Petrology of explosive Middle-Upper Triassic ultramafic rocks in the Mess Creek area, northern Stikine terrane

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Abstract
The Mess Lake facies of the Stuhini Group (Middle to Upper Triassic) in northwestern British Columbia includes a unit of pervasively serpentinized, olivine-rich, subaqueous lapilli breccia, lapilli tuff, and ash tuff. Relatively high whole-rock MgO concentrations (29-38 wt.%; loss on ignition-free) of pyroclastic samples from this unit reflect significant accumulation of olivine. These ultramafic pyroclastic rocks also exhibit strong enrichment in Ba and depletion in Nb+Ta relative to La, consistent with derivation from slab-metasomatized mantle asthenosphere in a volcanic arc setting. The restored parental liquid is a primitive, mantle-derived, arc magma that contained up to 16-20 wt.% MgO. The unit contains fresh volcanic glass indicating low-grade regional metamorphism, and suggesting that it postdates emplacement of the nearby Hickman pluton, which yielded 40Ar/39Ar hornblende ages of 222.2 ±2.8 Ma, 221.6 ±2.5 Ma, and 220.1 ±2.7 Ma. The Alaskan-type ultramafic plutons of the Polaris suite (Middle to Late Triassic) and a post-Hickman basaltic diatreme, containing picritic fragments, are spatially associated and broadly coeval with the ultramafic pyroclastic rocks of the Mess Lake facies, but a petrogenetic link has yet to be established.

Keywords: Stuhini Group, Triassic, pyroclastic, ultramafic, Stikinia

1. Introduction
The Stikine terrane (Stikinia) of the Canadian Cordillera (Fig. 1) is a Mesozoic volcanic arc (see Nelson et al., 2013 for recent overview) that hosts over 1000 Cu ±Au-Mo-Ag porphyry occurrences (British Columbia Geological Survey, 2015; Yukon Geological Survey, 2015). Logan and Mihalynuk (2014) estimated that ≥90% of the Cu mineralization in the Stikine and adjacent Quesnel terrane to the east formed during a relatively short-lived (~6 m.y.) mineralizing epoch centred at ~205 Ma, which spans the Triassic-Jurassic boundary. This episode of porphyry mineralization has been attributed to a thermal spike in the underlying mantle wedge that resulted in mobilization of hydrous, metal-rich fluids. Logan and Mihalynuk (2014) attributed the elevated geothermal gradient to arc-parallel tearing of the Panthalassan oceanic plate as it subducted beneath Stikinia at ~210 Ma, based on the appearance of rare, strongly alkaline lavas and ultramafic (picritic) rocks. In the Mess Lake area, ~130 km southwest of the town of Dease Lake, ultramafic olivine-rich pyroclastic tuff forms the base of the Mess Lake volcanic facies (Logan et al., 2000) of the Stuhini Group (Middle to Upper Triassic), mainly along the eastern margin of the Hickman pluton (Fig. 2). Possibly related to these pyroclastic rocks are the broadly coeval, spatially associated ultramafic intrusions of the Polaris suite (Middle to Late Triassic; Nixon et al., 1989; Logan and Koyanagi, 1994; Brown et al., 1996), which border the Hickman pluton. Establishing a genetic and temporal relationship between the Middle to Late Triassic ultramafic rocks would add further credence to the

Fig. 1. Terrane map of the northern Canadian Cordillera showing the location of the study area (modified from Nelson et al., 2013).
Fig. 2. a) Simplified geological map of the Mess Lake area (parts of NTS 104G 02, 03, 06, 07, 10, and 11; modified from Logan et al., 2000 and Mihalynuk et al., 1996), showing the Schaft Creek exploration camp and locations of samples analyzed for geochemistry (1-11; Table 2) and ⁴₀Ar/³⁹Ar geochronology (yellow stars). Key locations discussed in the paper are labeled A-E. b) Schematic stratigraphic column illustrating the relationships between stratigraphic and intrusive units in the study area.
Kilometres

Universal Transverse Mercator grid zone 9
NAD 1983 datum
Contour interval = 250 m

40Ar/39Ar dating site
Location of samples collected between 2009 -2011 (see table 1 for UTM coordinates and geochemical data)

**Legend**
**INTRUSIVE**
*Paleocene to Eocene*
- PeEd: biotite, sphene +/- hornblende granodiorite

*Middle Jurassic*
- MJSt: 3 Sisters suite - tonalite
- LDF: Forrest Kerr suite - biotite granite to tonalite

*Late Triassic to Early Jurassic*
- LTrJm: Loon Lake stock - quartz monzonite
- LTrS: Stikine assemblage

*Middle Triassic to Late Triassic*
- MLTrS: Polaris suite - dunitic, olivine pyroxenite, gabbronorite
- MLTrP: Middle to Upper Triassic

*Late Devonian*
- LEd: Forest Kerr suite - biotite granite to tonalite

*Early Devonian*
- EEd: Foliated to equigranular green chloritic pyroxene diorite

**STRATIFIED**
*Holocene*
- HoB: Big Raven Formation - Alkaline olivine basalt and hawaiite

*Miocene to Holocene*
- MQ: Mount Edizzi Complex - trachyte to alkaline olivine basalt and hawaiite, flows and breccias

*Lower to Upper Cretaceous*
- LTrS: Sustus Group - chert-pebble conglomerate, quartz sandstone, siltstone, and carbonaceous shale

**Middle Jurassic to Middle Cretaceous**
- MTrJ: Bowser Lake Group - greywacke, shale, local chert-pebble conglomerate and granule conglomerate lenses

