% passing a 2mm sieve and a 250 g split pulverized so > 85% passed a 75 µm sieve. Powdered specimen weighing 0.2 g was fused in a graphite crucible with 1.5 g of LiBO₂/Li₂B₄O₇ flux at 980°C for 30 minutes and bead dissolution in 100 ml of 5% ACS grade HNO₃. The major element oxides, along with Ba, Ni and Sc, were analyzed by ICP-ES (Inductively Coupled Plasma – Emission Spectroscopy) and most trace elements by ICP-MS (ICP – Mass Spectrometry). Aqua Regia leach was used to determine the remaining trace elements (Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl and Se), wherein 0.5 g of sample was digested for one hour in a solution of equal parts concentrated

HCl, HNO₃ and deionized H₂O at 95°C. The sample was then made up to a final volume containing 1 g of sample per 20 ml of solution using 5% HCl and then analyzed by ICP-MS. Total carbon and sulphur were determined using the Leco method, which involves adding a flux, igniting in an induction furnace, and measuring by adsorption in an infrared spectrometric cell. Loss on ignition (LOI) was determined on a specimen powder split by igniting at ~1000°C and measuring weight loss. Precision and accuracy were estimated from replicate analyses of trachyandesite reference material SO-19 (most elements), GS311-1 for total C and S, and DS11 for Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl and Se. Elements below the detection limit in greater than three specimens (Cr, Ni, Sc, Be, Sn, Ta, V, S, Mo, Zn, Cd, Bi, Ag, Au, Hg, Tl and Se) are not reported. Both precision and accuracy can be summarized as better than 2% for most major element oxides with most trace elements better than 5% except, Sb and W are 8.9% and 25% respectively (Table 1).

Optical and Scanning Electron Microscopy

Polished thin sections were examined using a petrographic microscope under reflected, plane-polarized and cross-polarized light. Scanning electron microscope (SEM) imaging was performed using a Tescan Mira 3 XMU SEM equipped with an Oxford Aztec X-Max EDS (energy dispersive spectrometer) operated at an accelerating voltage of 20 kV at the University of British Columbia (UBC) Okanagan, Fipke Laboratory for Trace Element Research (FiLTER). Prior to analysis, thin sections were carbon-coated using a Cressington sputter coater. Backscatter electron mode (BSE) provided imaging and Aztec analysis software was used for semi-quantification of elemental spectra. Approximately 123 analyses were completed and used to aid in mineral identification.

Electron Microprobe Analysis (EMPA)

Quantitative major element mineral compositions were obtained for specimens PIN 2, 3, 4 and 5 using a Cameca SX Five field emission EMP at FiLTER using Micro-Analysis Consultants Ltd. (MAC) reference materials for calibration: Si, Mn - garnet spessartine, Ti - sphene, Al, Fe - almandine garnet, Ca - wollastonite, Na - albite, Mg - diopside, K - orthoclase, P – apatite. The electron microprobe was operated in wavelength dispersive mode (WDS), at 15kV accelerating voltage with a beam current of 20 nA and a beam size of 2 μm . Precision and accuracy can be summarized as +/- 2% for all major elements.

LA ICP-MS Mineral Trace Element Analyses

Two specimens (PIN 3 and PIN 5) were selected for trace element analysis of minerals using an Agilent 8900 Triple Quadrupole ICP-MS operated in no gas mode, in conjunction with a Photon Machines Analyte 193 Excimer laser at FiLTER. Analyses were performed on in-situ minerals in polished thin sections. The ICP-MS (Ni cones) was tuned for maximum signal (Pb, Th, U), U/Th parity on NIST 610, minimum oxide formation (ThO %) and operated in low resolution mode (maximum sensitivity) at a RF power of 1550 W. Gases used are: Ar auxillary gas at 1L/min, Ar sample gas at 0.9 L/min, ultra-high-pure (UHP) laser He carrier gas at 0.6 L/min. and the beam train purge gas was UHP N₂. Elements selected for analysis are As, Rb, Sr, Sb, Ba, Pb, Th, U, the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) plus Y, the high-field strength elements (Zr, Nb, Hf, Ta) and transition metals (Sc, V, Cr, Mn, Co, Ni, Cu, Zn). Laser pulses were applied with a repetition rate of 6 Hz, a fluence of 4.95 J cm⁻², spot size of 40 μm , energy set-point of 5MJ, laser energy = 83% and voltage at 13 kV. Reference material

and mineral analyses involved 40s of background collection and 40s of analysis. Raw data were converted into final concentrations using Iolite (Paton et al. 2011) with Mg (wt. %), by electron microprobe analysis, as the internal standard. NIST 610 (8 analyses) acted as the external standard and instrument performance, precision and accuracy were monitored by 8 replicate analyses of NIST 612. Precision and accuracy are better than 2% for Cr, As, Tb, Ho, Tm, Lu, Hf and U, better than 5% for Ni, Cu Zn, Rb, Y, Zr, Ce, Pr, Gd, Dy, Er, Yb, Hf, Pb and Th, better than 10% for V, Mn, Co, Sr, Nd, Sm, and Eu, better than 15% for Sb and La, and better than 25% for Nb, Ba and Ta.

