TERMINAL STAGE OF A DYING RIFT

By

Andrew LaVigne

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Geological Sciences - Master of Science

ABSTRACT

TERMINAL STAGE OF A DYING RIFT

By

Andrew LaVigne

While most continental rifts progress toward rupture and eventual oceanic spreading, in certain circumstances, the rift may fail. Failed rifts provide a window into the transition from continental rifting to the formation of a passive margin, which in successful rifts is occluded by thick post rift sedimentary packages. Among the best-preserved failed rifts is the 1.1 Ga Midcontinent Rift (MCR) in North America. Within the MCR, the final stage of magmatism is preserved on Michipicoten Island. Here I present a geochemical and isotopic study of the Michipicoten Island Formation to probe conditions in the crust and mantle during the final stage. My results show that the volcanic units on Michipicoten Island have undergone magma mixing between rhyolitic and basaltic magma, dominating magmatic processes within the crust. During previous eruptive periods in the MCR, during which this observation has been made, the rhyolitic endmember has been interpreted to have experienced significant contribution from the Achaean crust based on profoundly unradiogenic ɛNd values. In contrast, the Michipicoten Island Formation exhibits some of the most radiogenic ϵNd_i values in the MCR, indicating that the source of evolved melts in the MCR changes from melting of existing Archean crust to juvenile material. The isotopic data from Michipicoten Island also shows that the depleted mantle is the single largest contributor of any geochemical reservoir. In the absence of a strong thermal plume component, melting of the depleted mantle requires decompression. The Michipicoten Island Formation was erupted during the geophysically-defined post-rift phase. My results require plate thinning to have continued during this late stage, with the implication that plate deformation persisted even though the crustal structure may not have recorded this deformation.

Copyright by ANDREW LAVIGNE 2019 This thesis is dedicated to my grandfather Michael Brink Thank you for inspiring me to be become a scientist

ACKNOWLEDGMENTS

I would like to thank the National Science Foundation for funding this research. I also would like to thank the Ontario Park Service for allowing us to conduct our research on Michipicoten Island. I am extremely grateful for all the time and effort my advisor Dr. Tyrone Rooney put into making this master's degree happen. I am also grateful for my graduate community taking time out of there busy schedules to help a young scientist. I would like to thank Dr. Val Finlayson and Dr. Jasper Konter for all the help they gave me during the isotopic analyses stage of this research. Finally, I would like to thank my friends and family whose support over these last few years has been invaluable.

TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	ix
KEY TO ABBREVIATIONS	xi
Introduction	1
Geologic Background G.1 Geological Setting G.2 Tectonic Setting G.3 Geologic Evolution of the Midcontinent Rift G.3.1 Initiation stage (1115-1110 Ma) G.3.2 Early Stage (1110-1105 Ma)	4 4 5 6
G.3.3 Hiatus Stage (1105-1101 Ma) G.3.4 Main Stage Volcanism (1101-1094 Ma) G.3.5 Late Stage (1094-1080 Ma) G.4 Geology of Michipicoten Island	6 7 7 8
Methods M.1 Major and Trace Element Analyses M.2 Isotopic Analyses M.3 Isotopic Age Correction M.3.1 Rb-Sr System M.3.2 Sm-Nd System M.3.3 Lu-Hf System M.3.4 U-Th-Pb System M.4 Isotopic Mixing	.11 .11 .13 .13 .14 .15 18 21
Results R.1 Petrography R.2 Geochemistry R.2.1 Major Elements R.2.2 Trace elements R.3 Isotope geochemistry	.25 .25 .27 .27 .27 .29 31
Discussion D.1 Effects of Alteration D.1.1 Major and Trace Elements. D.1.2 Effects of Alteration on Radiogenic Isotope Tracers D.2 Generation of Evolved Magmatism D.2.1 Fractional Crystallization. D.2.2 Crustal Anatexis D.2.3 Liquid Immiscibility. D.3 Temporal Evolution of the Michipicoten Island Formation D.4 Temporal Context of the Michipicoten Island Formation in the Framework of MCR Magmatic Stratigraphy.	.34 .34 .35 .38 .38 .39 .40 .41

D.4.1 Early Stage	44
D.4.2 Hiatus Stage	44
D.4.3 Main Stage	45
D.5 Hybridization of Late Stage Magmatism in the MCR	47
D.6 Mantle Sources of Late Magmatism in the MCR	48
D.7 Implication for Rift Failure	52
Conclusion	53
APPENDICES	55
APPENDIX A FIGURES	56
APPENDIX B TABLES	87
APPENDIX C STANDARDS	102
REFERENCES	113

LIST OF TABLES

Table 1: Major Elements Concentrations	88
Table 2: Trace Elements Concentrations	90
Table 3: Measured Isotopic Values	99
Table 4: Calculated Isotopic Values	101
Table 5: Major Element Standards	103
Table 6: Trace Element Standards	104

LIST OF FIGURES

Figure 1: Gravity Anomaly Map	57
Figure 2: MCR Stratigraphy	58
Figure 3: Geologic Map of Michipicoten Island	59
Figure 4: Photomicrographs	60
Figure 5: Classification Diagrams	61
Figure 6: Major Elements Diagrams	63
Figure 7: Flow Evolution Diagrams	65
Figure 8: Large Ion Lithophile Element Diagrams	66
Figure 9: First Row Transition Elements Diagrams	67
Figure 10: High Field Strength Element Diagrams	68
Figure 11: Primitive Mantle Normalized Trace Element Diagrams	70
Figure 12: Chondrite Normalized Rare Earth Element Diagrams	72
Figure 13: εNd _i v. εHf _i Digram	74
Figure 14: (⁸⁷ Sr/ ⁸⁶ Sr) _i ν. εNd _i Diagram	75
Figure 15: Pb Isotope Diagrams	76
Figure 16: Isocon Diagrams	78
Figure 17: Isochron Diagrams	79
Figure 18: MELTS Models	80
Figure 19: Chemical Comparison of Michipicoten Island Formation Samples to Experimentally Produced Liquids	81

Figure 20: Liquid Extraction Diagram	82
Figure 21: Primitive Mantle Normalized Comparison Diagrams	83
Figure 22: Ternary Magma Mixing Model	85

KEY TO ABBREVIATIONS

CC: Continental crust DM: Depleted mantle DMM: Depleted MORB mantle HFSE: High field strength elements HREE: Heavy rare earth elements ICP-MS: Inductively coupled plasma mass spectrometer LA-ICP-MS: Laser ablation- inductively coupled plasma mass spectrometer LILE: Large-ion lithophile element LIP: Large igneous provinces LREE: Light rare earth elements Ma: mega-annums MCR: Midcontinent Rift MORB: Mid-ocean ridge basalt **REE:** Rare earth element PPM: Parts per million PM: Primitive Mantle SE: Standard error SCLM: Sub-continental lithospheric mantle XRF: X-ray fluorescence spectrometer

Introduction

Fundamental to our understanding of the plate tectonic model is that continents must break apart to form oceanic basins. The process by which continents tear apart is known as continental rifting. Normal plate tectonic forces alone (i.e., the tensile forces in plates caused by plate motion) are often insufficient to break the hard continental crust (Buck and Karner, 2004). Thus, additional factors must be at play to generate a successful continental rift. One such factor is the impingement of a deep-seated thermo-chemical anomaly (i.e., a mantle plume). These plumes allow for the localization of strain and heating of the continental crust making the crust the crust weaker and more susceptible to rifting (Buck and Karner, 2004). The surface expressions of mantle plumes are of large igneous provinces (LIP). Large igneous provinces are defined as large (>0.1 Mkm²), intraplate magmatic provinces that are typically emplaced in a short period of time (1-5 million years (henceforth Ma, mega-annums)), but with a maximum duration of <50 Ma (Bryan and Ernst, 2008; Ernst, 2014). The time between the end of volcanism and the start of rift opening can be quite variable, anywhere from 2 Ma to 13 Ma (Courtillot et al., 1999). The highly correlated timing between rifting and the generation of large igneous provinces is an indicator that the two processes are linked. Stronger evidence that rifting and LIP generation are linked is the formation of triple junctions. Rift triple junctions are where three arms of a rift intersect, each arm being an area of thinned lithosphere due to graben or half graben formation. For most continental rifts, the triple junctions are both temporally and spatially linked to the interpreted plume head center, usually within 1000 km based on domal uplift (White and McKenzie, 1989; Courtillot et al., 1999). This information makes for a compelling model for the link between rifting, plume head emplacement, and the generation of LIPs.

The coupled plume-rift model for continental breakup requires a transition from active, plume-driven rifting to passive, plate-driven extension. This also requires a transition from faultdominated strain accommodation to diking strain accommodation. This transition is typically

marked by a renewed pulse of magmatic activity (Ernst, 2014). Important questions remain about the nature of this magmatism, and what sources are contributing to said magmatism during this transitional period. Unfortunately, it is difficult to obtain samples of rock that record rift processes because with successful continental rifting, transitional volcanic material is submerged and buried beneath the oceanic sediments (Stein et al., 2018). While we can infer the presence of this magmatism through the use of seismic tomography and magnetic anomaly mapping, sampling has proven difficult. Luckily there is a second type of rift known as a failed rift. These failed rifts do not succeed in forming oceanic basins and thus may preserve magmatism associated with the final stage of rifting in such a way that as to allow for sample collection.

While rifts and their associated LIPs that succeed in forming oceanic basins are common, rifts that fail are far less numerous, but no less important. Of the known LIPs associated with failed rifts, some have been highly deformed and eroded, like the Emeishan traps (Courtillot et al. 1999). Others like the Circum Superior and Matachewan - Mistassini are eroded down to their plumbing systems. This leaves just the Keweenaw Large Igneous Provence, associated with the extension of the Midcontinent Rift (MCR), and the Siberian Traps, which has been associated with the extension of West Siberian Basin, as the only well exposed failed rifts on Earth. The Western Siberian Basin and the Midcontinent rift both have synrift volcanism but in the Western Siberian Basin this volcanism is buried beneath intra rift sediments. In the Midcontinent Rift the synrift volcanics have been exposed do to uplifting during later orogenesis (Saunders et al., 2005). This makes the MCR the best target for sampling of late stage lavas in a failed rift systems.

Volcanism associated with the MCR has been broken down into four primary stages. First is the initiation stage, which has been associated with plume head impact beneath the MCR. Next is the early stage of volcanism, which has been interpreted as the result of melting from a primary plume source during initial extension (Cannon, 1992; Nicholson et al., 1997;

Miller and Nicholson, 2013; Stein et al., 2015). The next phase is known as the hiatus phase which, as its name suggest, is marked by a lack of volcanism. This reduction in flux may be due to the reduced extension or large-scale magmatic underplating (Nicholson et al., 1997; Miller and Nicholson, 2013). After this period of relative quiescence, volcanism is renewed with mixed plume depleted mantle source, which has been suggested by some authors as an indication of renewed extension within the rift (Cannon, 1992; Nicholson et al., 1997; Miller and Nicholson, 2013). The final stage of volcanism is known as the late stage and has not had nearly the same level of rigorous study as the previous stages, despite its potential to shed light on the aforementioned questions surrounding the final stages of rifting.

The late stage volcanics are much more localized: exposures are only found in the Keweenaw Peninsula (Lake Shore Traps), the Schoder-Lusten basalts, and Michipicoten Island (Michipicoten Island Formation). Recent dating by Fairchild et al. (2017) has shown that the youngest volcanic sequence in the Midcontent Rift is the Michipicoten Island Formation. The Michipicoten Island Formation is also the most significant volcanic sequence from the late stage of volcanism, and thus will be the focus of this study. Major and trace elements were analyzed to understand what processes are affecting the magma within the crust so we can understand what is impacting the magma as it ascends to the surface. By understanding what crustal processes are modifying the magmas, we can better assess the potential mantle sources contributing to late stage volcanism. From previous work (i.e. Nicholson et al., 1997; Miller and Nicholson, 2013) we have an understanding that the source of magmatism is linked to the tectonic situation within the MCR, thus understanding the source will inform us about the what is happening tectonically within the MCR.

Geologic Background

G.1 Geological Setting

The Keweenaw Large Igneous Province erupted an estimated 2 million cubic kilometers of volcanic material across the MCR's nearly 3000 km length (Cannon, 1992; Stein et al., 2014). Volcanic rocks were mostly deposited within the rift, forming one of the most pronounced positive gravity anomalies in North America (fig. 1). This volcanism occurred over 30 million years from 1110 Ma to 1080 Ma during a lull in the contemporaneous Grenville orogeny, making it an unusually long-lived large igneous province (LIP) (McLelland et al., 2001; Rivers, 2008; Swanson-Hysell et al., 2019). The MCR for its age of ~1.1 billion years, is exceptionally well preserved. Our understanding of the formation of LIPs typically comes from Permian or younger flood basalt sequences. Most of the Paleozoic and older LIP's are so eroded that only dikes and sills are left exposed (Ernst 2014). This preservation provides a rare opportunity to examine a Precambrian LIP.

G.2 Tectonic Setting

The Midcontinent rift formed between the Shawinigan phase and the Ottawa phase of the Grenville Orogeny, during a lull in orogenic activity. The pre-MCR crustal shortening associated with the Shawinigan phase ended at ~1140 Ma (Rivers, 1997). However, the beginning of the Ottawa phase of the Grenville Orogeny has proven difficult to precisely determine. Understanding when the Ottawa Phase began is crucial since crustal shortening during the Ottawa phase has often been invoked as the cause of MCR failure (Cannon, 1994; Ernst, 2014). Some authors (e.g. McLelland et al., 2001; Rivers et al., 2002) have suggested that the beginning of the Ottawa phase began with the end of magmatism at ~1090 Ma but recent dating by Fairchild et al. (2017) has pushed back the timing of the last phase of volcanism to 1083 Ma. Thus, independent constraints on when the Ottawa phase began, which is not dependent on simply the youngest magmatism, is required.

Granitic units closer to the Grenville front can give insight into when orogenesis resumed in Laurentia. Dating of units from the Adirondack Highlands, such as the deformed Hawkeye Granitic suite, reveals ages between 1103-1093 Ma; less deformed pyroxene bearing syenite has been dated at 1080 ± 4 Ma (Chiarenzelli and McLelland, 1991). The difference in the deformation is key to understanding when orogenesis must have begun. If the orogenesis had started after the emplacement of the syenite, then both the granite and the syenite would have the same level of deformation. Since the pyroxene-bearing syenite has undergone less deformation, then it can be assumed that it formed after the Ottawa phase of orogenesis had already begun (McLelland et al., 2001). While dating of metamorphosed units from the Adirondacks indicates when the Ottawa phase began, it does not necessarily indicate when rifting ceased. Swanson-Hysell et al. (2019) suggest that a series of angular unconformities, which has been roughly constrained to ~1091 Ma, represent the transition from active rifting to post rift thermal subsidence. If active rifting ceased at 1091 Ma, then why does magmatism continue to 1083 Ma on Michipicoten Island?