**Lower Jurassic to Middle Jurassic**
- MTrJ: Hazleton Group - Marine epiclastic and volcanic, and coarse clastic (conglomerate, grit, greywacke) rocks

**Middle to Upper Triassic**
- MTrS: Stuhini Group - Mess Lake facies - mafic to intermediate lapilli tuff, lesser ash, breccia & tuffite, Green and maroon, massive plagioclase and olivine-plagiophytic basaltic flows, sills and dykes, Episolastic sandstone interbedded with conglomerate

**Devonian to Lower Permian**
- DTrS: Stikine assemblage - foliated Paleozoic volcanic, clastic, and carbonate rocks

**KEY UNITS**

- **A** Hickman pluton - Stikine suite
- **B** Mess Lake facies ultramafic tuff (Fig. 3)
- **C** Mt. Hickman ultramafic complex - Polaris suite
- **D** Middle Scud ultramafite - Polaris suite
- **E** Yehinko ultramafite - Mess Creek facies ultramafic tuff

*Location of samples collected between 2009 -2011 (see table 1 for UTM coordinates and geochemical data)*

*40Ar/39Ar dating site*
We conclude that the ultramafic rocks that are cut by coeval plutonic rocks. Paleozoic rocks of the Stuhini Group deposition is marked by termination of magmatism, (see Discussion). The end of Triassic arc building and Stuhini Group contains voluminous augite and/or plagioclase porphyritic basalt and andesite that are coeval with Carnian to Norian (Fig. 2), where they form a 3-5 km long semi-continuous unit that is ≤100 m thick. Although the ultramafic rocks appear to have served as a locus for late brittle faulting and veining, thick sections are relatively undisturbed. One sub-vertical cliff face exposes a section ~35 m thick (Fig. 3a), cut by a thin (<1 m) hornblende-phryic basaltic dike with chilled margins (Fig. 3b). The outcrop exposes four fining-upward sequences, in which beds, normally graded from tuff breccia to olivine lapilli tuff, are capped by units of rhythmically stratified ash tuff (Figs. 3-5). Each fining-upward sequence has a sharp base, locally marked by low-amplitude scouring of underlying ash tuff, and may record a separate eruption event. The contact between fine lapilli tuff and overlying rhythmically-stratified ash tuff is gradational in all cases. The bomb and lapilli-sized fragments contain abundant black-weathering, euhedral to subhedral, serpentine-after-olivine pseudomorphs and have cuspatate to embayed margins (Fig. 4a), suggesting minimal deformation during and since deposition. Lapilli are typically vesicular although, in some cases, the internal vesicular microstructure

2. Geological background

The Stikine terrane is a composite volcanic arc comprising Devonian to Jurassic volcanic and sedimentary assemblages that are cut by coeval plutonic rocks. Paleozoic rocks of the Stikine assemblage (Monger, 1977) record the first of three episodes of island-arc formation. The second and third episodes are represented by two unconformity-bound Middle Triassic-Lower Jurassic successions: 1) the Stuhini Group (Middle-Upper Triassic), which consists predominantly of subaqueous, mafic to felsic volcanic and related sedimentary rocks; and 2) the Hazelton Group (Lower-Middle Jurassic) comprising subaqueous to subaerial, volcano-sedimentary rocks (Brown et al., 1996; Logan et al., 2000; Barresi et al., 2015). The Stuhini Group contains voluminous augite and/or plagioclase porphyritic basalt and andesite that are coeval with Carnian to Rhaetian sedimentary rocks (Souther, 1977; Logan et al., 2000; Mihały, 1999; Logan and Iverson, 2013). Logan et al. (2000) reported that aplitic dikes extend outward from a hornblende biotite granodiorite to quartz monzonite intrusion on the east-facing slope above Mess Creek and cut the Mess Lake facies of the Stuhini Group. They correlated this plutonic body with the main phase of the Hickman pluton (~221 Ma; Holbe, 1988; this study), implying that the Mess Lake facies is older than ~221 Ma, which may be at odds with our results (see Discussion). The end of Triassic arc building and Stuhini Group deposition is marked by termination of magmatism, deposition of Late Norian to Rhaetian limestones (Sinwa Formation), and deformation.

Plutonic suites coeval with arc volcanism include Forrest Kerr (Late Devonian), More Creek (Early Mississippian), Stikine, Polaris, and Copper Mountain (Late Triassic), Texas Creek, Aishihik, and Long Lake (Early Jurassic), and Three Sisters (Middle Jurassic; Logan et al., 2000; Zagorevski et al., 2014). The Hickman pluton in the eastern half of the study area (Fig. 2) is a composite intrusion and part of the Stikine Suite (Brown et al., 1996; Logan et al., 2000).

2.1. Late Triassic ultramafic magmatism

The Stuhini Group consists mainly of basaltic to andesitic volcanic rocks that are accompanied by rare felsic volcanic rocks. Ultramafic volcanic rocks are volumetrically minor, but seem to be distributed throughout northwestern Stikinia, including the Mess Lake, Telegraph Creek, Endeavour Mountain, and Atlin Lake areas (Brown et al., 1996; Mihały, 1999; Logan et al. 2000). In the Mess Creek area, ultramafic volcanic rocks of the Mess Lake facies unconformably overlie Permian Stikine assemblage limestone and are overlain by massive plagioclase-phryic basalts, massive to weakly stratified mafic tuffs, and plagioclase + augite-phryic basaltic andesite.