LA-ICP-MS Titanite Dating

Titanite from specimen PIN 4, was dated, *in situ*, via laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) at FiLTER, UBC Okanagan. Instrumentation includes a Photon Machines Analyte 193 Excimer laser coupled to an Agilent 8900 triple quadrupole ICP-MS. The setup was optimized before each analytical run using the Standard Reference Material 'NIST610' to maximize signal while maintaining a $^{238}\text{U}/^{232}\text{Th}$ ratio within 3% of the certified value. Helium, at a rate of 0.7 L/min, was used as the ablation cell carrier gas. It was mixed with Ar (0.9 L/min) before the plasma using an in-house glass mixing valve/signal smoothing device. Dwell times of 50 ms were used for U and Pb isotopes. The laser was operated with a spot size of 30 μm at a repetition rate of 8 Hz and a fluence of 5 J/cm². Each spot was pre-ablated with two laser bursts to clear the surface followed by a 30 second delay and then 30 seconds of ablation. Unknown analyses were bracketed with known standards (as described in the main text) to quantify potential instrument drift during the analysis session. Isotope ratios were corrected for drift and downhole fractionation using the primary reference material, titanite MKED1 ($^{206}\text{Pb}/^{238}\text{U}$ age of 1517.32 ± 0.32 Ma; Spandler et al., 2016) and processed using the Iolite software package (Paton et al. 2010,

2011) v. 4.3.8. Secondary reference materials ‘Fish Canyon’ (Lanphere and Baadsgaard 2001; Kuiper et al. 2008) and ‘Mount McClure’ (Schoene and Bowring 2006) were analyzed to monitor and verify analytical procedures and resulting data. The resulting ^{207}Pb corrected $^{206}\text{Pb}/^{238}\text{U}$ weighted mean ages of the secondary reference materials are within systematic uncertainty (2%) of accepted values. Eight repeat analyses of Fish Canyon yielded a ^{207}Pb corrected $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 27.9 ± 1 Ma (mean square weighted distribution (MSWD) = 0.99; accepted age of 28.201 ± 0.012 Ma) while 8 repeat analyses of Mount McClure yielded a ^{207}Pb corrected $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 528 ± 5 Ma (MSWD = 0.65; accepted age of 523.51 ± 1.47 Ma). The full data set (unknowns and standards) is given in manuscript Table 4. All geochronology plots were made with the open source R package, ChrontouR v. 1.2.3 (Larson 2020).

REFERENCES

- Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., and Wijbrans, J.R., 2008, Synchronizing rock clocks of Earth history: *Science*, v. 320, p. 500–504, <https://doi.org/10.1126/science.1154339>.
- Lanphere, M.A., and Baadsgaard, H., 2001, Precise K–Ar, $^{40}\text{Ar}/^{39}\text{Ar}$, Rb–Sr and U/Pb mineral ages from the 27.5 Ma Fish Canyon Tuff reference standard: *Chemical Geology*, v. 175, p. 653–671, [https://doi.org/10.1016/S0009-2541\(00\)00291-6](https://doi.org/10.1016/S0009-2541(00)00291-6).
- Larson, K.P., 2020, ChrontouR: Geochronology contouring plots in R (Software): OSFHOME, Center for Open Science, <https://doi.org/10.17605/OSF.IO/P46MB>.
- Paton, C., Woodhead, J.D., Hellstrom, J.C., Hergt, J.M., Greig, A., and Maas, R., 2010, Improved laser ablation U–Pb zircon geochronology through robust downhole fractionation

correction: *Geochemistry, Geophysics, Geosystems*, v. 11, Q0AA06,
<https://doi.org/10.1029/2009GC002618>.

Paton, C., Hellstrom, J., Paul, B., Woodhead, J., and Hergt, J., 2011, Iolite: Freeware for the visualisation and processing of mass spectrometric data: *Journal of Analytical Atomic Spectrometry*, v. 26, p. 2508–2518, <https://doi.org/10.1039/c1ja10172b>.

Schoene, B., and Bowring, S.A., 2006, U–Pb systematics of the McClure Mountain syenite: thermochronological constraints on the age of the $^{40}\text{Ar}/^{39}\text{Ar}$ standard MMhb: *Contributions to Mineralogy and Petrology*, v. 151, 615, <https://doi.org/10.1007/s00410-006-0077-4>.

Spandler, C., Hammerli, J., Sha, P., Hilbert-Wolf, H., Hu, Y., Roberts, E., and Schmitz, M., 2016, MKED1: A new titanite standard for in situ analysis of Sm–Nd isotopes and U–Pb geochronology: *Chemical Geology*, v. 425, p. 110–126,
<https://doi.org/10.1016/j.chemgeo.2016.01.002>.