G.3 Geologic Evolution of the Midcontinent Rift

Several divisions have been proposed to separate rift magmatism based on chemical composition (Shirey et al., 1994; Marshall, 1996; Davis and Green, 1997; Nicholson et al., 1997; Heaman et al., 2007; Vervoort et al., 2007; Miller and Nicholson, 2013). Here we utilize the nomenclature proposed by Miller and Nicholson (2013). This naming convention combines both geochemistry and geochronology to divide the magmatic activity into five distinct groups: initiation, early, hiatus, main, and late stage.

G.3.1 Initiation stage (1115-1110 Ma)

The initiation of the Midcontinent Rift began at 1115 Ma with the emplacement of intrusions in the Nipigon Embayment area (Heaman et al., 2007). The geochemical trace element

characteristics of these sills seems to indicate that the plume impacted around this time (Hollings et al., 2007). During this time period, only intrusions are preserved, with surface volcanics absent. It has been proposed that this may be due to an increase in the rate of erosion due to crustal doming (Miller and Nicholson, 2013).

G.3.2 Early Stage (1110-1105 Ma)

This group is represented by the first flows of Keweenaw LIP that are dominantly picritic in composition. The early flows from this group have relatively primitive compositions and ɛNd values near zero, which has been inferred to be the plume signature (Shirey et al., 1994). However, up section, the composition of the lavas becomes progressively more negative in terms of ɛNd. These observations have been interpreted as indicating a progressive increase in crustal contamination (Shirey et al., 1994). It has been suggested that this indicates that the initial melts were able to move quickly through the cold continental crust, but as time progressed these basalts heated the crust and started assimilating it into the melt (Shirey et al., 1994). Miller and Nicholson (2013) interprets the isotopic data, along with elevated Th/Yb (i.e. >1), as the result of fractional crystallization and assimilation in deep crustal magma chambers. This is in agreement with existing models that suggest sialic magmas were generated as the result of deep crustal anataxis (Vervoort and Green, 1997; Vervoort et al., 2007).

G.3.3 Hiatus Stage (1105-1101 Ma)

This time period is defined by the deposition of sediments and the absence of volcanism. A notable exception to this are the occurrence of Group 5 basalts at Mamainse Point, and limited rhyolite volcanism throughout the rift (Shirey et al., 1994; Miller and Nicholson, 2013). At Mamainse Point, where volcanism continued during this phase, much of the stratigraphic record is represented by sedimentary units. For example, the Great Conglomerate and the Basaltic Clast Conglomerate occupies ~50% of the stratigraphy during this hiatus phase. Despite the

hiatus in volcanism, existing interpretations suggest that the plume continued generating melt (Miller and Nicholson, 2013). It has been suggested that during this time there was extensive ponding of mafic melts at the crust-mantle boundary, generating a magmatic underplate. This underplate can be observed geophysically in gravity models from the MCR region.

G.3.4 Main Stage Volcanism (1101-1094 Ma)

The main stage represents a time period of renewed and vigorous volcanic activity, emplacing the majority of the volcanic material found within the MCR. Lava flows from the main stage, like the first flows of the early stage, show little evidence of crustal assimilation (Shirey et al., 1994; Nicholson et al., 1997). This has been interpreted as the result of long-lived crustal magma chambers having generated an insulating marginal zone, thus protecting the melt from contamination with in the continental crust (Miller and Nicholson, 2013). As magmatism progressed during this stage, magmatism became more primitive(e.g. became more Mg rich)(Paces, 1988; Paces and Bell, 1989a; Klewin and Berg, 1991). This has been interpreted to be the result of an increase in magmatic flux and the plumbing system becoming better developed over time (Shirey et al., 1994; Miller and Nicholson, 2013). Another observable trend seen throughout the rift during this time period is the change in isotopic values from near primitive εNd_i values (plume-like, εNd_i near 0) towards more positive values (depleted upper mantle like). This change has been interpreted as the commencement of mixing between asthenospheric melt and melt from the plume (Paces, 1988; Paces and Bell, 1989b; Shirey et al., 1994).

G.3.5 Late Stage (1094-1080 Ma)

Volcanism from this stage is localized as the Lake Shore Traps (LST) in the Keweenaw Peninsula and the Porcupine Mountains in northern Michigan, and the Michipicoten Island Formation on Michipicoten Island Ontario (Fig: 2). In the Keweenaw and Porcupine Mountains,

the LST overlies the main stage Portage Lake Volcanics and are intercalated with the Copper Harbor Conglomerate. On Michipicoten Island, the Michipicoten Island Formation overlies a series of late stage sills, which intruded the main stage volcanism of the Quebec Mine Member. Miller and Nicholson (2013) interpreted these late stage volcanics to be the result of mixing of remnant plume components with depleted asthenospheric components, though existing data supporting this argument is limited. Annells, (1974) concluded that the late stage lavas on Michipicoten Island were the result of basaltic melts mixing with remnant upper crustal melts based on major and minor element data from a few flows, and a limited geochemical dataset.

G.4 Geology of Michipicoten Island

Michipicoten Island is the 3rd largest island in Lake Superior, and it is almost entirely composed of igneous material associated with the Midcontinent Rift. Michipicoten Island is located on the most northern segment of the rift eastern arm (Fig. 1). The intra-rift volcanism dips towards the central rift axis and is bounded to the north by one of the rift graben faults known as the Michipicoten Island Fault. The igneous rocks of the island can be subdivided into three general formations: the Quebec Mine Member, the Michipicoten Island Intrusives, and the Michipicoten Island Formation (fig. 3). The Michipicoten Island Formation will be the focus of this study. The Mamainse Point Formation mostly consists of coarse-grained olivine tholeiite basalts flows ~855 m thick. Based on their similar characteristics, Mamainse Point Formation basalts have been thought to be stratigraphically related to the Mamainse Point Sequence (Annells, 1973). This idea is further supported by paleomagnetic data. Fairchild et al. (2017) points out that the mean paleomagnetic pole of the Mamainse Point Formation on Michipicoten Island (Palmer and Davis, 1987) overlaps with the mean pole from Mamainse Point Sequence (Swanson-Hysell et al., 2014).

The Michipicoten Island Intrusives intrude the Mamainse Point Formation and were was emplaced at 1086.5 +1.3/-3.0 Ma (Palmer and Davis, 1987), and makes up ~50% of the surface

area of the island (Annells, 1974). The intrusives were emplaced in two stages: the First Intrusive Phase comprises a quartz porphyry and a felsite. The Second Intrusive Phase is composed of a granitic phase and basaltic andesite phase.

The Michipicoten Island Formation lies unconformably atop the intrusions. The Mamainse Point Formation is locally separated from the intrusions by a polymictic conglomerate. The Michipicoten Island Formation is composed of 5 major units: the Cuesta Member, the Channel Lake Member, the Quebec Harbor Member, the South Shore Member, and the Davieaux Island Member, lying stratigraphically in that order (fig. 3). The Cuesta Member is a plagioclase-phyric andesite that is divided into two flows referred to as the Cuesta Upper Flow and Cuesta Lower Flow. The Cuesta Member is between ~255 m and ~340 m thick with the Cuesta Lower Flow making up ~50% of the outcrop on the west side of the island but pinching out on the east side (fig. 3)(Annells, 1974). The Channel Lake Member is comprised of aphyric basaltic andesites ~260 m thick (Annells, 1974). Individual flows from this unit are between <1 m to 10 m thick with the exact number of flows uncertain. The next major unit is the Quebec Harbor Member a ~275 m thick appyric andesite (Annells, 1974). This member is comprised of multiple flows but due to poor preservation and a lack of outcrops the number and thickness of flows cannot be determined. On the west side of the island between the Channel Lake Member and the Quebec Harbor Member is a small outcrop of lithic tuff that has been dated to be 1084.35 ± 0.20 Ma (Fairchild et al., 2017). Atop the Quebec Harbor Member is the well-preserved South Shore Member, an olivine-free and plagioclase-phyric basalt. The South Shore Member is ~265 m thick in total, this unit is comprised of twenty one individual flows that are <1 m to >30 m thick (Fairchild et al., 2017). The youngest unit is the Davieaux Island Member, which forms a string of islands off the southern coast of Michipicoten Island. The Davieaux Island Member is a single ~195 m thick flow of feldspar and guartz-rich rhyolite (Annells, 1974). The exact relation between the South Shore Member and the Davieaux Island

Member is unclear since there is no contact between the two units. This rhyolite unit has been dated at 1083.52 ± 0.23 Ma, making it the youngest flow in the MCR (Fairchild et al., 2017).

Methods

M.1 Major and Trace Element Analyses

A total of 78 samples were collected from Michipicoten Island. Samples were taken from flow interiors, when possible, to minimize the effects of contamination from vesicle fill of secondary quartz and chlorite. Units sampled include the Upper and Lower Cuesta Member, the Channel Lake Member, the Quebec Harbor Member, the South Shore Member and the Davieaux Island Member.

Samples were cut in to ~30g billets, then polished to remove the saw marks. Once saw marks were removed, samples were washed twice in deionized water in an ultrasonic bath to remove any surface contamination. Samples were then crushed using a steel jaw crusher, and subsequently powdered with an alumina mill. These powders were fused into glass disks using a lithium tetraborate flux at 1:3 sample: flux ratio following the methods of Rooney et al. (2012)

Major and trace elements concentrations were analyzed at Michigan State University. Major elements were determined using a Bruker S4 Pioneer X-Ray Fluorescence Spectrometer (XRF). These disks were then analyzed for trace elements using a Photon-Machines Analyte G2 Excimer laser and Thermo Scientific ICAP Q quadrupole inductively coupled plasma mass spectrometer (ICP-MS). Standard deviation on replicated analyses is less than 5%, except for low concentrations (< 2 pmm) of Cr and Ni. Samples were run over four sessions. Major elements from the XRF were used as internal standards for trace element analysis and processed using Thermo Qtegra software. Machine drift was handled by analyzing the sample in triplicate and applying drift correction using known concentrations in geological standards BHVO-2 and JB1a.

M.2 Isotopic Analyses

Isotopic analyses were conducted at the University of Hawaii at Manoa School of Earth Science and Technology (SOEST) laboratory. Samples were first processed at Michigan State University

using a metal-minimal technique. Sample were cut into ~10g billets and crushed, then picked for freshness to reduce the effects of secondary alteration. Groundmass that was accepted for analyses was generally dark and glassy without the presence of secondary mineral such as chlorite. The picked sample groundmass was then leached in 6M hydrochloric acid for >16 hours at University of Hawaii at Manoa following a protocol modified from Koppers et al. (2003). Single dissolutions were used to separate Pb–Sr–Nd isotopes following Konter and Storm (2014) and Hf isotopes following Connelly et al. (2006). The analyses took place on a Nu Plasma HR multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS).

The initial separation of Pb and Sr from the rest of the matrix took place using a Sr-Spec resin column. The cut that was not used for the Sr-Pb cleanup would be later used for the Nd and Hf separation. The Sr cut went through a second column of Sr-Spec resin to remove any remaining interfering elements, following the same procedure as the first separation but without the lead step. Sr isotopic analyses were normalized to ⁸⁶Sr/⁸⁸Sr ratio of 0.1194 to correct of mass fractionation. Kr interference was corrected for using a multi-dynamic program developed by (Konter and Storm, 2014). The blank on Sr analysis was ~70 pg.

After initial Sr-Pb separation, the Pb cut is passed though AG1-X8 resin to separate any remaining unwanted elements. TI spike (NIST SRM 997; 205 TI/ 203 TI = 2.3889) was used to correct for drift. The blank on Pb analysis was ~70 pg.

After the Sr and Pb steps, Nd was the next element to be removed from the matrix. This matrix is dissolved in ascorbic acid to reduce the Fe³⁺ to Fe²⁺, then passed through two columns of TRU resin, which separates and purifies the REE from the matrix. To separate the Nd from the REE, the REE cut was placed in a column of LN resin for chromatographic separation. The analysis of Nd used a multi-dynamic program to correct for REE interference and mass bias, normalizing samples to the accepted present-day ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 (Konter and Storm, 2014). Drift was corrected for using Jndi-1 standard using standard sample bracketing. Blank on Nd was ~ 40 pg.

The remaining sample left over after the previous separations was used for the hafnium separation following a modified method from Connelly et al. (2006); the full method is described in Finlayson et al. (2018). Each sample is placed on a bed of AG50-x8 resin and washed with a HCI-HF mixture to remove the high field strength elements (HFSE) from the rest of the matrix. The final treatment is to remove the Ti from the sample, because refractory Ti can build up on the sample cone and create an electrical barrier to Hf, generating imprecise Hf results (Blichert-Toft et al., 1997). To remove the Ti, the HFSE cut is placed on a bed of DGA resin and Ti is removed by washing sample with 3.5 M HNO₃.

M.3 Isotopic Age Correction

While the act of correcting isotopic data is commonplace in the geochemistry community, most studies don't publish the method by which they generated their corrected age. This is compounded by the fact that many of the published equations assume that a researcher measured the parent/daughter ratio using isotope dilution. Our analyses don't use isotopic dilutions. The lack of detailed method on how a researcher conducted their age correction can lead to a reproducibility problem. Thus, I outline in detail the methods used for age-correcting our data. Like all age corrections for an isotopic system, we assume that the isotopic systems has remanded closed since eruption.

The equation for obtaining the original radiogenic isotopic ratio is:

(equation 1.1)

$$I_i = I - R\left(e^{\lambda t} - 1\right)$$

Where λ is the decay constant and t is the age of the sample in years. I_i is the original daughter isotopic ratio and I is the daughter isotopic ratio today. R is the parent isotopic ratio.

M.3.1 Rb-Sr System

We do not measure the parent isotopic ⁸⁷Rb/⁸⁶Sr on the Multi-Collector ICP-MS, so it has to be derived from the ⁸⁷Sr/⁸⁶Sr ratio and the Rb and Sr concentration (Faure, 1986): *(equation 2.1)*

$$\frac{{}^{87}Rb}{{}^{86}Sr} = \frac{C_{Rb} \times {}^{87}Rb}{Rb_{wt}} \times \frac{Sr_{wt}}{C_{Sr} \times {}^{86}Sr}$$

Where C refers to concentration and wt refers to atomic weight (de Laeter et al., 2003).

Both the atomic weight of Sr and atomic abundance of ⁸⁶Sr are dependent on the ⁸⁷Sr/⁸⁶Sr of the samples.

First arranging all Sr isotopes in terms of the most abundant isotope i.e. ⁸⁸Sr.