In addition to these ultramafic pyroclastic deposits, ultramafic plutonic rocks of the Polaris suite, described as Alaskan-type intrusions by Nixon et al. (1989), also occur along the margins of the Hickman batholith (Fig. 2). These ultramafic intrusions comprise chromite-bearing serpentinitized dunite and clinopyroxenite (+olivine), and include the Hickman ultramafic complex and Middle Scud ultramafite (Nixon et al., 1989; Brown et al., 1996). Brown et al. (1996) reported a third ultramafic pluton on the western side of the batholith, named the Yehiniko ultramafite.

2.1.1. Ultramafic tuff of the Stuhini Group

The Stuhini Group ultramafic pyroclastic rocks are well exposed ~12 km south-southeast of the Schaft Creek camp (Fig. 2), where they form a 3-5 km long semi-continuous unit that is ≤100 m thick. Although the ultramafic rocks appear to have served as a locus for late brittle faulting and veining, thick sections are relatively undisturbed. One sub-vertical cliff face exposes a section ~35 m thick (Fig. 3a), cut by a thin (<1 m) hornblende-phryic basaltic dike with chilled margins (Fig. 3b). The outcrop exposes four fining-upward sequences, in which beds, normally graded from tuff breccia to olivine lapilli tuff, are capped by units of rhythmically stratified ash tuff (Figs. 3-5). Each fining-upward sequence has a sharp base, locally marked by low-amplitude scouring of underlying ash tuff, and may record a separate eruption event. The contact between fine lapilli tuff and overlying rhythmically-stratified ash tuff is gradational in all cases. The bomb and lapilli-sized fragments contain abundant black-weathering, euhedral to subhedral, serpentine-after-olivine pseudomorphs and have cuspatate to embayed margins (Fig. 4a), suggesting minimal deformation during and since deposition. Lapilli are typically vesicular although, in some cases, the internal vesicular microstructure.
Logan et al. (2000) described the Stuhini Group ultramafic rocks as largely altered to serpentine, chlorite and talc. Most lapilli consist of olivine, pseudomorphed by serpentine ± magnetite and calcite (Fig. 6) in a fine-grained brown groundmass of chlorite, sericite, and other clay minerals; the lapilli float in a matrix of serpentinized olivine, devitrified ash, and chlorite. Less commonly, lapilli are composed entirely of vesicular palagonitized glass (scoria; Fig. 6e). Clinopyroxene is sparse, as are clasts of non-cognate lithologies. Despite pervasive alteration, most ash tuff samples contain bubble-wall shards of partially palagonitized to fresh glass (Fig. 6b).

Brown et al. (1996) mapped ultramafic cumulate rocks at the margin in the Hickman batholith in the Telegraph Creek area, in the northwestern corner of the study area (Yehiniko ultramafite; Fig. 2). Reconnaissance sampling in 2010 indicated that some of these rocks are ultramafic lapilli tuff rather than intrusive rocks. Detailed investigation of the Yehiniko ultramafic body, conducted during this study, revealed abundant ultramafic pyroclastic rocks with ubiquitous, relict olivine (Fig. 6f). Brown et al. (1996) also described other occurrences of Upper
Triassic or older ultramafic volcanic rocks in the Endeavour Mountain area, ~30 km east-northeast of Schaft Creek (Fig. 2), supporting the idea of widespread ultramafic volcanism in northwestern Stikinia.

2.1.2. The Hickman pluton

The Hickman pluton of the Stikine suite consists mainly of massive to weakly-foliated, medium grained, equigranular, hornblende biotite granodiorite to quartz monzonite with subordinate tonalite and quartz diorite (Brown et al., 1996; Logan et al., 2000). The pluton also contains gabbroic and dioritic phases. Potassium-argon and Rb-Sr geochronology on biotite and hornblende suggests a minimum emplacement age of ~221 Ma for the Hickman pluton (Holbek, 1988; Brown et al., 1996). At the Schaft Creek deposit, quartz and feldspar-porphyrritic apophyses of the Hickman pluton, with a U-Pb zircon age of 220 +15/-2 Ma (Logan et al., 2000) cut Stuhini Group country rocks and are associated with mineralization. At its southern limit of exposure, the Hickman pluton is cut by a mafic diatreme breccia of unknown age. The breccia consists of cm- to dm- sized hydrothermally altered granitoid and mafic volcanic clasts in a fine-grained plagioclase-phyric basaltic matrix. The mafic volcanic population includes fragments of augite and olivine (now largely chlorite)-phyric basalt/picrite, which we sampled due to its primitive mineralogy and composition, and possible genetic ties to ultramafic rocks of the Mess Lake facies and/or Polaris suite.

2.1.3. Ultramafic cumulate rocks of the Polaris suite

Evaluating the possibility of a genetic relationship between the Middle to Late Triassic ultramafic intrusions of the Polaris suite (Nixon et al., 1989; Brown et al., 1996) and the ultramafic pyroclastic rocks of the Stuhini Group is important for understanding the extent, timing and duration of the Middle to Late Triassic magmatism in northwestern Stikinia. The Mount Hickman ultramafic complex, on the southeastern margin of the Hickman pluton (Fig. 2), consists mainly of olivine-clinopyroxenite and gabbro; serpentinitized dunite is locally
exposed on its southern and northern flanks. The Middle Scud body on the west side of the Hickman pluton, ~15 km west of Mount Hickman ultramafic complex, contains sheared and pervasively serpentinized biotite-rich peridotite.