For the stable isotopes of Sr we used the natural abundances (de Laeter et al., 2003).
We can use the natural abundance because, while their true abundance will change based on the ⁸⁷Sr/⁸⁶Sr the ratio, stable isotopes will remain constant.

$$\frac{{}^{84}Sr}{{}^{88}Sr}, \quad \frac{{}^{86}Sr}{{}^{88}Sr}, \quad \frac{{}^{88}Sr}{{}^{88}Sr}$$

 For the radiogenically produced ⁸⁷Sr the ⁸⁷Sr/⁸⁸Sr ratio can be determined using the measured value:

(equation 2.2)

•

$$\frac{{}^{87}Sr}{{}^{88}Sr} = \frac{{}^{87}Sr}{{}^{86}Sr} \times \frac{{}^{86}Sr}{{}^{88}Sr}$$

The abundance of the different Sr isotopes in the sample can be determined by:

(equation 2.3)

$${}^{84}Sr = \frac{\frac{8^4Sr}{8^8Sr}}{Sr_{sum}} \qquad {}^{86}Sr = \frac{\frac{8^6Sr}{8^8Sr}}{Sr_{sum}}$$

$${}^{87}Sr = \frac{\frac{{}^{87}Sr}{{}^{88}Sr}}{Sr_{sum}} \qquad {}^{88}Sr = \frac{\frac{{}^{88}Sr}{{}^{88}Sr}}{Sr_{sum}}$$

Where

$$Sr_{sum} = \frac{^{87}Sr}{^{88}Sr} + \frac{^{84}Sr}{^{88}Sr} + \frac{^{86}Sr}{^{88}Sr} + \frac{^{88}Sr}{^{88}Sr}$$

This allows us to determine the atomic weight of Sr in this sample, as required for equation 2.1: *(equation 2.4)*

$$Sr_{wt} = {}^{84}Sr_m \times {}^{84}Sr + {}^{86}Sr_m \times {}^{86}Sr + {}^{87}Sr_m \times {}^{87}Sr + {}^{88}Sr_m \times {}^{88}Sr$$

The atomic weight of an element is equal to the sum of the masses (m) of each isotope multiplied by the abundance of the isotope.

All terms are dependent on the ⁸⁷Sr/⁸⁶Sr ratio and are required for equation 2.1 have been solved for.

M.3.2 Sm-Nd System

We do not measure parent isotopic ¹⁴⁷Sm/¹⁴⁴Nd on the Multi-Collector ICP-MS so it has to be derived from the ¹⁴³Nd/¹⁴⁴Nd ratio and the Sm, Nd concentrations.

(equation 3.1)

.

$$\frac{{}^{147}Sm}{{}^{144}Nd} = \frac{C_{Sm} \times {}^{147}Sm}{Sm_{wt}} \times \frac{Nd_{wt}}{C_{Nd} \times {}^{144}Nd}$$

Where C refers to concentration and wt refers to atomic weight (de Laeter et al., 2003).

Both the atomic weight of Nd and atomic abundance of ¹⁴⁴Nd are dependent on the ¹⁴³Nd/¹⁴⁴Nd of the samples.

First expressing all Nd isotopes in terms of the most abundant isotope i.e. ¹⁴²Nd.

For the nonradiogenic isotopes of Nd we used the natural abundances. We can use the natural abundance for this because, while their true abundance will change based on ¹⁴⁷Nd/¹⁴⁴Nd, the ratio between stable isotopes will remain constant (de Laeter et al., 2003).

^{142}Nd	^{144}Nd	^{145}Nd	¹⁴⁶ Nd	^{148}Nd	¹⁵⁰ Nd
$\overline{^{142}Nd}$ '	$\overline{^{142}Nd}$				

 For the radiogenically produced ¹⁴³Nd isotope the ¹⁴³Nd/¹⁴²Nd ratio can be determined using the measured ¹⁴³Nd/¹⁴⁴Nd

(equation 3.2)

$$\frac{{}^{143}Nd}{{}^{142}Nd} = \left(\frac{{}^{143}Nd}{{}^{144}Nd}\right)_m \times \frac{{}^{144}Nd}{{}^{142}Nd}$$

The abundance of the different Nd isotopes in this sample can be determined by:

(equation 3.3)

$${}^{142}Nd = \frac{\frac{142}{142}Nd}{Nd_{sum}} \qquad {}^{143}Nd = \frac{\frac{143}{142}Nd}{Nd_{sum}} \qquad {}^{144}Nd = \frac{\frac{144}{142}Nd}{Nd_{sum}} \qquad {}^{145}Nd = \frac{\frac{145}{142}Nd}{Nd_{sum}}$$

$${}^{146}Nd = \frac{\frac{146}{142}Nd}{Nd_{sum}} \qquad {}^{148}Nd = \frac{\frac{148}{142}Nd}{Nd_{sum}} \qquad {}^{150}Nd = \frac{\frac{150}{142}Nd}{Nd_{sum}}$$

Where

$$Nd_{sum} = \frac{^{142}Nd}{^{142}Nd} + \frac{^{143}Nd}{^{142}Nd} + \frac{^{144}Nd}{^{142}Nd} + \frac{^{145}Nd}{^{142}Nd} + \frac{^{146}Nd}{^{142}Nd} + \frac{^{148}Nd}{^{142}Nd} + \frac{^{150}Nd}{^{142}Nd}$$

This allows us to generate the atomic weight of Nd in this sample required for equation 3.1 *(equation 3.4)*

$$\begin{aligned} Nd_{wt} &= \ ^{142}Nd_m \times ^{142}Nd + \ ^{143}Nd_m \times ^{143}Nd + \ ^{144}Nd_m \times ^{144}Nd + \ ^{145}Nd_m \times ^{145}Nd \\ &+ \ ^{146}Nd_m \times ^{146}Nd + \ ^{148}Nd_m \times ^{148}Nd + \ ^{150}Nd_m \times ^{148}Nd \end{aligned}$$

The atomic weight of an element is equal to the sum of the masses (m) of each isotope multiplied by the abundance of the isotope.

All terms are dependent on the ¹⁴³Nd/¹⁴⁴Nd ratio and are required for equation 3.1 have been solved for.

While the initial ¹⁴³Nd/¹⁴⁴Nd is an important ratio, the limited fractionation between Nd and Sm coupled with the long half life of ¹⁴⁷Sm, makes the difference between the ¹⁴³Nd/¹⁴⁴Nd_i of individual samples quite small (Janoušek et al., 2016). Thus, commonly ¹⁴³Nd/¹⁴⁴Nd ratio is expressed relative to the chondrite uniform reservoir (CHUR), which as the name suggests, is defined as a mantle source with the same Sm-Nd concentrations and isotopic ratios as C1 chondrite (Bouvier et al., 2008). When comparing the¹⁴³Nd/¹⁴⁴Nd of the sample to that of CHUR, differences between samples become larger. This comparison is referred to as epsilon notation (ϵ).

The equation for εNd is:

$$\varepsilon_{Nd} = \left(\frac{\frac{1^{43}Nd}{1^{44}Nd}}{\frac{1^{43}Nd}{1^{44}Nd}} - 1\right) \times 10^4$$

To use this notation properly, the samples must be corrected to initial ¹⁴³Nd/¹⁴⁴Nd, but we can't compare the initial ¹⁴³Nd/¹⁴⁴Nd of our sample to the CHUR. So, we must age correct ¹⁴³Nd/¹⁴⁴Nd CHUR as well. The ¹⁴⁷Sm/¹⁴⁴Nd of CHUR has already been defined by Bouvier et al. (2008) and thus does not need to be derived.

$$\frac{{}^{143}Nd}{{}^{144}Nd}_{CHUR\,i} = \frac{{}^{143}Nd}{{}^{144}Nd}_{CHUR} - \frac{{}^{147}Sm}{{}^{144}Nd}_{CHUR} (e^{\lambda t} - 1)$$

M.3.3 Lu-Hf System

We do not measure parent isotopic ratio ¹⁷⁶Lu/¹⁷⁷Hf on the Multi-Collector ICP-MS so it has to be derived from the ¹⁷⁶Hf /¹⁷⁷Hf concentration of Lu and Hf.

(equation 4.1)

$$\frac{{}^{176}Lu}{{}^{177}Hf} = \frac{C_{Lu} \times {}^{176}Lu}{Lu_{wt}} \times \frac{Hf_{wt}}{C_{Hf} \times {}^{177}Hf}$$

Where C refers to concentration and wt refers to atomic weight (de Laeter et al., 2003).

Both the atomic weight of Hf and atomic abundance of ¹⁷⁷Hf is dependent on the ¹⁷⁶Hf/¹⁷⁷Hf of the samples.

First expressing all Hf isotopes in terms of the most abundant isotope i.e. ¹⁸⁰Hf.

• For the stable isotopes of Hf we used the natural abundances (de Laeter et al., 2003).

$$\frac{174}{180}Hf, \quad \frac{177}{180}Hf, \quad \frac{178}{180}Hf, \quad \frac{178}{180}Hf, \quad \frac{179}{180}Hf, \quad \frac{180}{180}Hf$$

• For the radiogenically produced ¹⁷⁶Hf isotope the ¹⁷⁶Hf/¹⁷⁷Hf ratio can be determined using the measured value.

(equation 4.2)

$$\frac{{}^{176}Hf}{{}^{180}Hf} = \left(\frac{{}^{176}Hf}{{}^{177}Hf}\right)_m \times \frac{{}^{177}Hf}{{}^{180}Hf}$$

The abundance of the different Hf isotopes in this sample can be determined by:

(equation 4.3)

$${}^{174}Hf = \frac{\frac{174}{180}Hf}{Hf_{sum}} \qquad {}^{176}Hf = \frac{\frac{176}{180}Hf}{Hf_{sum}} \qquad {}^{177}Hf = \frac{\frac{177}{180}Hf}{Hf_{sum}}$$

$${}^{178}Hf = \frac{\frac{178}{180}Hf}{Hf_{sum}} \qquad {}^{179}Hf = \frac{\frac{179}{180}Hf}{Hf_{sum}} \qquad {}^{180}Hf = \frac{\frac{180}{180}Hf}{Hf_{sum}}$$

Where

$$Hf_{sum} = \frac{174}{180}Hf + \frac{176}{180}Hf + \frac{177}{180}Hf + \frac{177}{180}Hf + \frac{178}{180}Hf + \frac{179}{180}Hf + \frac{179}{180}Hf + \frac{180}{180}Hf$$

This allows us to generate the atomic weight of Hf in this sample required for equation 4.1 *(equation 4.4)*

$$Hf_{wt} = {}^{174}Hf_m \times {}^{174}Hf + {}^{176}Hf_m \times {}^{176}Hf + {}^{177}Hf_m \times {}^{177}Hf + {}^{178}Hf_m \times {}^{178}Hf + {}^{179}Hf_m \times {}^{179}Hf + {}^{180}Hf_m \times {}^{180}Hf$$

The atomic weight of an element is equal to the sum of the masses (m) of each isotope multiplied by the abundance of the isotope.

Now we have derived all the terms required for equation 4.2 to be solved, which in turn allows for 4.1 to be completed.

Like the Sm-Nd system the Lu-Hf system, has a long half-life and little fractionation, thus it is commonly put into epsilon notation.

(equation 4.5)

$$\varepsilon_{Hf} = \begin{pmatrix} \frac{176 Hf}{177 Hf_{i}} \\ \frac{176 Hf}{177 Hf_{cHUR i}} - 1 \end{pmatrix} \times 10^{4}$$

Using the equation 1.1 the CHUR ¹⁷⁶Hf/¹⁷⁷Hf can be corrected for the age of the sample. We used ¹⁷⁶Hf/¹⁷⁷Hf and ¹⁷⁶Lu/¹⁷⁷Hf for CHUR from Bouvier et al. (2008).

M.3.4 U-Th-Pb System

Because we measured all of the Pb isotopes and ²⁰⁴Pb is the only non-radiogenically produced isotope of Pb, we can use a different method than the one used for the other isotopic systems. *(equation 5.1)*

$${}^{206}Pb = \frac{1}{\left(1 + \frac{1}{\frac{206Pb}{204Pb}}\right) + \left(\frac{\frac{207Pb}{204Pb}}{\frac{206Pb}{204Pb}}\right) + \left(\frac{\frac{208Pb}{204Pb}}{\frac{206Pb}{204Pb}}\right)}$$

Since the abundance of the radiogenic isotopes are solved, the abundance of ²⁰⁴Pb is:

$${}^{204}Pb = 1 - ({}^{206}Pb + {}^{207}Pb + {}^{208}Pb)$$

Now that we know the abundances of the different Pb isotopes are we can find the atomic weight of Pb in our sample

(equation 5.2)

$$Pb_{wt} = {}^{204}Pb_m \times {}^{204}Pb + {}^{206}Pb_m \times {}^{206}Pb + {}^{207}Pb_m \times {}^{207}Pb + {}^{208}Pb_m \times {}^{208}Pb$$

The atomic weight of an element is equal to the sum of the masses (m) of each isotope multiplied by the abundance of the isotope.

As with the previous isotopic systems we need to find the parent stable isotope ratio *(equation 5.3)*

$$\frac{^{238}U}{^{204}Pb} = \frac{C_U \times ^{238}U}{U_{wt}} \times \frac{Pb_{wt}}{C_{Pb} \times ^{204}Pb}$$
$$\frac{^{232}Th}{^{204}Pb} = \frac{C_{Th} \times ^{232}Th}{Th_{wt}} \times \frac{Pb_{wt}}{C_{Pb} \times ^{204}Pb}$$

The equation for the ²³⁵U/²⁰⁴Pb can be simplified because ²³⁸U/²⁰⁴Pb was calculated.

$$\frac{{}^{235}U}{{}^{204}Pb} = \frac{{}^{238}U}{{}^{204}Pb} \times \frac{{}^{235}U}{{}^{238}U}$$

M.4 Isotopic Mixing

Most continental magmatism is not derived from solely one source, but are rather a mix between two or more sources. Thus, to model the interaction between sources we need equations that describe what the mixing lines should look like, which we can then compare to our data.

These equations describe the mixing between source "a" and source "b". ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr will be used as an example, but this can be done for any of the common heavy radiogenic isotopic systems.

If we start with mixing between two reservoirs for ⁸⁷Sr/⁸⁶Sr.

(equation 6.1)

$$\binom{{}^{87}Sr}{{}^{86}Sr}_m = \frac{f_b{}^{87}Sr_b + [1 - f_b]{}^{87}Sr_a}{f_b{}^{86}Sr_b + [1 - f_b]{}^{86}Sr_a}$$

Where: f_b is fraction of component b

Equation 6.1 simplified if we assume that 86 Sr is equivalent to Sr concentration (86 Sr ~ Sr) *(equation 6.2)*

$$\left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_{mix} = \frac{f_b Sr_b \left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_b + [1 - f_b]Sr_a \left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_a}{f_b Sr_b + [1 - f_b]Sr_a}$$

Appling this to the Nd system

(equation 6.3)

$$\left(\frac{^{143}Nd}{^{144}Nd}\right)_{mix} = \frac{f_b N d_b \left(\frac{^{143}Nd}{^{144}Nd}\right)_b + [1 - f_b] N d_a \left(\frac{^{143}Nd}{^{144}Nd}\right)_a}{f_b N d_b + [1 - f_b] N d_a}$$

Equations 6.2 and 6.3 can be used to solve for the mixing iteratively. To define the equation that describes the mixing line between endmembers we must combine equation 6.2 and 6.3 into a single equation.

If we rewrite equation 6.2 to solve for f_b

$$f_{b} = \frac{[Sr]_{a} \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{a} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix} \right)}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix} ([Sr]_{b} - [Sr]_{a}) - [Sr]_{b} \left(\frac{^{87}Sr}{^{86}Sr}\right)_{b} + [Sr]_{a} \left(\frac{^{87}Sr}{^{86}Sr}\right)_{a}}$$

We can then place it into equation 6.3 to have one uniform equation that describes the mixing line between the two components.

(equation 6.4)

$$\begin{pmatrix} \frac{\left[Sr\right]_{a}\left(\left(\frac{8^{7}Sr}{8eSr}\right)_{a}-\left(\frac{8^{7}Sr}{8eSr}\right)_{mix}$$

Which can be simplified to

$$\left(\frac{^{143}Nd}{^{144}Nd}\right)_{mix} = \frac{[Sr]_a[Nd]_b \left(\frac{^{143}Nd}{^{144}Nd}\right)_b \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_a - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix}\right) + [Sr]_b[Nd]_a \left(\frac{^{143}Nd}{^{144}Nd}\right)_a \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_b\right)}{[Sr]_a[Nd]_b \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_a - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix}\right) + [Sr]_b[Nd]_a \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_b\right)} - \frac{(Sr)_a[Nd]_b \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_a - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix}\right) + [Sr]_b[Nd]_a \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_b\right)} - \frac{(Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b \left(\frac{^{87}Sr}{^{86}Sr}\right)_a - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix}\right) + [Sr]_b[Nd]_a \left(\frac{(Sr)_a[Nd]_a \left(\frac{(Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b (Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b \left(\frac{(Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_b[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_a[Nd]_b (Sr)_b[Nd]_b (Sr)_b (Sr)_b (Sr)_b (Sr)_b (Sr)_b (Sr)_b (Sr)_b (S$$

Results

R.1 Petrography

Here, we use the organization scheme originally proposed by Annells (1974), which divides the different units on Michipicoten Island largely based on petrological and mineralogical differences. The order of this section follows the order of eruption of the Michipicoten Island Formation.

The Cuesta Lower Flow has an abundance of large glomerocrysts and phenocrysts, which make up about 50% of the volume of the sample (fig. 4). Both phenocryst and glomerocryst phases include plagioclase, clinopyroxene, orthopyroxene, biotite and oxides. Plagioclase phenocrysts are euhedral and oscillatory zoned; some exhibit sieve texture with occasional clinopyroxene and/or oxide chadocrysts. Both clinopyroxene and orthopyroxene phenocrysts phases are anhedral. Oxides and biotite phenocryst phases are subhedral. Groundmass within the Cuesta Lower Flow is primarily plagioclase and oxides.

Like the Cuesta Lower Flow, the Cuesta Upper Flow has an abundance of large glomerocrysts and phenocryst phases, but phenocrysts only make up about 40% of the sample by volume. Both phenocryst and glomerocryst phases include plagioclase, clinopyroxene, oxides, and what appear to be replaced olivine crystals (fig. 4). These sparsely replaced olivine crystals seem present in both the glomerocrysts and as phenocryst phases but can be difficult to distinguish from vesicles because the vesicles are filled with a similar alteration product. The plagioclase phenocrysts are euhedral, oscillatory zoned, and some are sieved with occasional clinopyroxene and or oxides forming in the spaces. Clinopyroxene phenocrysts are subhedral and the oxide phenocrysts are anhedral. Groundmass in the Upper Cuesta Member is comprised primarily of plagioclase and oxides.

The Channel Lake Member is largely aphanitic, with phenocrysts making up <1-5% of the volume of the samples (fig. 4). Phenocryst phases include plagioclase, clinopyroxene and oxides. Plagioclase phenocrysts are euhedral, some with sieve or skeletal texture and
sometimes containing clinopyroxene grains. Both clinopyroxene and oxide phenocrysts are anhedral and the oxides are often embayed. The groundmass contains plagioclase, oxides and minor clinopyroxene in the lower flows; clinopyroxene is absent in the upper flows. Sparsely distributed coarser grained semi-spherical mesostasis is present within some of the flows. This mesostasis has irregular shapes and boundaries, containing plagioclase and minor clinopyroxene. Some of the clinopyroxene that comprises the mesostasis is bladed in texture.

The West Sand Bay Tuff member lies between the Channel Lake and the Quebec Harbor Members. This tuff is comprised of subangular green and red clasts with a light green matrix. This matrix is fined grained with minor plagioclase and quartz. The clasts have been highly altered but appear to be vesicular basalt and quartz porphyry. Annells (1974) reports identifying clasts from the Cuesta flows, but this is not apparent in our samples.

The lower flows of the Quebec Harbor Member are comparatively phenocryst rich, up to 10% phenocrysts (fig. 4). Two samples were taken from the lower flows (fig. 3). Phenocryst phases in the lower section consist of plagioclase, clinopyroxene and oxides. The plagioclase crystals are often euhedral, oscillatory zoned, and with sieve texture. While most are euhedral, some are anhedral with highly rounded edges. Clinopyroxene in the lower flows are anhedral, embayed and occasionally elongated. Oxides are euhedral and occasionally embayed. Cumulates, mostly consisting of plagioclase with minor oxides, are common. Annells (1974) reports augite phenocrysts with "spongy texture" in thin sections he observed, but these are not present in our samples. Groundmass phases include plagioclase, clinopyroxene and oxides. The upper flows of the Quebec Harbor Member are phenocryst poor (<1% volume crystals) and are often altered. The result of this alteration is a groundmass made up of oxidized hematite and chlorite. Where phenocrysts are present, they are euhedral plagioclase. The groundmass consists of plagioclase, oxides and minor clinopyroxene.

The South Shore Member has few phenocrysts, only making up ~1% of the sample volume (fig. 4). The phenocrysts consist of plagioclase, clinopyroxene and occasional oxides.

Most of the phenocrysts are isolated crystals, but there are some cumulates. Plagioclase and oxide phenocrysts are subhedral to anhedral, while clinopyroxene is anhedral. Groundmass consists mostly of plagioclase, clinopyroxene, and oxides. The groundmass commonly shows plagioclase in a trachytic texture.

The Davieaux Rhyolite is microcrystalline, with no phenocryst phases that we have observed (fig. 4). Layers of oxides and silicates are folded and show plasticity of the rhyolite flow. There are lenses of ~100 µm anhedral quartz and potassium feldspar in the sample that appear to be secondary based on oxidation rims around these lenses. Microcrystalline phases include quartz, potassium feldspars and altered oxides. Annells (1974) also observed the texture of the Davieaux Rhyolite and did report rare highly altered feldspars phenocrysts. Annells (1974) indicated that the lack of well-preserved glass in this unit suggests it has been subjected to devitrification from hydrothermal activity.

R.2 Geochemistry

While the groupings of the Michipicoten Island Formation were made on the basis of petrography, these divisions are also apparent in the geochemistry. Rock type classification of samples is based on Le Bas et al. (1986). The Michipicoten Island Formation follows a subalkaline tholeiitic trend (fig. 5)

R.2.1 Major Elements

The oldest major volcanic unit in the Michipicoten Island Formation is the Cuesta Member, which is divided into the Upper and Lower Flow. The lower flow is andesitic in composition based on total alkali-silica diagram, with SiO₂ concentration of ~57 wt. % and 5.5 wt. % K₂O wt. % + Na₂O wt. % (fig. 5). Although samples were taken at different stratigraphic positions, it appears, based on the lack of significant geochemical changes in the major or trace elements between samples, that these samples are all from the same flow. The Upper Cuesta Flow is

also an andesite, but with a higher SiO₂ content of 61 wt. % (fig. 5). In major element variation diagrams the Questa Lower Flow lies between the South Shore Member and the Channel Lake Member, or with the more mafic Channel Lake samples. The Questa Upper flow plots with the Channel Lake Member, but with the slightly more silica rich compositions (fig. 6).

The next youngest unit is the Channel Lake Member. The unit is chemically the most variable of any unit in the Michipicoten Island Formation in total alkali-silica space, ranging from low-SiO₂ andesites to rhyolite (SiO₂ wt. % 57-74 avg. 64.5 wt. %) (fig 5). The most evolved flow occurs near the bottom of the section, while the least evolved flows occur near the top of the sequence. The Channel Lake Member has a well-developed trend line with the normally compatible elements MgO, FeO, TiO₂, and CaO all decreasing with SiO₂. P₂O₅ also exhibits a decreasing trend (fig. 6). The normally incompatible elements K₂O and Na₂O increase with silica. The lower SiO₂ wt. % samples have an increasing trend in Al₂O₃ wt. % when compared to SiO₂ wt. %, but the samples with more than 60 wt. % SiO₂ have a decreasing Al₂O₃ trend with increasing SiO₂. The flow-by-flow diagram (fig. 7) shows a general decrease in SiO₂ concentration up section, but faulting of this particular unit is common and may complicate any interpretation (Annells, 1974).

Above the Channel Lake Member is the Quebec Harbor Member. Only a few flows of the Quebec Harbor Member were collected due to limited accessible exposure. This unit is dacitic in composition (fig. 5). This unit has been divided into an unaltered lower section and an altered upper section. Two samples were taken from the unaltered lower part, and compositionally they appear to be a part of the same flow. Samples from this unit are dacitic in composition (~ 70 wt. % SiO₂), breaking the general trend seen in the Channel Lake Member of becoming less evolved up stratigraphy (fig.7). In major element space the Quebec Harbor Member samples plot along with the Channel Lake Member dacites (fig. 6).

The South Shore Member is the most mafic of any of the units in the Michipicoten Island Formation, ranging from basaltic to basaltic andesite in composition (2.1-5.5 wt. % MgO, 49-56

wt. % SiO₂). This member becomes slightly more SiO₂ and TiO₂ rich up section. A sawtooth pattern is evident in the flow by flow diagrams of decreasing incompatible elements followed by a sharp increase; this is the opposite for the compatible elements. This pattern can be most easily seen in SiO₂ and CaO (fig. 7). Like the Channel Lake Member, the South Shore Member has a clear trend line, and the two trend lines intersect and about ~56 wt. % SiO₂ to from a nearly continuous Michipicoten Island Formation trend. In most major element spaces, the Channel Lake Member and the South Shore Member behave similarly and with identical slopes. MgO, FeO, and CaO decrease, while K₂O and Na₂O increase with SiO₂. Unlike the Channel Lake member, TiO₂ does not change when compared to SiO₂ and the majority of South Shore Member Member Samples form an increasing trend in P₂O₅ vs. SiO₂ (fig. 6)

The Davieaux Island Member is a rhyolite and is the most silica rich (72 wt. % SiO₂) of any of the Michipicoten Island Formation units, except the samples from the Channel Lake Member, which appear to be altered (fig. 5). Unlike the rest of the Michipicoten Island Formation the Davieaux Island rhyolite is alkaline instead of sub-alkaline. The rhyolite lies at the end of many of the major element trend lines like FeO, TiO₂ and Al₂O₃, but falls off the trend line in Na₂O, CaO and K₂O (fig. 6).

R.2.2 Trace elements

The Cuesta Upper and Lower flows of the Michipicoten Island Formation exhibit moderate concentrations in the first row transition elements and in high field strength elements (HFSE), when compared to the other Michipicoten Island Formation samples in most trace element spaces; and often overlap with the more mafic samples of the of the Channel Lake Member (fig. 9, 10). This is not true, however, for Ni and Cr in the Cuesta Lower Flow, which has higher concentrations of these elements in comparison to the majority of the other units. Both the Questa Upper and Lower Flows have higher Eu concentrations than the other Michipicoten Island Formation the the other Michipicoten Island Formation units. The samples taken from the upper part of the Cuesta Upper Flow are

quite variable in the large ion lithophile elements (LILE) (fig. 8). From the primitive mantle normalized trace element diagrams we can see that the Cuesta members have strong negative Ti and Sr anomalies (fig. 11). The chondrite normalized REE diagram shows that the flows have a high Eu concentration when compared to other samples, with similar concentrations in REE (fig. 12).

The Channel Lake Member, which lies above the Cuesta Flows, is the most chemically diverse unit of any from the Michipicoten Island Formation. From the array formed by the Channel Lake member, a trend line can be observed in both the first row transition elements (decreasing with increasing SiO₂) and HFSE (increasing with increasing SiO₂), except for Eu, which decreases with increasing SiO₂ (fig. 9, HSFx). The Channel Lake trace element concentrations often lie between the South Shore Member (most mafic) and the Davieaux Island Member (most silicic), with the exception of some HFSE where the Channel Lake Dacites have the highest concentration of Zr, Hf, U, and LREE. Primitive Mantle normalized values appear similar to those of the Cuesta Member, but most have stronger Sr and Ti anomalies (fig. 11). In the Chondrite normalized REE diagrams, the Channel Lake Member has a greater Eu anomaly (fig. 12).

The Quebec Harbor Member is more restricted in its trace element concentrations than the Channel Lake Member stratigraphically below it. The unaltered samples from the Quebec Harbor Member have relatively low first row transition element concentrations but high HFSE concentrations (fig. 9, HFSEx). The unaltered Quebec Harbor Member trace element patterns overlap with those of the Channel Lake Member dacites. The trace element patterns in the Primitive Mantle and Chondrite diagrams are comparable to those of the Channel Lake dacites (fig. 11 and 12). Samples from the altered section show how pervasive the alteration can be, causing samples to fall off the trend line even in the fluid immobile elements like Zr and Hf (fig. HFSEx). It should be noted that sample TOR0000QL, despite being taken from the altered region as denoted in Annells (1974) of the Quebec Harbor Member, mostly plots with unaltered

samples in HFSE and first order transition element space but falls off the trend line in large ion lithophiles (fig. 9, 10, 8).

Lying atop the altered section of the Quebec Harbor Member is the South Shore Member. This unit is the next most variable geochemically after the Channel Lake Member. This unit also forms a trend line in trace element space like that of the Channel Lake Member, with the same trajectory. The South Shore Member has the highest Sc, V and Co and these elements decrease with SiO₂, but very low Ni and Cr, which varies little with SiO₂ (fig. 9). The HFSE in the South Shore Member are the lowest of any Michipicoten Island Formation unit and increase in concentration with SiO₂ (fig. HSFx). This unit has the weakest Sr and Ti anomalies on the Primitive Mantle diagram (fig. 11) and only a slight Eu anomaly in the Chondrite normalized REE plot (fig 11, RIx)

The Davieaux Island Member forms the top unit of the Michipicoten Island Formation stratigraphic section and is geochemically distinct. This unit has a low concentration of the first row transition elements, often forming the most extreme samples of the trend line created by the other Michipicoten samples (fig. 9). The Davieaux Island Member HFSE concentrations are often off the trend line above (i.e. Y, Th, Ta) or below (i.e. Zr, Hf, U, La, Eu) but also lie at the end of the trend line in some spaces (Nb, Yb) (HSFx). From the Primitive Mantle normalized trace element diagram, we can see the Davieaux Island Member has the strongest Sr and Ti anomaly of any of the Michipicoten samples (fig. 11). From the chondrite normalized REE diagram we can observe that the Davieaux Island Rhyolite is depleted in LREE when compared to the Channel Lake dacites but has enriched HREE as well as the strongest Eu anomaly (fig. 12).