**3. Methods**

### 3.1. $^{40}$Ar/$^{39}$Ar methodology

Laser $^{40}$Ar/$^{39}$Ar step-heating analysis was carried out at the Geological Survey of Canada Noble Gas laboratory in Ottawa, Ontario. Unaltered pieces (0.25-1.0 mm) of hornblende were picked from four gabbroic to granodioritic samples of the Hickman pluton (Stikine suite). Individual hornblende separates were loaded into aluminum foil packets along with grains of Fish Canyon Tuff Sanidine (FCT-SAN) to act as flux monitor (apparent age = 28.201 ± 0.023 Ma; 1σ, Kuiper et al., 2008). The sample packets were arranged radially inside a copper canister. The samples were submitted for a 60 MWh irradiation in high flux position 5c at the research reactor of McMaster University in Hamilton, Ontario, Canada.

Upon return from the reactor, samples were split into one or more aliquots each and loaded into individual 1.5 mm-diameter holes in a copper planchet. The planchet was then placed in the extraction line and the system evacuated. Heating of individual sample aliquots in steps of increasing temperature was achieved using a Merchantek MIR10 10W CO$_2$ laser equipped with a 2 mm x 2 mm flat-field lens. The released Ar gas was cleaned in the extraction line over two hot SAES™ NP-10 getters of St 707 alloy (Zr-V-Fe) held at ~400°C (to remove nitrogen, oxygen, hydrocarbons, water and other active gases) and a room-temperature getter containing HY-STOR® 201 calcium-nickel alloy pellets (to remove hydrogen), and then analyzed isotopically using a Nu Instruments Noblesse noble gas mass spectrometer, equipped with a Faraday detector and three ion counters. For the first aliquots of each sample, the analyses were run in single ion counter peak-hopping mode for small signals (‘SC’ mode as described in Kellett and Joyce, 2014), and in cases where the $^{40}$Ar signal exceeded ion counting tolerance, a Faraday plus single ion counter peak-hopping routine was used. For Aliquot #2 of sample ZE09-059A all steps were run in ion counter multi-collection mode (‘MC-Y’ mode of Kellett and Joyce, 2014), except for the 7.5W step for which the $^{40}$Ar signal exceeded the ion counter tolerance. This step was run using full multi-collection mode (‘MC-O’ mode of Kellett and Joyce, 2014). Baselines were measured before each analysis. Blank measurements were made throughout the analytical sessions (Table 1). Mass fractionation and detector efficiencies were determined from repeated measurements of air aliquots, whereby $^{40}$Ar and $^{36}$Ar signals were measured on all collectors. $^{40}$Ar/$^{36}$Ar ratios were then determined for each collector individually, and for each combination of collectors (excluding $^{40}$Ar on the Faraday/$^{36}$Ar on each ion counter). Raw data from the mass spectrometer were processed using in-house Excel® data handling macros that use average, linear or non-linear regression protocols based on the equations of Koppers (2002).

Error analysis on individual steps follows numerical error analysis routines outlined in Scaillet (2000); error analysis on grouped data follows algebraic methods of Roddick (1988). Corrected argon isotopic data are listed in Table 1, and presented in Figure 7 as spectra of gas release or inverse-isochron plots per Roddick et al. 1980. In the case of sample ZE09-059A for which two aliquots were run, the spectrum plotted contains step-heating data from both aliquots, alternately shaded and normalized to the total volume of $^{39}$Ar released for each aliquot. Such plots provide a visual image of replicated heating profiles, evidence for $^{40}$Ar-loss in the low temperature steps, and the error and apparent age of each step. Reported plateau ages are defined as ages derived from three or more consecutive heating steps that are statistically equivalent, and comprise greater than 50% of the total $^{39}$Ar released. MSWD is defined as the mean square of weighted deviates.

Neutron flux gradients throughout the sample canister were evaluated by analyzing the FCT-SAN sanidine flux monitors included with each sample packet and interpolating a linear
Fig. 6. a) Cross-polarized photomicrograph of a lapilli composed of mm-scale pervasively serpentinized olivine (Srp) that contains fine euhedra of magnetite set in a scoriaceous, very fine-grained groundmass of devitrified glass. Sample 1. b) Plane-polarized light image of an ash tuff at the top of fining-upward sequence 1 (Figs. 3 and 5). Concavo-convex, bubble-wall shards of clear to light brown, partially palagonitized, glass (Gl) comprise >40% of the rock. c) and d) Plane and cross-polarized images of a vesicular lapilli tuff (Sample 4). Olivine, both as part of larger lapilli or as individual crystals has been completely replaced by serpentine, magnetite, and calcite. Dashed pink line in c) outlines the margin of a ~2 mm lapilli. e) Plane-polarized light image of a palagonitized lapillius of scoria (dark brown outlined by dashed pink line) in crystal-rich ash tuff at the top of fining-upward sequence 4. f) Cross-polarized photomicrograph of a lapilli tuff from the Yehiniko occurrence, previously interpreted as a Polaris suite intrusion. Although the sample has been extensively altered to serpentine (after olivine), sercite, and chlorite, relict fresh olivine is abundant. Cal: calcite, Chl: chlorite, Mag: magnetite, Ol: olivine, Ser: sercite, Serp: serpentine, V: vesicle (now infilled by chlorite).
Table 1: CO₂ laser step-heating ⁴⁰Ar/³⁹Ar data. All uncertainties quoted at 2σ unless otherwise indicated.

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Table 1. Continued.

| Power* | Volume 1/104 cc | \(^{39}\text{Ar}/^{36}\text{Ar}\) ± | \(^{39}\text{Ar}/^{39}\text{Ar}\) ± | \(^{40}\text{Ar}/^{36}\text{Ar}\) ± | \(f_{m}^{*}\) | App. Age ± | Inverse Isochron Data |
|--------|-----------------|----------------|----------------|----------------|----------------|----------------|------------------|------------------|------------------|
| 3.0    | 0.0006          | 0.2019 ± 0.0013 | 2.853 ± 0.351 | 0.588 ± 0.026 | 93.165 ± 3.430 | 64.0 ± 33.495 | 594.1 ± 3.298 | 98.9 ± 63.1 | 0.0170 ± 0.0018 |
| 3.5    | 0.0004          | 0.1784 ± 0.0020 | 3.403 ± 0.511 | 0.187 ± 0.022 | 72.391 ± 4.390 | 72.0 ± 30.253 | 82.6 ± 2.514 | 95.1 ±  **#** | 0.0138 ± 0.0027 |
| 3.9    | 0.0006          | 0.0759 ± 0.0015 | 2.685 ± 0.350 | 0.440 ± 0.002 | 41.683 ± 2.692 | 17.6 ± 32.469 | 5.024 ± 0.259 | 69.3 ±  **#** | 0.0289 ± 0.0032 |
| 4.2    | 0.0002          | 0.0982 ± 0.0035 | 0.629 ± 0.785 | 0.019 ± 0.029 | 42.581 ± 6.658 | 68.3 ± 13.496 | 13.367 ± 0.171 | 160.9 ±  **#** | 0.0235 ± 0.0065 |
| 4.6    | 0.0004          | 0.0638 ± 0.0026 | 1.866 ± 0.558 | 0.135 ± 0.041 | 37.357 ± 7.034 | 16.8 ± 39.597 | 8.799 ± 0.212 | 103.6 ±  **#** | 0.0276 ± 0.0118 |
| 5.0    | 0.0007          | 0.0925 ± 0.0056 | 8.003 ± 0.322 | 0.020 ± 0.009 | 40.508 ± 7.299 | 61.8 ± 19.330 | 0.523 ± 0.058 | 62.5 ±  **#** | 0.0248 ± 0.0484 |
| 5.5    | 0.0050          | 0.0138 ± 0.0056 | 7.464 ± 0.142 | 0.212 ± 0.018 | 23.791 ± 0.404 | 17.6 ± 97.202 | 0.940 ± 0.049 | 245.2 ± 0.185 | 0.0326 ± 1.2458 |
| 6.0    | 0.0060          | 0.0086 ± 0.0100 | 5.980 ± 0.886 | 0.497 ± 0.010 | 11.886 ± 0.174 | 2.0 ± 206.365 | 0.062 ± 0.007 | 222.6 ± 3.5 | 0.0374 ± 0.0128 |
| 6.5    | 0.0048          | 0.0005 ± 0.0011 | 5.627 ± 0.568 | 0.499 ± 0.010 | 40.956 ± 0.098 | 8.7 ± 206.167 | 0.484 ± 0.012 | 225.4 ± 3.4 | 0.0316 ± 0.0125 |
| 7.0    | 0.0086          | 0.0013 ± 0.0009 | 5.549 ± 0.564 | 0.214 ± 0.013 | 41.856 ± 0.056 | 2.1 ± 197.839 | 5.9 ± 0.017 | 300.8 ± 1.7 | 0.0384 ± 0.0283 |
| 7.5    | 0.0215          | 0.0007 ± 0.0012 | 6.384 ± 0.568 | 0.214 ± 0.013 | 41.357 ± 0.012 | 1.2 ± 192.211 | 5.9 ± 0.017 | 306.0 ± 1.7 | 0.0374 ± 0.0283 |
| 8.0    | 0.0408          | 0.0001 ± 0.0011 | 7.687 ± 0.957 | 0.214 ± 0.013 | 41.656 ± 0.012 | 1.2 ± 192.211 | 5.9 ± 0.017 | 306.0 ± 1.7 | 0.0374 ± 0.0283 |
| 8.5    | 0.0799          | 0.0003 ± 0.0011 | 8.147 ± 0.957 | 0.214 ± 0.013 | 42.156 ± 0.012 | 1.2 ± 192.211 | 5.9 ± 0.017 | 306.0 ± 1.7 | 0.0374 ± 0.0283 |
| 9.0    | 0.1050          | 0.0011 ± 0.0011 | 8.605 ± 0.957 | 0.214 ± 0.013 | 42.656 ± 0.012 | 1.2 ± 192.211 | 5.9 ± 0.017 | 306.0 ± 1.7 | 0.0374 ± 0.0283 |
| 9.5    | 0.1500          | 0.0015 ± 0.0011 | 9.164 ± 0.957 | 0.214 ± 0.013 | 43.156 ± 0.012 | 1.2 ± 192.211 | 5.9 ± 0.017 | 306.0 ± 1.7 | 0.0374 ± 0.0283 |

*a As measured by laser in % of full nominal power (10W). Ages marked with an asterisk (*) or a pound symbol (#) were those used in the plateau or inverse isochron age calculation, respectively.

*b Nominal J (±0.30%, 1σ) from GSC Irradiation Batch #61, referenced to Fish Canyon Tuff Sandstone=25.281 ±0.023 Ma (1σ, Kuiper et al., 2008).

c Fraction \(^{129}\text{Ar}/^{36}\text{Ar}\) as percent of gas in all aliquots.

d Errors on ages from each heating step are analytical only and do not reflect error in irradiation parameter J.

Plateau and inverse isochron age errors are quoted at 2σ and incorporate the error in J, but not the error in decay constants.