R.3 Isotope geochemistry

Eight samples were chosen for analysis of Nd, Sr, Hf, and Pb isotopes. One sample was chosen from each of the thinner units of the Davieaux Island Member, Quebec Harbor Member,

Cuesta Upper and Lower Members. From the larger units (i.e. the Channel Lake Member and the South Shore Member), two samples were chosen. Isotopic data is age corrected to 1100 Ma.

Samples from the Michipicoten Island Formation have radiogenic (¹⁴³Nd/¹⁴⁴Nd)_i ratios, except for sample TOR0000S1. This same trend can be seen in the Hf isotopic data (fig. 13). The Cuesta, South Shore, Davieaux Island Members lies above the mantle array in ϵ Nd_i vs. ϵ Hf_i space, while the sample from the Quebec Harbor Member lie below. The Channel Lake Member has one sample above the mantle array and one just below (fig 13). Most of the samples have near or greater than chondritic ϵ Nd_i (-0.5 - +6.5) and ϵ Hf_i (-1.5 - +4.0) values. This isn't the case for sample TOR0000S1, which has negative ϵ Nd_i (-3.9) and ϵ Hf_i (-12.2). This is unexpected since the other sample from the South Shore Member has the highest ϵ Nd_i and ϵ Hf_i of any sample reported from the MCR.

Most of the Michipicoten Island Samples have near chondritic (0.703125) ⁸⁷Sr/⁸⁶Sr initial values, except for TOR0000S1 from the South Shore Member and the sample from the Davieaux Island Member (fig. 14). TOR0000S1 has a more radiogenic (⁸⁷Sr/⁸⁶Sr)_i and plots closer to rocks from Wawa Greenstone Belt adakites, andesites and basalts in the (⁸⁷Sr/⁸⁶Sr)_i vs. εNd (Turek et al., 1982; Polat and Münker, 2004). The sample from the Davieaux Island Member has a less radiogenic (⁸⁷Sr/⁸⁶Sr)_i value and plots away for the other sample (fig. 14).

Age-corrected Pb isotopic data (²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb)_i shows that samples from the Michipicoten Island Formation vary over a large range and lie above the northern hemisphere reference line (NHRL) (fig. 15). In comparison to the Mamainse Point data, the Michipicoten Island samples lie in a parallel array to the Group 5 samples from Mamainse point. Group 5 is the most crustally-contaminated series of lava flows in the Mamainse point sequence (Shirey et al., 1994). Analyses of Mamainse Point (²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb)_i data shows that values radiate from a common point; the samples from Michipicoten Island, however, do not radiate from this point. The Davieaux Island Member plots at the upper end of the Michipicoten

Island array in the (²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb)_i space. In the (²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb)_i space it plots well below the NHRL. The Cuesta Upper flow lies slightly above the line. The rest of the Michipicoten Island Formation samples lie along the NHRL, and in a similar region as the Mamainse Point samples (fig. 15)

Discussion

D.1 Effects of Alteration

D.1.1 Major and Trace Elements

To understand the geochemistry of the Michipicoten Island Formation we must first assess what effects alteration has had on the different units. The presence of secondary alteration within the Michipicoten Island Formation is well noted (Annells, 1974). The majority of the alteration types seem to be chloritization and silicification. The first physical manifestation of alteration is found within the core of the Cuesta Upper Flow, where there is a secondary deposit of pyrite. Stratigraphically above this deposit, the Cuesta Upper Flow becomes red and plagioclase is the only remnant phase in this section. The other phases appear to have become red oxidized hematite and chlorite. Comparing the chemistry of a sample from the lower unaltered section (TOR0000QS) and a sample from the upper altered section (TOR0000QQ) on a isocon diagram we can observe element mobility between samples (fig. 1t1)(Grant, 2005). From the isocon diagram it appears that Mg, Rb, K, Ba, Ca, Pb, Cs and Sr were mobile based on these sample plotting away from the concentration of the altered sample (C^a = C^m) line.

The alteration observed in the Upper Cuesta Flow continues into the base of the Channel Lake Member. This has resulted in the unit being a similar red color. It also has chalcedony and quartz being deposited in thin fractures and veins, as well as forming agates. At the top of the Channel Lake Member, alteration is also observed, changing the color of the basalt groundmass to dark reds and greens. Closely spaced veining of calcedony, quartz and calcite are within these fractures. Within some of the flows, veining is so pervasive that the sample appears brecciated. Based on the isocon diagram, Pb, Ca, Sr, K, Rb were mobile (fig. 16).

The Quebec Harbor Member has the largest amount of alteration of any of the units within the Michipicoten Island Formation. The physical result of this alteration is that much of

this unit is a bright red color. This alteration allowed for preferential erosion and resulted in the formation of many of the bays on the south side of Michipicoten Island (fig. 3). By comparing the least altered of the altered samples from the altered section of the Quebec Harbor Member and the unaltered Quebec Harbor Member samples, we can observe that K, Rb, Ca, Sr and Mn appear to have been mobilized (fig. 16). When we compare the most altered Quebec Harbor Member Member to the least altered, the elements fall completely off the C^a = C^m line. This may indicate that alteration was so pervasive that it changed the mass of the sample or that the samples are not comagmatic, thus changing the relative proportions of the different elements and pulling all the samples off the C^a = C^m line.

Above the altered section of the Quebec Harbor Member, the South Shore Member is far less altered. Some alteration was concentrated around the edges of columnar jointing, with visible alteration penetrating about 5 mm into the basalt. Two of the flows were highly altered, appearing deep red. Based on the isocon diagram, K, Rb, Sr, P and Cs have been mobilized. Interestingly, Ni and Co fall off the $C^a = C^m$ line; since these elements are typically relatively immobile elements, this may indicate the difference in proportions of oxides between the two samples.

Only one sample was taken from the Davieaux Island Member, which makes an isocon plot impossible. There are strong physical and chemical indicators that this unit has been altered with respect to its LILE. This is evident in the strong positive Pb, K, and Rb anomalies in the primitive mantle diagram. Fractures within the Davieaux Island Member are bleached white and kaolinized, and some of these fractures are filled with quartz or calcite (Annells, 1974).

D.1.2 Effects of Alteration on Radiogenic Isotope Tracers

The effects of alteration are also present in the isotopic systems. The Lu-Hf and the Sm-Nd systems are based upon relatively fluid immobile elements, and thus are unlikely to have been impacted by the alteration processes. These elements are usually close to the isocon lines (fig

iscx). The Rb-Sr isotopic system and the U-Th-Pb isotopic system have more potential for disruption due to alteration because of the relatively fluid mobile elements in these systems.

To help to assess whether the varying isotopic systems are open or closed, isochron plots were utilized. These plots come with some assumptions that must be kept in mind. One of the assumptions is that the individual samples are comagmatic (i.e. all coming from the same source). The second assumption is that all the samples are of the same age (or at least to within error of each other)(Faure, 1986).

Whole rock Rb-Sr isochron ages of the Channel Lake Member were conducted by Chaudhuri and Faure (1967) then later corrected by (Baragar, 1978). The data from these units were imprecise, resulting in the generation of an age that is clearly incorrect of 887 ± 78 Ma; more accurate zircon dating places the age of the Channel Lake Member at no younger than 1084.35± 0.20 Ma (Fairchild et al., 2017). When we apply a linear line of regression to our samples from the Michipicoten Island Formation, we get an age of ~ 854 Ma. Based on more accurate zircon dating we know actual age of the Michipicoten Island Formation is somewhere between 1086 and 1083 Ma this would, indicate that the isotopic system has been perturbed in some fashion so as to reduce the apparent age from the whole rock chemistry (Palmer and Davis, 1987; Fairchild et al., 2017). An explanation for calculating a young date might be that the samples are not all comagmatic, which is the first order assumption for generating a isochron age; additionally any perturbation that resulted in a decrease in the Rb concertation or increase in Sr concentration post eruption would alter ⁸⁷Rb/⁸⁶Sr, and cause a lowering of the slope and thus causing lower isochron age (eqn. 2.1).

From the isochron diagrams, the Rb-Sr system appears to be mostly closed, with most samples plotting near the chondritic line. Sample TOR0000S1 plots above this line, which may indicate some element mobility, or it may indicate that the source of magmatism for this sample was more radiogenic (fig. 17). The Davieaux Island Member plots below the chondritic isochron

line in an anomalously high ⁸⁷Rb/⁸⁶Sr vs. ⁸⁷Sr/⁸⁶Sr, likely indicating that this system wasn't closed for the Davieaux Island Member (Faure, 1986).

For both the Sm-Nd and Lu-Hf isotopic systems, the isochron diagrams show that the systems appear to be closed (fig.17). The two South Shore Member samples fall the furthest off the chondritic isochron. As discussed above, falling off the line isn't necessarily the result of an open system but may be due to mixtures of non-chondritic reservoirs. With the South Shore Member, it would seem that TOR0000S1 mixed with a low ¹⁴⁷Sm/¹⁴⁴Nd source resulting in low ¹⁴³Sm/¹⁴⁴Nd at present. This same pattern holds true for the Lu-Hf isotopic system, but TOR0000S1 falls even further from the chondrite isochron.

The Pb isochrons show that the U-Th-Pb isotopic systems do not seem completely closed in some samples. The Cuesta Upper Flow and Quebec Harbor Member plot away from the chondritic isochrons in all the Pb isotopic plots (fig. 17). This indicates that the Pb system was open for the Cuesta Upper Flow and Quebec Harbor Member. The Davieaux Island Member appears to be only perturbed in ²³⁸Th/²⁰⁸Pb v. ²⁰⁸Pb/²⁰⁴Pb (fig.17). This would seem to indicate there was some thorium mobility in the rhyolite. This also explains why in the in ²⁰⁸Pb/²⁰⁴Pb v. ²⁰⁶Pb/²⁰⁴Pb space the Davieaux Island Member falls far below the NHRL. In the other isotopic spaces, the Davieaux Island member plots where one would expect along the isochron based on where the other Michipicoten samples plot.

From the isochron plots some samples' isotopic signatures are unlikely to be solely the original magma composition. The ⁸⁷Sr/⁸⁶Sr and ²⁰⁸Pb/²⁰⁴Pb ratios from the Davieaux Island Member have likely been affected by some secondary process. It also appears likely that secondary prosses have affected the Cuesta Upper Flow and Quebec Harbor Member Pb isotopic data. For the Davieaux Island Member, Cuesta Upper Flow and Quebec Harbor Member Member the isotopic systems that appear to have been impacted by secondary prosses data are plotted but should not be used for interpretation.

D.2 Generation of Evolved Magmatism

D.2.1 Fractional Crystallization

Fractional crystallization is a commonly invoked process that causes evolution in the composition of a magmatic system. Indeed, fractional crystallization can help explain many of the patterns seen in the geochemistry of the Michipicoten Island Formation. This effect can most clearly be seen in the change in the Eu anomalies (fig. con). Eu is unlike the rest of the REE because it can be both trivalent (the norm for REE, a 3⁺ charge) and divalent (a 2⁺ charge). This divalent nature allows Eu to substitute for Ca in plagioclase. This allows us to understand how much plagioclase crystallization has occurred between melts. The least evolved (most mafic, Mg+Fe rich) unit, the South Shore Member, has a small Eu anomaly in the chondrite normalized diagram, while the most evolved (most silicic or most Mg+Fe depleted) unit, the Davieaux Island Member, has the strongest negative Eu anomaly (fig. 12). The accumulation of plagioclase can explain why the Cuesta flows have higher Eu concentrations than samples from the Channel Lake Member that have similar weight percent SiO₂. This is supported petrographically where we observe that there is plagioclase accumulation within the Cuesta Members. The Cuesta Member also appears to have an accumulation of Fe-Ti oxides, which explains the elevated Cr concertation (fig. 9). Fractional crystallization of monazite or allanite can also possibly explain why the Davieaux Island Member is depleted in the LREE compared the diorites of the Channel Lake Member (Miller and Mittlefehldt, 1982). The trend lines observed are complex and thus require modeling to further explain the variations.

Due to the evolved nature of the Michipicoten Island Formation, Rhyolite MELTS was chosen as the preferred modeling program (Gualda et al., 2012). Models where run at a wide range of internal compositions (TOR0000S1, TOR0000S2, TOR0000RC, and TOR0000RJ) with variable water concentration (0.5% to 5%) and different oxygen fugacities (Δ QFM 1.5 to -0.5 and Δ NNO 1 to -1). Models were also run under variable pressure conditions (0.2 to 10 kbar). MELTS models were unable to fully reproduce the entire trend line for all the major element

compositional spaces (fig. 18). The models do get closer to reproduction of the liquid line of the descent under lower pressures (<2.5 kbar), low water concentrations (<2 wt. %) and oxidizing conditions (Δ NNO = 0). The failure of the MELTS models to accurately reproduce the entire trend lines seen in the major elements would argue that pure fractional crystallization is not the sole process contributing to the evolution of the Michipicoten Island Formation. Thus, we will examine other methods for magma evolution i.e. crustal anatexis and liquid Immiscibility.

D.2.2 Crustal Anatexis

Another commonly invoked method by which magmas can evolve is through crustal anatexis. Within the MCR, this process has been most commonly used to explain the highly evolved nature of rhyolites, and their corresponding extremely non-radiogenic εNd_i values (Nicholson, 1990; Vervoort and Green, 1997; Vervoort et al., 2007). These extremely non-radiogenic εNd_i values are interpreted as coming from the old Archean crust. If this were the case, then we should see a correlation between the less radiogenic values in εNd_i and εHf_i and increasing SiO₂; this is not observed within the Michipicoten Island Formation. Indeed, the Davieaux Island rhyolite (the most silicic sample), has positive εNd_i and εHf_i . In contrast sample TOR0000S1 from the South Shore member is the most mafic but has non-radiogenic εNd_i and εHf_i values. The lack of correlation does not rule out crustal anatexis as a whole. It simply suggests that if there was a significant amount of anatexis, then it must come from a younger, more radiogenic source.

One such possible radiogenic source are the previous flows from the early and main stages of MCR volcanism. By the end of the main stage of volcanism, the volcanic pile has reached an approximate thickness of 20 km between the Michipicoten Island Fault and the Keweenaw fault. This provides a potential source of anatectic melt. From the numerous melting experiments that have been conducted, the amount of water in the system has the most control over the final composition of the melt (Helz, 1976; Spulber and Rutherford, 1983; Beard and

Lofgren, 1989). Thy et al. (1990) compiled data from many of these experiments to help explain the origin of some of the rhyolites found in Iceland. Using these insights we can observe in the Al₂O₃ vs. SiO₂ plot that the high SiO₂ sample from the Michipicoten Island Formation overlap with partial melts of a basaltic source (fig. 19) (Thy et al., 1990). Melting of previous MCR volcanic material has been used to explain the origin of isotopically primitive rhyolites in the Portage Lake Volcanics (Nicholson, 1990). Thus, it seems likely that anatectic melts derived from a partial melting of a basaltic source contributed to the Michipicoten Island Formation geochemical evolution.