**Atmospheric** \(^{40}\text{Ar}/^{36}\text{Ar}=295.5**

**Decay Constant** \((^{40}\text{K} \lambda_{\text{t}}) = 5.463 \pm 0.214 \times 10^{-10}/\text{yr} (2\sigma, \text{Min et al., 2000})**

Blanks were measured before and after aliquot analysis and levels varied between \(^{40}\text{Ar}=2.5 \times 10^{-7} \text{nmol,}^{39}\text{Ar}=1.8 \times 10^{-10} \text{to} 5.4 \times 10^{-10} \text{nmol,}^{38}\text{Ar}=1.8 \times 10^{-10} \text{to} 1.4 \times 10^{-9} \text{nmol,}^{37}\text{Ar}=1.3 \times 10^{-10} \text{to} 2.3 \times 10^{-10} \text{nmol,}^{36}\text{Ar}=1.1 \times 10^{-10} \text{to} 1.4 \times 10^{-9} \text{nmol, all at ±10 % uncertainty (2σ). Nucleogenic interference corrections (±2σ) are} \((^{40}\text{Ar}/^{36}\text{Ar})K=0.025 \pm 0.005, (^{40}\text{Ar}/^{39}\text{Ar})K=0.011 \pm 0.010, (^{40}\text{Ar}/^{39}\text{Ar})C=0.002 \pm 0.002, (^{39}\text{Ar}/^{36}\text{Ar})C=0.00068 \pm 0.00004, (^{39}\text{Ar}/^{37}\text{Ar})C=0.00003 \pm 0.00003, (^{39}\text{Ar}/^{36}\text{Ar})C=0.00028 \pm 0.00016.**
Fig. 7. Hornblende $^{39}$Ar/$^{36}$Ar age spectra and Ca/K ratios as a function of stepped release of $^{39}$Ar during heating of samples: a) ZE09-059A, b) ZE09-059B, c) ZE09-060, and d) ZE09-061. Inverse $^{36}$Ar/$^{39}$Ar vs. $^{36}$Ar/$^{40}$Ar isochron diagrams for samples: e) ZE09-059A and f) ZE09-060, respectively.
fit against calculated J-factor and sample position. The error on individual J-factor values is conservatively estimated at ±0.6% (2σ). Because the error associated with the J-factor is systematic and unrelated to individual analyses, correction for this uncertainty is not applied until ages from isotopic correlation diagrams are calculated (Roddick, 1988). Errors in the plateau and inverse isochron ages do not include the errors of decay constants. Nucleogenic interference corrections in the plateau and inverse isochron ages do not include the correlation diagrams are calculated (Roddick, 1988). Errors for this uncertainty is not applied until ages from isotopic systematic and unrelated to individual analyses, correction (9 of 11 heating steps) plot along a line that regresses to an essentially atmospheric 40Ar/36Ar composition of 323 ±32, and gives an age of 221.6 ±2.5 Ma (Fig. 7f; MSWD = 1.4). Although indistinguishable from the plateau age, the isochron age includes almost all of the heating steps and has a more acceptable MSWD, and is therefore the preferred cooling age for this sample. This age is indistinguishable from that of sample ZE09-059B (Fig. 7b).

Sample ZE09-061 is a medium-grained to pegmatitic hornblende gabbro. Weakly zoned hornblende is variably altered and locally contains altered biotite inclusions. One aliquot was analyzed, yielding a slightly hump-shaped release spectrum. Six mid- to high-temperature steps, however, give a plateau age of 220.1 ±2.7 Ma (Fig. 7d; MSWD = 1.02, 85% of total 39Ar). The fusion step, which gives an apparent age of 209 ±5 Ma, was not included.

4.2. Geochemistry

Pyroclastic samples have high volatile contents (7-13 wt.% LOI; Table 2) that reflect, in part, extensive serpentinization of olivine. All pyroclastic samples have high concentrations of MgO (29-38 wt.%, LOI-free) and Ni (1100-1700 ppm), low concentrations of Al2O3 (4-6 wt.%) and, with the exception of sample 9, low concentrations of alkalis (Na2O + K2O ≤0.3 wt.%). The high absolute MgO and Ni-Cr concentrations and strong negative correlations between MgO and the relatively immobile, conserved oxides (Al2O3, TiO2, P2O5; not shown) suggest that the geochemical variability among the ultramafic pyroclastic rocks is mainly controlled by accumulation of olivine. Samples define a nearly vertical array that projects towards ~Fo00 on Mg vs. Fe cation unit plot, along an olivine control line (Fig. 8a). Primary liquid compositions were calculated by fractional removal of olivine from each sample at upper crustal pressure (P = 0.1 GPa) until the resulting parental
### Table 2: Major and Trace Element Compositions of Late Triassic Ultramafic Rocks


<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Major Elements (wt. %)</th>
<th>Trace Elements (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>TiO₂</td>
</tr>
<tr>
<td>ZE11-649A</td>
<td>40.72</td>
<td>0.10</td>
</tr>
<tr>
<td>ZE11-649D</td>
<td>40.10</td>
<td>0.21</td>
</tr>
<tr>
<td>ZE11-649F</td>
<td>39.98</td>
<td>0.27</td>
</tr>
<tr>
<td>ZE11-648C</td>
<td>39.18</td>
<td>0.26</td>
</tr>
<tr>
<td>ZE11-648D</td>
<td>39.57</td>
<td>0.20</td>
</tr>
<tr>
<td>ZE11-644A</td>
<td>45.60</td>
<td>0.31</td>
</tr>
<tr>
<td>ZE11-644B</td>
<td>42.43</td>
<td>0.62</td>
</tr>
<tr>
<td>ZE11-645A</td>
<td>40.25</td>
<td>0.43</td>
</tr>
<tr>
<td>ZE11-645B</td>
<td>42.46</td>
<td>0.20</td>
</tr>
<tr>
<td>ZE10-172</td>
<td>41.81</td>
<td>0.28</td>
</tr>
<tr>
<td>ZE09-062</td>
<td>44.25</td>
<td>0.91</td>
</tr>
</tbody>
</table>