D.2.3 Liquid Immiscibility

Magma unmixing through immiscibility results in the separation of an iron rich ferrobasalt and a rhyolite. Experimental results show that a point of liquid immiscibility can occur once the magma reaches 90-95% crystallization and temperatures of 1,010-1,040 C° (Dixon and Rutherford, 1979; Philpotts, 1982; McBirney, 1996). The partitioning of elements between the two magmas leaves a pronounced geochemical signature. The ferrobasalt will be enriched in the REE and HFSE, due to its more depolymerized nature, leaving the rhyolite depleted in these elements (Hess, 1971). The depletion of REE and HFSE in the rhyolitic melt is the opposite of the normal fractional crystallization process, which typically concentrates REE and HFSE in the rhyolitic melt. Based on the partitioning of REE and HFSE, we would expect the Davieaux Island Member rhyolite to have low REE and HFSE concentrations if magma unmixing is playing a role. Since the Davieaux Island Member is the most enriched in terms of the HFSE and HREE elements, it suggests that magma unmixing didn't play a role in the generation of the Michipicoten Island Formation (fig. MPx, 12).

D.3 Temporal Evolution of the Michipicoten Island Formation

The geometry and structure of Michipicoten Island allowed for the preservation of a nearly complete stratigraphic sequence of units. This has exposed a petrologically and geochemically diverse record of a silicic volcanic center, and sampling of this stratigraphy allows for the examination of its evolution. In this section we will describe the magmatic history of the Michipicoten island formation based on the different member's stratigraphic position.

The Michipicoten Island Formation volcanic system began with the Cuesta Lower and Upper Flows. These first two pulses of magmatism carried a relatively large abundance of phenocrysts (CPX+PLG+OX ± BIO) (fig. 4). We interpret this as resulting from an incipient and inefficient magmatic plumbing system. In these early flows, magma stalled within the crust for long enough to generate abundant phenocrysts and glomerocrysts. As the system evolved into the Channel Lake Member, phenocryst phases are less abundant (fig. 4). The loss of phenocrysts is accompanied by a general trend from more evolved (~67 wt. % SiO₂) towards less evolved-up section (~ 55 wt. % SiO₂). This would seem to indicate that melt is spending less time within the crust before eruption. Thus, either the magmatic plumbing system is becoming more efficient, or the magmatic flux is increasing.

The Quebec Harbor Member represents a break in the general progression of decreasing SiO₂ with time, jumping from ~55 wt. % SiO₂ at the end of the Channel Lake Member to ~67% wt. SiO₂ in the Quebec harbor member (fig. 7). The change in geochemistry is also marked with a change in the petrology, with generally aphanitic flows seen throughout the Channel Lake Member, shifting to plagioclase-phyric flows in the Quebec Harbor Member (fig. 4). Examining a Cenozoic flood basalt sequence in East Africa, Krans et al. (2018) observed that plagioclase-phyric flows often occur after a hiatus in volcanism, and this was interpreted to be the result of plagioclase mobilization from the magma mush after recharge. While some anhedral plagioclase crystals may have been picked up this way, the lack of a sharp increase in the Eu concentration between the high SiO₂ Channel Lake samples and the Quebec Harbor

Member suggest that there wasn't a large amount of plagioclase accumulation, rather the majority of the plagioclase crystalized from the liquid (fig. 10). The Quebec Harbor member represents a period of reduced flux, allowing for the crystallization of plagioclase crystals preeruption.

After the low flux period, which produced the Quebec Harbor member, the South Shore member is produced. This unit has returned to the aphanitic texture seen in the Channel Lake Member (fig. 4). The geochemistry also appears to have returned to the Channel Lake-like system as well. This suggests that the magmatic flux has increased from the Quebec Harbor Member. The seemingly rapid change from the evolved geochemistry of the Quebec Harbor Member back to a system that is more similar to the Channel Lake Member, suggests that the more efficient magmatic plumbing system created by the end of the Channel Lake Member remained intact despite the slowdown in flux between the Channel Lake Member and the South Shore Member. Unlike the Channel Lake Member, it appears that the magmatic system has become stabilized in TiO_2 (i.e. unchanging with SiO_2) (fig.6). This is the first evidence of the Michipicoten Island Formation becoming buffered and indicates the Ti must be highly compatible in the solid phase (Lee et al., 2014). With the eruption of the last of the South Shore Member the volcanic system shuts down.

The formation of the Davieaux Island Member represents the last gasp of this magmatic system. The exact relationship between the Davieaux Island Member and the South Shore Member is unclear due to the lack of a contact between the units. However, we do know that less than 1 million years passed between eruptions, because the West Sand Bay Member is dated at 1084.4 Ma, (below the Quebec Harbor Member) and the Davieaux Island Member 1083.5 Ma. The shift from basaltic andesites in the South Shore Member to rhyolite in the Davieaux Island Member clearly represents a shift in the nature of the magmatic system. Previously when the Michipicoten Island Formation contained high silica products (e.g. Quebec Harbor Member) it was marked with an increase in the abundance of phenocrysts, but the

Davieaux Island rhyolite is conspicuously devoid of phenocrysts (fig. 4). A mechanism for generating crystal poor rhyolites is compression and melt extraction (Bachmann and Bergantz, 2004; Hildreth, 2004). This would seem to be further supported by the geochemistry in which the Davieaux Island Member seemingly falls off the Zr trend line formed by the other Michipicoten Island Formation samples (fig. 10). This signature can be generated by melt initially following the typical liquid line of descent with increasing Zr with increasing SiO₂, then once the melt reaches zircon saturation and 50% crystallinity it can be compressed and extraction will cause the erupted of a rhyolite with depleted in Zr (fig.20) (Deering and Bachmann, 2010).

D.4 Temporal Context of the Michipicoten Island Formation in the Framework of MCR Magmatic Stratigraphy

Magmatism within the MCR has been broken into four stages: Initiation, early, main, and late, each with some unique geochemical characteristic. The initiation stage is composed of ultramafic to mafic intrusives related to melting from the impacting plume and thus drawing any comparison to the late stage magmas would be futile (Heaman et al., 2007; Miller and Nicholson, 2013). The early stage is largely composed of basaltic material with some studied evolved melts found in the North Shore Volcanic Group (NSVG) (Dosso, 1984; Vervoort and Green, 1997; Vervoort et al., 2007). Magmatism from the hiatus stage is rare and is only found at Mamainse Point. The Mamainse Point formation is also the most well characterized geostratigraphic section within the MCR volcanics, making it a useful comparator to the Michipicoten Island sample suite. Basaltic volcanism from the main stage can be found throughout the rift but silicic volcanism is more prevalent on the western arm of the MCR. This study is the first rigorous geochemical study of late stage volcanism within the MCR. It is thus important to understand the similarities in geochemistry between the late stage magmas and

previous magmatic stages because they can provide insight into how the Michipicoten Island Formation formed.

D.4.1 Early Stage

Evolved magmas are rare during the early stage of magmatism in the MCR. The evolved melts from the early flows of the NSVG have a broadly similar trace element pattern to the Michipicoten Island Formation, especially in the highly incompatible elements, although the slope across REE is steeper than the Michipicoten Island Formation samples (fig. 21) (Vervoort and Green, 1997). It should be noted that a steep slope to the REE is a common feature of the early stage basalts (Shirey et al., 1994; Nicholson et al., 1997). Isotopically, the melts produced from this stage have only a slightly non-radiogenic values of ca. -5 to 0 ϵ Nd (Vervoort and Green, 1997; Vervoort et al., 2007). Evolved melts during this time migrated though the cold continental crust with little interaction, and evolve by fraction crystallization and assimilation of previous MCR material or high Sm/Nd crust (Vervoort and Green, 1997).

D.4.2 Hiatus Stage

There is very little volcanism preserved from the hiatus stage. Dating of silicic clasts from the Copper Harbor Conglomerate in the Keweenaw Peninsula by Davis and Paces (1990) indicate that during the hiatus stage there was some silicic volcanism in the western arm of the MCR (fig. 2). The only place where hiatus volcanism is preserved in their original flows is within the Mamainse Point Sequence. The flows from the Mamainse Point Sequence have been broken into 8 distinct groups based on their geochemistry (Klewin and Berg, 1990). The flows from the hiatus stage are referred to as Group 5. The Group 5 lavas from Mamainse Point can be broken into three subgroups 5 a, b and c (Klewin and Berg, 1991). These basalts appear to have different trace element patterns, with Group 5b having the lowest enrichment in trace elements (Fig. 21). Despite this, Klewin and Berg (1991) were able to show that the Group 5a magmas

could be reproduced by simple mixing of ~80% 5b melt and ~20% rhyolitic melt, which the authors use as their crustal melt analog. The Group 5c magmas are more complex, requiring both fractional crystallization and crustal contamination to produce the trace element enrichment. The Group 5c trace elements follow a very similar trace element pattern to the Michipicoten Island Formation (fig. 21). Isotopically the Group 5 basalts from Mamainse Point appear to be quite different from those of the Michipicoten Island Formation with more non-radiogenic ϵ Nd- ϵ Hf values and lie between the primitive mantle and the continental crust. The isotopic data from the Group 5 lavas at Mamainse Point led Shirey et al. (1994) to interpret the source for these lavas was the primitive mantle (i.e. plume) with variable amount of continental crust.

D.4.3 Main Stage

Lying beneath the late stage volcanic of the Michipicoten Island Formation is the Quebec Mine Member basalts, which are texturally similar to the main stage lavas found at Mamainse Point (Annells, 1974). The main stage lavas at Mamainse Point have been broken into 3 groups: Groups 6, 7 and 8. Group 8 type lavas are only found at Mamainse Point and have a geochemical signature unlike any other volcanics found in the MCR (Shirey et al., 1994; Nicholson et al., 1997). Trace element patterns are similar between the Group 6 and 7 but Group 6 has higher trace element concentrations (21). Group 6 trace elements patterns, in particular, resemble the trace element pattern of the Michipicoten Island Formation in the more compatible trace elements (fig. 21). Isotopically, Group 6 and 7 lavas lie between the primitive mantle and depleted mantle components, with Group 6 closer to the primitive mantle and Group 7 closer to the depleted mantle in ϵ Nd- ϵ Hf space (fig. 13). Shirey (1994) interpreted these isotopic data to indicate that the main stage volcanism is the result of variable amounts of the plume and depleted mantle; this has been supported by other authors working on other main stage volcanic sequences (Paces, 1988; Paces and Bell, 1989b; Nicholson et al., 1997). The

majority of the Michipicoten Island samples plot near the Group 6 and 7 basalts from Mamainse Point, though are farther off the mantle array (fig. 13).

Evolved magmatism from this stage is has been predominantly studied in two formations, the NSVG on the western shore of Lake Superior and the Portage Lake Volcanics (PLV) in the Keweenaw Peninsula. The trace element patterns of the main stage NSVG icelandites appear similar to the samples from Michipicoten Island, although the rhyolite taken from the main stage volcanism doesn't show the depletion in Zr, Hf, Sm, Nd and LREE that the Davieaux Island Member exhibits (fig. 21 and 11). In the NSVG the rhyolitic and granophyric magmas have highly non-radiogenic ε Nd_i values (-15 to -2) (Vervoort and Green, 1997; Vervoort et al., 2007). The intermediate magmas (icelandites and andesites) from the main stage have less non-radiogenic ε Nd_i values (-9 to 0, most < -4) (Dosso, 1984; Vervoort and Green, 1997). The difference in isotopic signature between the rhyolites and the intermediate magmas has been interpreted to be the result of the melting of the highly non-radiogenic Archean crust producing rhyolitic and granophyric magmas, while the intermediate magma (like the evolved melts of the main stage) are the result of fractional crystallization with little interaction from the crust (Vervoort and Green, 1997).

Nicholson (1990) noted that many of the rhyolites in the Portage Lake Volcanics, found in the Keweenaw Peninsula, fall broadly into two categories: type 1 and type 2. These magma types were defined on the basis of petrologic differences. Most notably, type 2 shows the presence of quartz phenocrysts, whereas in type 1 magmas quartz is only present in the groundmass. From a petrographic standpoint, the Davieaux Island Rhyolite would appear most similar to the type 1 rhyolites. From a trace element perspective the Davieaux Island Member is most similar to the type 1, with a more sloped REE pattern and not as pronounced Eu anomaly in comparison to the type 2 rhyolites (Nicholson, 1990). The Davieaux Island Member deviates from both groups in ϵ Nd_i values: the type 2 rhyolites have ϵ Nd values between -13.3 to -15.9, while type 1 have ϵ Nd_i values between -0.3 to -4.7, the Davieaux Island Member has ϵ Nd value

of 2.4. The type 1 Rhyolites have been interpreted to have been the result of fractional crystallization of the Portage Lake Volcanics and melting of the previous basalt.

The late stage volcanics Michipicoten Island Formation, from a trace element perspective, appear most similar to the Group 5 basalts from Mamainse Point (erupted during the hiatus stage) and icelandites from the NSVG during the main phase of magmatism. Isotopically, however, the Michipicoten Island Formation samples are different from the Group 5 basalts and are most similar to main stage basalts from Mamainse Point (Groups 6 and 7). A common interpretation for evolved magmatism with highly incompatible trace enrichments and radiogenic ϵ Nd_i values is that it is the result of melting and assimilation from previous MCR volcanics (Nicholson and Shirey, 1990; Vervoort and Green, 1997; Vervoort et al., 2007).

D.5 Hybridization of Late Stage Magmatism in the MCR

The formation of intermediate lavas, like those observed on Michipicoten Island, may be the result of mixing of a rhyolitic melt with a basaltic melt. As discussed above, the Michipicoten Island Formation trace element patterns look similar to those of the Group 5 magmas from Mamainse Point. Klewin and Berg (1991) showed that this trace element pattern can be reproduced through fractional crystallization and rhyolite mixing. This has been physically observed at Mamainse Point where basalts appear to be intermingling with rhyolites (Matthews and Rooney, 2009). A requirement for any silicic melt that has mixed with the Michipicoten Island Formation is that the rhyolite must contain radiogenic Nd and Hf isotopic values as well as non-radiogenic Sr isotopic values (unlike the Archean continental crust); otherwise mixing of the rhyolite would cause a crustal contamination signature. If the rhyolite might cause a perturbation towards the PM source, since most of the MCR flood basalts have a strong PM isotopic signature. Isotopically, it is impossible to tell the difference between direct crustal anataxis of earlier MCR material and mixing of rhyolites that are formed from the same source.

Petrographically, however, there is evidence for magma mixing. The spherical mesostasis observed in the Channel Lake Member is texturally similar to the "magmatic inclusions" discussed in Bacon (1986), which are interpreted to be undercooled mafic melts that are mixing/mingling with the host evolved magmas. Thus, it is apparent that some amount of magma hybridization is playing a role in the formation of the late stage magmas on Michipicoten Island.