**Note:** Detection limits in parentheses.
Fig. 8. a) Mg vs. Fe\textsuperscript{TOT} in cation units, showing the compositions of ultramafic lapilli tuff (black circles; samples 1-5, 8-10), olivine clinopyroxenite from Mount Hickman ultramafic complex (white circle; sample 11) and two ultramafic clasts from a basaltic breccia (white squares; samples 6-7). Cation units are calculated by dividing the wt.% oxide value by molecular weight, multiplying by number of cations in oxide formula, and recasting to 100%. The thin dashed lines are the calculated loci of fractional removal of olivine using PRIMELT3 MEGA.XLSM (Herzberg and Asimow, 2015). The radiating lines are isopleths of constant Fe content coexisting with liquids as determined by the Fe-Mg exchange coefficient (KD=0.30) and adjusted for Fe\textsuperscript{3+}/Fe\textsuperscript{TOT}=0.10. The stoichiometric compositions of olivine and clinopyroxene are shown for reference. b) N-MORB normalized trace element patterns of samples collected during 2009-2011 mapping.

A relatively low Fe\textsuperscript{3+}/Fe\textsuperscript{TOT} ratio (0.05) was chosen to account for the effect of olivine accumulation, which reduces the Fe\textsuperscript{3+}/Fe\textsuperscript{TOT} ratio of the cumulate rock relative to its parental magma. The calculated primary liquids have high MgO concentrations of 16-20 wt.% (LOI-free), consistent with the paucity of clinopyroxene and plagioclase in the pyroclastic rocks. All of the ultramafic samples are orthopyroxene normative (5-25% by weight). However, because of the high mobility of alkalis and the reduction in Mg/Si ratios that result from conversion of olivine (Mg\textsubscript{2}SiO\textsubscript{4}) to serpentine (Mg\textsubscript{3}Si\textsubscript{2}O\textsubscript{5}(OH\textsubscript{4})), the composition of the parental magma cannot be shown to be subalkaline (Si-saturated) with certainty (Kitayama and Francis, 2014). The high LOI concentrations and pervasive serpentinization, coupled with the lack of correlation between the mobile (e.g., Ba) and immobile (e.g., Zr) elements (not shown), suggest that LIL contents of the Stuhini Group ultramafic rocks should be considered with caution. In nearly all instances, the absolute abundances of the immobile trace elements are lower than those of mid-ocean ridge basalts (MORB), consistent with dilution by olivine accumulation. The ultramafic rocks have relatively flat MORB-normalized heavy rare earth element (HREE) profiles (Tb/Yb\textsubscript{MORB} = 1.1-1.5), but display relative enrichments in light (L)REE (Ce/Yb\textsubscript{MORB} = 3-10), and marked depletions in high field strength elements (HFSE) relative to REE of similar compatibility (Nb/La\textsubscript{MORB} <0.3; Zr/Nd\textsubscript{MORB} = 0.3-0.6).

The single phlogopite-rich olivine clinopyroxenite sample (sample 11, Table 2) from the Mount Hickman ultramafic complex has a relatively high concentration of MgO (~14 wt.%) and CaO (~17 wt.%) and low concentration of Al\textsubscript{2}O\textsubscript{3} (~4.5 wt.%), which reflects the predominant control of clinopyroxene accumulation on the sample’s chemistry. The sample also contains abundant cumulus magnetite (>10%), which is reflected in its anomalously high Fe content (Fig. 8a). The phlogopite clinopyroxenite sample is depleted in Nb-Ta relative to the similarly compatible LREE, and strongly enriched in LILE, consistent with derivation from a calc-alkaline parental liquid.

The diatreme clasts (6 and 7, Table 2) are picritic (MgO ≥16 wt.%) and their strongly altered groundmass accounts for the elevated LOI (4-8 wt.%). In addition to containing ubiquitous clinopyroxene, samples 6 and 7 are distinguished from pyroclastic samples by lower concentrations of MgO and FeO and higher concentrations of Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, alkalis, and incompatible trace elements. These mineralogical and compositional differences, however, do not preclude a genetic relationship between the clasts and the pyroclastic samples, and future studies may examine possible links.
5. Discussion

5.1. The age of ultramafic volcanism in northern Stikinia

New 40Ar/39Ar ages from four granodioritic to gabbroic samples indicate that the Hickman pluton cooled through the hornblende closure temperature (400-600°C; Reiners et al., 2005) at ~220-222 Ma, consistent with the previous determination by Holbek (1988). The observation of fresh to partially palagonitized glass in the ultramafic tuff of the Mess Lake facies < 10 km east of the Hickman pluton indicates that the pyroclastic rocks did not experience significant regional metamorphism (Jakobsson and Moore, 1986), suggesting that they may postdate emplacement of the Hickman pluton. This interpretation contradicts that of Logan et al. (2000) who considered the aplitic dikes cutting volcanic rocks of the Mess Lake facies to be co-magmatic with a granodioritic to quartz monzonitic body that they regarded as part of the Hickman pluton farther west (Fig. 2). However, although direct geochronologic data from this eastern plutonic body are lacking, alkaline geochemistry and associated Cu mineralization suggest that its eastern half includes a Late Triassic-Early Jurassic phase belonging to the ca. 195-210 Ma Copper Mountain plutonic suite (Loon Lake stock; cf. Logan et al., 2000). In short, the relative timing of the Mess Lake ultramafic rocks and the Hickman pluton remains unclear. The issue will be addressed by future work including U-Pb (xenocrystic/detrital zircon) and Sm-Nd (whole rock) geochronology of the ultramafic rocks, and 40Ar/39Ar geochronology of crosscutting hornblende-phyric basaltic dikes (Fig. 3b).

5.2. Emplacement and petrology of the Middle to Upper Triassic ultramafic pyroclastic rocks

The ultramafic pyroclastic rocks of the Mess Lake facies were deposited during at least four cycles of explosive eruption, as recorded by four sharp-based fining-upward sequences. Partially palagonitized, highly-vesicular, scoria (Fig. 6e) and the concavo-convex morphology of bubble-wall glass shards suggest that the ultramafic rocks of the Mess Lake facies were fragmented by violent exsolution of volatiles, rather than by hydrovolcanic explosion (McPhie et al., 1993; Thompson-Stiegler, 2008). We speculate that the lack of epipelite rocks between each sequence might indicate minimal time gaps between eruptive events.

The calculated MgO contents indicate the Mess Lake facies ultramafic pyroclastic rocks were derived from volatile-rich picritic magmas, undergoing olivine crystallization. The immobile trace element profiles of the pyroclastic rocks resemble many arc-related, calc-alkaline magmatic suites, which are widely regarded as melts of sub-arc asthenosphere metasomatized by fluids ± melts emanating from subducted oceanic lithosphere (Pearce and Peate, 1995). Alternatively, calc-alkaline trace element systematics of the tuffs may be attributed to lithospheric contamination of relatively unfractonated (tholeiitic) parental magmas as commonly proposed for Archean and Proterozoic igneous suites (e.g., Maurice et al., 2009; Milidragovic et al., 2014; Sandeman et al., 2014). The mass contribution that is required from such a contaminant may be estimated using reservoir-sensitive trace element ratios that are also insensitive to early stages of olivine-predominant fractional crystallization and accumulation (Pearce, 2008). On a Th/Yb vs. Nb/Yb ratio plot (Fig. 9) the ultramafic pyroclastic rocks of the Mess Lake facies plot above the asthenospheric MORB-ocean island basalt (OIB) array. Their position above the array requires either 1) melting of a fluid/melt metasomatized asthenospheric mantle source; or 2) a depleted N-MORB type magma modified by addition of ~10-20% middle and upper crust. Greater amounts of contamination by lower crust would be required to generate the relatively high Th/Yb ratios of the ultramafic pyroclastic rocks. Although this study is in its preliminary stages, we favour the first alternative, in which melting of slab-metasomatized sub-arc asthenosphere is the main control on the trace element profiles of the ultramafic pyroclastics, for three reasons. First, the relatively high volatile contents required for the buoyant ascent of a picritic magma are more consistent with an arc setting. Second, the pseudomorphed olivine crystals are largely euhedral and show no evidence of disequilibrium, which may be expected from assimilation of Sr-rich crustal rocks. Third, Pb, which is strongly enriched in the middle and upper crust (15-17 ppm; Rudnick and Gao, 2003) and depleted in N-MORB (0.30 ppm; Sun and McDonough, 1989), is below detection limit (<5 ppm) in all ultramafic samples.

![Fig. 9. Th/Yb vs. Nb/Yb (after Pearce, 2008), showing the compositions of ultramafic pyroclastic rocks, olivine clinopyroxenite from the Mount Hickman ultramafic complex, and picritic clasts from a basaltic breccia (symbols as in Fig. 8). The compositions of N-MORB, E-MORB, and OIB are from Pearce (2008); upper continental crust (UC), middle continental crust (MC), lower continental crust (LC) and bulk continental crust (BC) are from Rudnick and Gao (2003). Mixing lines between N-MORB and UC and LC compositions are shown, with small white circles representing 10% mixing steps.](image-url)
6. Summary and conclusions

Preliminary examination of Middle to Upper Triassic ultramafic volcanic rocks in the Mess Lake area indicates multiple eruptive cycles, evidenced by at least four fining-upward sequences in which sharp-based beds, normally graded from tuff breccia to olivine lapilli tuff, are capped by units of rhythmically stratified ash tuff. Some of the pyroclastic rocks appear to be fresh and contain unaltered glass that is well suited for geochemical studies of magmatic compositions (both major and trace) and volatile contents. Reconstructed primary magma compositions suggest high-MgO (16-20 wt.%) primitive liquids, saturated in olivine only. The ultramafic pyroclastic rocks have typical calc-alkaline trace element signatures (Pearce and Peate, 1995), consistent with derivation from metasomatized, sub-arc asthenospheric mantle. Future studies will examine possible genetic links between the pyroclastic deposits, mafic-ultramafic cumulate intrusions of the Polaris Suite, and diatreme(s) containing picritic clasts.

Fresh volcanic glass in the ultramafic tuffs adjacent to the Hickman pluton and diatreme(s) cutting the Hickman pluton support the idea that ultramafic volcanism, as a whole, is younger than the hornblende age of the Hickman pluton (~222 to 220 Ma). This is at odds with the observations of Logan et al. (2000), who reported that aplite dikes emanating from a hornblende granodioritic to quartz monzonitic body, which they considered correlative with the Hickman pluton, cut volcanic rocks of the Mess Lake facies. Uranium-lead, $^{40}$Ar/$^{39}$Ar, and Sm-Nd geochronology will be used to better constrain the emplacement age of the ultramafic rocks, and isotopic studies (Rb-Sr and Sm-Nd) will be used to assess the contributions of different reservoirs during ultramafic magma petrogenesis and, ultimately, to help further characterize mantle conditions during the deposition of the Stuhini Group and spatially associated ultramafic plutons.

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