D.6 Mantle Sources of Late Magmatism in the MCR

Traditionally there has been discussion of four distinct isotopic reservoirs contributing to the MCR volcanics: the Primitive Mantle (PM), the Depleted Mantle (DMM), Sub Continental Lithospheric Mantle (SCLM), and the Archean Continental Crust (CC) (Nicholson and Shirey, 1990; Shirey et al., 1994; Shirey, 1997; Vervoort and Green, 1997; Vervoort et al., 2007). The Primitive Mantle isotopic composition for the MCR within the Nd system is thought to be chondritic, which has been interpreted as melting from an upwelling thermochemical anomaly such as a plume source (Nicholson and Shirey, 1990; Shirey et al., 1994; Shirey, 1997; Vervoort and Green, 1997; Wirth et al., 1997; Vervoort et al., 2007). The chondritic nature of the plume has also been applied to the Sr isotopic system (Nicholson and Shirey, 1990; Shirey et al., 1994). Since the Nd and Sr isotopic systems both indicate the plume source is chondritic then it would stand to reason that the Hf isotopic composition of the plume would be chondritic as well. In this study we use the chondritic Nd and Hf isotopic values from Bouvier et al. (2008) and Sr isotopic values from Workman and Hart (2005). From current work being conducted on the Mamainse Point Sequence (not part of this project), the Pb isotopic data radiate out of a single point. This most likely represents the plume component, since this component is the only one that all the Mamainse Point basalts share (Rooney et al., 2018). The depleted MORB mantle is another source that is thought to be contributing as a source of magmatism in the MCR, although this source seems to be primarily restricted to the main stage of volcanism (Shirey et

al., 1994; Nicholson et al., 1997; Miller and Nicholson, 2013). This source is defined by its radiogenic Nd and Hf, and unradiogenic Sr and Pb isotopic characteristics. For this reservoir we use the depleted mantle Nd isotopic value from Bennett (2003), Hf from Blichert-Toft et al (1997), Sr from Workman and Hart (2005) and Pb from Zindler and Hart (1986).

The continental crust is a more variable source reservoir. Underlying the MCR in the Michipicoten Island region is the Wawa Greenstone Belt. As discussed in the in the crustal anatexis section, the contamination derived from old Archean crust would not have to be very significant to alter the isotopic signature of the Michipicoten Island Formation, and thus must be considered. The Wawa Greenstone Belt is a sub-province of the Superior Craton and is thought to have formed as a result of subduction accretion complexes (Polat and Kerrich, 2000). The Wawa Greenstone Belt is the closest pre-rift crustal formation to Michipicoten Island. Despite an initial positive cNd-cHf isotopic signature during formation, isotopic ingrowth in the Wawa Greenstone Belt has resulted in strongly negative ɛNd and ɛHf values due to low Sm/Nd and Lu/Hf ratios (fig. 13)(Polat and Münker, 2004). The Pb isotopic system is much more difficult to constrain since there has been no whole rock Pb isotopic study of the Wawa Greenstone Belt. In an effort to try to constrain our crustal end member in terms of Pb, we examine the Mamainse Point sequence (Shirey et al., 1994). The array created by the Group 5 magmas, which are considered to be the most crustally contaminated of the Mamainse Point basalts, demonstrate the influence of the continental crust. We can place our crustal endmember at the end of this array opposite of the plume source (Rooney et al., 2018).

The role of the lithospheric mantle in the generation of the Michipicoten Island Formation is more difficult to assess. The complete lack of mantle xenoliths from the region means that there are no direct measurements of the SCLM in the region. Carbonatite magma from the Seabrook Lake Carbonatite, which has been interpreted as primary melts from the SCLM, shows ϵ Nd_i of +4.5 and an initial ⁸⁶Sr/⁸⁷Sr of 0.70265 (Bell and Blenkinsop, 1987). This differs from the isotopic characteristic proposed by Shirey et al. (1994). Recent work on the trace

elements of metabasalts of the Coldwell Complex indicates that they are the result of melting of a metasomatized SCLM. Two samples taken from the outer metabasaltic unit have negative εNd values (Good and Lightfoot, 2019). Our project places isotopic constraints (Nd, Hf, Sr, and Pb) on the SCLM by utilizing samples from the Wolfcamp Basalts at the interior of the Coldwell Complex, which have positive εNd_i values (Rooney et al., 2018). We will use those preliminary results to constrain our SCLM end member. With these main components defined we can now attempt to assess their contribution to the Michipicoten Island Formation.

To assess what the relative contribution of each source (PM, DMM, SCLM, and CC) the most direct approach would be to create a four component unmixing model to quantitatively assign the contribution of each component. The reason we were unable to conduct such a model is due to the sources of magmatism not being as well defined for the Midcontent Rift system as they are for other rift systems. Thus, creating a numerical unmixing model would be prone to significant error because the solution would lack an illustrative topology of the mixing relationships. For our purposes, it is important to examine such mixing relationships and the relative position of the Michipicoten Island samples in relation to the endmembers noted above. To address this, we create ternary mixing models whereby two reservoirs where chosen (A and B) and a mixing line was solved for iteratively between the two (eqn. 5.2 and 5.3). Then, for every iteration of that mix, a new mixing line was created between the A-B mix fraction and a new component C.

From the isochron diagrams we know that the Nd and Hf isotopic systems are the most reliable in terms of closure (fig. 17). The source for the Nd and Hf isotopic systems also has the most well-defined magmatic endmembers, which make the (¹⁴³Nd/¹⁴⁴Nd)_i vs. (¹⁷⁶Hf/¹⁷⁷Hf)_i plot ideal for the mixing models (fig. 22). From mixing these sources in Nd, Hf isotopic space we can observe that most samples lie within the DMM, CC (continental crust), and SCLM mixing field. The two South Shore Members lie just on the outside of the mixing field with TOR0000S1 near the CC-SCLM line, and TOR0000RQ near the DMM-SCLM line. The DMM might have had a

less radiogenic signature 1.1 billion years ago than our equations predict which, would explain why TOR0000RQ is not captured in the mixing field. As for TOR0000S1, there are more nonradiogenic examples of the Wawa Greenstone Belt that could be contributing as the crustal source. The units that lie within the mixing fields that lie above the mantle array can be attributed to < 2% mixing of the continental crust and samples lying below the mantle can be attributed to <2% mixing of the subcontinental lithospheric mantle respectively. An issue with the ¹⁴³Nd/¹⁴⁴Nd vs. ¹⁷⁶Hf/¹⁷⁷Hf isotopic diagram is that the PM source can be replicated through the mixture of DMM, SCLM, and CC, thus other isotope spaces must be analyzed to assess whether the plume source is present and whether the samples plot within the same mixing field as in the (¹⁴³Nd/¹⁴⁴Nd)_i vs. (¹⁷⁶Hf/¹⁷⁷Hf)_i plot. Additional ternary mixing models were created in $(^{206}Pb/^{204}Pb)_i$ vs. $(^{143}Nd/^{144}Nd)_i$ and $(^{206}Pb/^{204}Pb)_i$ vs. $(^{176}Hf/^{176}Hf)_i$ plots, which unlike in the (¹⁴³Nd/¹⁴⁴Nd)_i vs. (¹⁷⁶Hf/¹⁷⁶Hf)_i plot, the PM component doesn't lie within the DMM, SCLM and CC mixing field due to the more radiogenic ²⁰⁶Pb/²⁰⁴Pb signature of the PM. From these diagrams, we observe that the Michipicoten Island samples plot near the PM source and outside of the DMM, SCLM and CC field. These two facts mean that the primitive mantle is a required magmatic source for the Michipicoten Island Formation.

Our model may not be able to give us exact numbers on how much of each source contributed to the Michipicoten Island Formation samples, but they do illustrate how much control the different components have. Because the concentration of elements in the continental crust and the lithospheric mantle are so much higher than the PM and the DMM reservoirs, the fact that most of the samples lie near the DMM and PM components indicates that they must be contributing the largest proportion of melt. The depleted mantle signature in the late stage magmas of the Michipicoten Island Formation is an interesting outcome since this source indicates decompression of the asthenosphere must have continued during this late stage of magmatic activity. Such an interpretation has implications for geodynamic models of rift development and the eventual failure of the MCR.

D.7 Implication for Rift Failure

The original interpretation of the Great Lakes International Multidisciplinary Program on Crustal Evolution (GLIMPCE) seismic lines resulted in the interpretation that MCR failure was due to far-field effects of the Grenville orogeny (Cannon and Hinze, 1992; Cannon, 1994). Reinterpretation of the GLIMPCE lines by Stein et al. (2015) using numerical stepwise structural restoration models called into question whether the MCR failed due to orogenesis, instead suggesting that successful rifting of Amazonia and Laurentia resulted in the removal the stress required for continued continental rifting of the MCR after the early stage of volcanism. Swanson-Hysell et al. (2019) point out that an Amazonia-Laurentia rifting model is difficult to reconcile with the timing of the Ottawa phase of the Grenville Orogeny and that the Amazonia – Laurentia rift would have had to have formed and then shortly afterwards been inverted. Instead, Swanson-Hysell et al. (2019) used dating of the unconformities, which are referred to as "post-rift unconformity" at ~1091 as an indicator of when the transition from active rifting to thermal subsidence began. Swanson-Hysell et al. (2019) concluded that the cessation of active rifting at 1091 Ma is correlative with the beginning of the Ottawa phase of Grenville orogeny.

Dating of volcanic bodies from the Adirondack highlands indicates that the Ottawa phase of the Grenville Orogeny had begun by 1080 ± 4 Ma (Chiarenzelli and McLelland, 1991; McLelland et al., 2001). The DMM signature within the Michipicoten Island Formation suggests that thinning of the lithospheric mantle continued until 1083 Ma - this is within error of beginning of orogenesis. This would seem to indicate that these two events are likely correlated and lends additional evidence to the Cannon (1994) model for the MCR failure as a result of far-field effects of the Grenville orogeny.

Conclusion

The Michipicoten Island Formation is the youngest exposed volcanic sequence from the final stage of volcanism within the failed Midcontent rift. As such it preserves the conditions during final stages of activity within this rift. Lavas within the Michipicoten Island Formation are more evolved than would be anticipated from a terminal oceanic rifting environment. Within an advanced oceanic rifting environment, such as Afar (East Africa), the silicic magmatism is accompanied by primitive basaltic magmatism. Within the Michipicoten Island Formation, we lack primitive basaltic magmatism and only have examples of evolved magmatic activity. Our major and trace element chemistry form an array from relatively undifferentiated to differentiated compositions extending from basaltic andesites to rhyolites. The continuum of compositions is unusual for rifting environments, and likely reflects mixing of rhyolitic and basaltic magmas. The major and trace element data of the Michipicoten Island Formation resembles other units within the MCR - notably hybridized Group 5 basalts from Mamainse Point. However, our new isotopic data show significant differences between the Michipicoten Island Formation and other evolved magmatism within the MCR. These older evolved magmas appear to be the result of mixing between the primitive mantle and old continental crust; the Michipicoten Island Formation isotopically appears to resemble the main stage of volcanism that was the result of mixing between the depleted mantle and the primitive mantle during a period of extension. Our results show that these sources continued to contribute to the final stages of magmatism within the MCR. Importantly, Archean continental crust was no longer significantly contributing to the final stage, suggesting that Archean crustal material may not be present at this late stage of rifting... This implies that magma chambers of the Michipicoten Island Formation were located within the previous volcanic units, which may have contributed chemically but would be difficult to resolve isotopically because of their similar composition. Previous episodes of evolved magmatic activity within the MCR tended to coincide with hiatuses in magmatism. During these hiatus stages, extension is thought to have waned and lavas from this period appear to be dominated

by melts derived from a plume source mixed with the continental crust; little contribution from the depleted upper mantle is observed. Unlike these older hiatus events, the Michipicoten Island Formation appears to continue to have the same isotopic characteristics as the previous main stage of volcanism. The implication of this observation is that decompression melting of the depleted upper mantle continued during this final stage of magmatic activity. Such an observation has a profound impact on geodynamic models for the development and failure of the MCR, as it implies plate thinning continued to ca. 1083 Ma. Future work will examine the disconnect between evidence within the crust of a much earlier cessation in the manifestation of extension, and the results presented here that require continued thinning of the lithospheric mantle. APPENDICES

APPENDIX A

FIGURES





Gravity anomaly map modified from Stein et al. (2015). Arrow indicating the Michipicoten Island gravity high.

Figure 2: MCR Stratigraphy



Stratigraphic columns of magmatic and sedimentary units found within the MCR. Dates in bold are from Fairchild et al. (2017) and other dates are from Palmer and Davis (1987). Upper right map is a magnetic anomaly map of the Lake Superior region. Figure modified from Fairchild et al. (2017).



Figure 3: Geologic Map of Michipicoten Island

Geologic map of Michipicoten Island. Figure modified from Fairchild et al. (2017) original map from Annells (1974). Pink pentagons are the sample locations.



Crossed polarized light images taken at 2X magnification of samples from the Michipicoten Island Formation. **a**. Davieaux Island Member. **b**. South Shore Member. **c**. Quebec Harbor Member. **d**. Channel Lake Member. A magmatic inclusion is in the center of the image. **e**. Cuesta Upper Flow. The image highlights a glomerocryst **f**. Cuesta Lower Flow.





a. Total Alkali Silica classification diagram (Le Bas et al., 1986) and alkaline v. sub-alkaline discrimination line (Irvine and Baragar, 1971). **b**. Discrimination diagram of tholeiitic v. calcalkaline (Irvine and Baragar, 1971). FeO* is the total iron calculated as FeO.
Figure 5 (cont'd)







Major elements diagrams of the Michipicoten Island Formation. Key is ordered by stratigraphic position



Figure 7: Flow Evolution Diagrams



Flow evolution diagrams showing the change in the major elements with relative stratigraphic position.



Figure 8: Large Ion Lithophile Element Diagrams

Large ion lithophile element v. silica



Figure 9: First Row Transition Elements Diagrams

First row transition elements v. silica



Figure 10: High Field Strength Element Diagrams

High field strength elements v. silica





Figure 11: Primitive Mantle Normalized Trace Element Diagrams

Primitive mantle normalized trace element. Faded purple region indicating the range of the Michipicoten Island Formation. Samples ordered by stratigraphic position and normalized to McDonough and Sun (1995)

Figure 11 (cont'd)



Figure 12: Chondrite Normalized Rare Earth Element Diagrams



Chondrite normalized rare earth element diagrams. Dashed line in the Quebec Harbor Member graph indicate sample was taken from the altered section as mapped by (Annells, 1974). Faded purple region indicating the range of the Michipicoten Island Formation. Samples ordered by stratigraphic position and normalized to McDonough and Sun (1995).

Figure 12 (cont'd)







εNd_i v. εHfi plot showing the Michipicoten Island Formation samples with Groups 5, 6 and 7 from Mamainse Point. Also shown are carbonatite magmas and alkaline basalts from the Coldwell Complex. Wawa Greenstone Belt (WSB) data is from Polat and Münker (2004) and is added to the plot because it is the closest Archean crustal material to Michipicoten Island. All data is age corrected to 1100 Ma. Mantle array from Chauvel et al. (2008). Depleted MORB mantle (DMM) composition from Bennett (2003) and Blichert-Toft et al. (1997). Primitive Mantle composition is chosen to be chondritic and thus must lie at 0,0 in εNd, εHf space. Red circles indicate samples where their original isotopic signature were likely perturbed by alteration.





(⁸⁷Sr/⁸⁶Sr)_i v. εNd_i plot showing the Michipicoten Island Formation samples with carbonatite magmas and alkaline basalts from the Coldwell Complex. As well as Portage Lake Volcanic (PLV) samples from Nicholson and Shirey (1990). Archean crustal field created from Sr isotopic data from Turek et al. (1982) and Nd isotopic data from Polat and Münker (2004). Red circles indicate samples that their original isotopic signature was likely perturbed by alteration.



Figure 15: Pb Isotope Diagrams

Pb isotope plots showing the Michipicoten Island Formation samples with Groups 5, 6 and 7 from Mamainse Point. Also shown are alkaline magmas from the Coldwell Complex. Location of

Figure 15 (cont'd)

the primitive mantle is based on the convergence the Mamainse Point data. Red circles indicate samples where their original isotopic signature were likely perturbed by alteration. **a.** ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb. **b.** ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb. Location of the continental crust (CC) Pb isotopic ratio based on Mamainse Point Group 5, which is interpreted to be a mix between PM and CC sources. DMM isotopic composition based on Zindler and Hart (1986).



Figure 16: Isocon Diagrams

Isocon diagrams. These diagrams show the element mobility by plotting the element concentration unaltered sample on the x axis against an altered sample but one of similar origin on the y axis. Element concentrations were multiplied by a scaling factor to bring them to within the plot region because element concentrations were vastly different between members. The black line is the slope and is equal to 1, thus if the concentration in the altered sample is the same as the unaltered then it will fall on this line. Blue lines indicating the \pm 10% of the slope equal to 1.

Figure 17: Isochron Diagrams



Isochron plots of the Michipicoten Island Formation. Blue line is the 1100 Ma chondritic isochron. Y axis values are the measured isotopic values, X values are calculated (e.q. 1.2, 2.2, 3.2, 4.4). **a**. ⁸⁷Sr/⁸⁶Sr versus ⁸⁷Sr/⁸⁶Rb **b**. ¹⁷⁶Hf/¹⁷⁷Hf versus ¹⁷⁶Lu/¹⁷⁷Hf **c**. ¹⁴³Nd/¹⁴⁴Nd versus ¹⁴⁷Sm/¹⁴⁴Nd **d**. ²⁰⁸Pb/²⁰⁴Pb versus ²³²Th/²⁰⁴Pb **e**. ²⁰⁷Pb/²⁰⁴Pb versus ²³⁵U/²⁰⁴Pb **f**. ²⁰⁷Pb/²⁰⁴Pb versus ²³⁵U/²⁰⁴Pb





Liquid lines of descent for a range of MELTS models. Conditions for these models were pressure set at 2 kbar, oxygen fugacity set at NNO = 0 and the starting composition was sample TOR0000S2. Model varied by concentration of water added.

Figure 19: Chemical Comparison of Michipicoten Island Formation Samples to Experimentally Produced Liquids



 Al_2O_3 versus SiO_2 plot showing the Michipicoten Island Formation samples compared to experimentally produced liquids from melting of basalt under different hydration conditions.. A. Lowest H₂O field. B. Moderate H₂O field C. Highest H₂O field. Figure modified from Thy et al. (1990).



Figure 20: Liquid Extraction Diagram

Figure from Deering and Bachmann (2010) showing the behavior of Zr during liquid extraction.



Figure 21: Primitive Mantle Normalized Comparison Diagrams

Primitive mantle normalized trace element diagrams from different regions of the MCR. Faded purple region indicating the range of the Michipicoten Island Formation. Samples ordered by Figure 21 (cont'd)

stratigraphic position and normalized to primitive mantle (McDonough and Sun, 1995). **a**. Mamainse Point samples from the main stage of volcanism divided based on the work of Klewin and Berg (1991) and new trace element concentrations from Rooney (in progress). **b**. Mamainse Point samples from the hiatus of volcanism divided based on the work of Klewin and Berg (1991) and new trace element concentrations from Rooney (in progress). **c**. North Shore Volcanic Group samples from both the main and early stages of volcanism (Vervoort and Green, 1997). Icelandite are solid lines with circles and the rhyolite is a dashed line with stars.



Figure 22: Ternary Magma Mixing Model

Ternary magma mixing model plots. Red circles indicate samples where their original isotopic signature were likely perturbed by alteration. Dark blue lines are mixing lines between PM, SCLM and DMM. Light blue lines are mixing lines between PM, SCLM and CC. Red lines are mixing lines between PM, DMM and CC. This model was created by first iteratively calculating a primary mixing line between two endmembers, then for each iteration a secondary mixing line is generated between the mix and the third endmember. Each point represents an iterative calculation. Only select secondary mixing lines are shown. **a.** Hf vs. Nd isotopic mixing plot. PM, SCLM and DMM mixing field (dark blue) generated with primary mixing between DMM and PM, at every 10%. Secondary mixing of (DMM, PM)_{mix} with the SCLM lines at every 10% mix of PM,

Figure 22 (cont'd)

points at every 1% mix of SCLM. PM, SCLM and CC mixing field (light blue) with primary mixing between PM and SCLM at every 1% mix. Secondary mixing (PM, SCLM)mix with the CC lines between 99% and 90% mix of PM with points at every 1% mix of CC. PM, DMM and CC mixing field (red) generated by with primary mixing between DMM and PM at every 10% mix. Secondary mixing (DMM, PM)_{mix} with the CC points at every 1% mix. **b.** Pb versus Nd isotopic mixing plot. PM, SCLM and DMM mixing field (dark blue) generated by the primary mixing between DMM and SCLM points at every 1% mix. Secondary mixing (DMM, SCLM)_{mix} with the PM, lines between 0% and 3% SCLM points at every 1% PM. PM, SCLM and CC mixing field (light blue) primary mixing between SCLM and CC points at every 1% mix. Secondary mixing (SCLM, CC)_{mix} with the PM, lines every 10% between 100 and 10% SCLM points at every 1% PM. PM, DMM and CC mixing field (red) generated by with primary mixing between DMM and CC points at every 1%. Secondary mixing (DMM, CC)_{mix} with the PM, lines between 99 and 90% with 0% DMM points at every 1% PM. c. Pb versus Hf isotopic mixing plot. PM, SCLM and DMM mixing field (dark blue) generated by the primary mixing between DMM and SCLM points at every 1%. Secondary mixing (DMM, SCLM)_{mix} with the PM, lines between 0% and 5% SCLM points at every 1% PM. PM, SCLM and CC mixing field (light blue) with primary mixing between SCLM and CC points at every 1%. Secondary mixing (SCLM, CC)_{mix} with the PM, lines every 10% between 100% and 10% SCLM points at every 1% PM. PM, DMM and CC mixing field (red) generated by with primary mixing between DMM and CC points at every 1%. Secondary mixing (DMM, CC)_{mix} with the PM, lines between 99 and 95% with 0% of DMM points at every 1% of PM.

86

APPENDIX B

TABLES

Table 1: Major Elements Concentrations

Sample	Unit Member	SiO2 (%)	TiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MnO (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	P2O5 (%)	LOI (%)	Sum (%)
TOR0000 SB	Michipicoten Island	63.58	1.08	13.11	7.13	0.15	1.62	3.85	4.43	1.81	0.24	2.79	97
TOR0000 SD	Cuesta Lower Flow	56.57	1.94	14.31	10.34	0.23	2.87	5.88	3.49	2.08	0.5	1.6	98.21
TOR0000 SE	Cuesta Lower Flow	55.87	2.01	14.19	11	0.23	3.03	6.11	3.29	2.11	0.52	1.46	98.36
TOR0000 SF	Cuesta Lower Flow	55.87	1.97	14.03	10.65	0.22	3.08	6.41	3.21	2.02	0.51	1.85	97.97
TOR0000 SG	Cuesta Lower Flow	56.31	1.97	14.22	10.49	0.25	3.04	5.64	3.53	2.13	0.51	1.74	98.09
TOR0000 QQ	Cuesta Upper Flow	55.76	1.61	15.47	8.22	0.13	4.16	1.3	2.08	7.17	0.52	3.22	96.42
TOR0000 QR	Cuesta Upper Flow	58.23	1.54	15.23	7.94	0.11	2.89	2.4	2.67	5.71	0.48	2.61	97.2
TOR0000 QS	Cuesta Upper Flow	59.06	1.44	15.02	7.7	0.15	1.7	5.8	3.88	1.18	0.46	3.39	96.39
TOR0000 QJ	Channel Lake Member	67.43	0.53	13.94	4.11	0.1	0.5	2.9	4.78	1.73	0.1	3.6	96.12
QK	Channel Lake Member	67.91	0.54	14.05	4.18	0.1	0.53	2.96	4.83	1.77	0.1	2.77	96.97
QL	Channel Lake Member	70.73	0.52	13.65	3.84	0.07	0.68	0.33	3.75	5.08	0.1	1.06	98.75
QM	Channel Lake Member	67.42	0.58	14.04	4.47	0.11	0.6	2.89	5.02	1.83	0.12	2.68	97.08
QN	Channel Lake Member	73.37	0.58	13.26	2.03	0.02	0.24	1.23	3.5	4.54	0.12	0.89	98.89
QO	Channel Lake Member	67.46	0.58	14.13	4.44	0.12	0.64	2.92	4.85	1.91	0.12	2.6	97.17
QT	Channel Lake Member	67.05	0.64	14.11	4.64	0.11	0.7	3.2	4.77	1.72	0.14	2.69	97.08
	Channel Lake Member	66.81	0.61	14.06	4.62	0.11	0.68	3.09	4.68	1.67	0.13	3.32	96.46
	Channel Lake Member	66.74	0.6	13.96	4.48	0.11	0.65	3.17	4.68	1.62	0.13	3.63	96.14
QW TOR0000	Channel Lake Member	66.94	0.66	14.1	4.69	0.11	0.73	3.3	4.69	1.6	0.14	2.8	96.96
QX TOR0000	Channel Lake Member	72.75	0.51	13.52	1.61	0.03	0.17	0.71	3.31	5.38	0.1	1.68	98.09
QY TOR0000	Channel Lake Member	65.74	0.74	14.04	5.3	0.12	0.91	3.61	4.54	1.57	0.16	3.04	96.73
QZ TOR0000	Channel Lake Member	66.09	0.73	14.14	4.91	0.12	0.82	3.6	4.58	1.5	0.17	3.11	96.66
R1 TOR0000	Channel Lake Member	58.99	1.45	14.84	8.84	0.16	3.45	1.6	4.05	3.42	0.43	2.57	97.23
R3 TOR0000	Channel Lake Member	57.22	1.58	14.45	9.38	0.26	2.86	6.51	3.57	0.99	0.41	2.55	97.23
R4 TOR0000	Channel Lake Member	57.72	1.6	14.38	9.75	0.18	2.62	0.34	3.78	1.09	0.4	1.96	97.86
R5 TOR0000	Channel Lake Member	62.49	1.49	13.56	8.14	0.09	1.88	3.17	2.24	4.38	0.4	1.93	97.84
R6 TOR0000	Channel Lake Member	62.66	1.08	14.3	6.59	0.14	1.21	4.47	4.14	1.55	0.25	3.49	90.24
R7 TOR0000	Channel Lake Member	56.76	1.00	14.07	10.46	0.10	2 75	6.72	3.56	0.91	0.63	1.8	98.01
R8 TOR0000	Channel Lake Member	55.86	1.92	13.74	10.40	0.22	26	6.84	3 44	0.86	0.61	3.28	96.53
R9 TOR0000	Channel Lake Member	56.89	1.92	13.81	10.41	0.26	2.68	6.81	3.53	0.86	0.61	2.03	97.78
RA TOR0000	Channel Lake Member	53.97	2.02	14.29	13.05	0.19	4.35	2.96	3.81	1.58	0.64	3	96.86
KB TOR0000	Channel Lake Member	56.25	1.92	13.77	10.74	0.22	2.68	6.91	3.57	0.78	0.6	2.38	97.44
TOR0000	Channel Lake Member	56.44	1.96	13.89	10.81	0.22	2.71	6.87	3.62	0.78	0.6	1.92	97.9
TOR0000 RE	Channel Lake Member	56.18	1.91	13.84	10.5	0.24	2.76	6.81	3.48	0.76	0.55	2.79	97.03
TOR0000 RE	Channel Lake Member	64.95	0.75	14.2	5.39	0.12	0.85	3.8	4.19	1.45	0.16	3.88	95.86
TOR0000 RG	Channel Lake Member	64.69	0.79	14.38	5.76	0.13	0.97	3.86	4.24	1.61	0.18	3.12	96.61

Major elements concentrations were analyzed at Michigan State University on a Bruker S4 Pioneer X-Ray Fluorescence Spectrometer (XRF).

Table 1 (cont'd)

Sample	Unit Member	SiO2 (%)	TiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MnO (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	P2O5 (%)	LOI (%)	Sum (%)
TOR0000 RH	Channel Lake Member	64.56	0.8	14.32	5.59	0.14	0.98	3.58	4.53	1.9	0.18	3.17	96.58
TOR0000 RI	Channel Lake Member	67.36	0.65	14.19	4.97	0.1	1.45	0.63	4.45	3.96	0.14	1.83	97.9
TOR0000 RJ	Channel Lake Member	58.33	1.51	15.03	8.76	0.12	3.64	4.29	3.55	2.27	0.44	1.89	97.94
TOR0000 RK	Channel Lake Member	57.95	1.41	14.85	9.11	0.16	3.74	2.03	3.16	4.22	0.41	2.77	97.04
TOR0000 RH	Channel Lake Member	64.56	0.8	14.32	5.59	0.14	0.98	3.58	4.53	1.9	0.18	3.17	96.58
TOR0000 RI	Channel Lake Member	67.36	0.65	14.19	4.97	0.1	1.45	0.63	4.45	3.96	0.14	1.83	97.9
TOR0000 RJ	Channel Lake Member	58.33	1.51	15.03	8.76	0.12	3.64	4.29	3.55	2.27	0.44	1.89	97.94
TOR0000 RL	Channel Lake Member	59.02	1.4	15.08	8.41	0.13	2.92	4.37	3.78	2.02	0.42	2.29	97.55
TOR0000 RM	Channel Lake Member	62.93	1.12	14.36	7.17	0.11	2.49	1.01	4.46	3.59	0.29	2.25	97.53
TOR0000 RN	Channel Lake Member	63.68	1.09	13.88	7.17	0.12	2.97	0.88	3.05	4.59	0.22	2.14	97.65
TOR0000 RO	Channel Lake Member	61.95	1.1	14.61	7.19	0.16	3.68	0.78	3.69	4.27	0.22	2.13	97.65
TOR0000 T1	Channel Lake Member	61.63	1.24	14.73	7.3	0.14	3.47	1.44	2.82	4.4	0.31	2.34	97.48
TOR0000 S8	Channel Lake Member	58.3	1.74	15.35	9.24	0.15	3.43	1.71	7.15	0.08	0.44	2.3	97.59
TOR0000 S5	Quebec Harbor Member altered	68.51	0.66	13.51	5.01	0.06	1.13	0.42	4.12	4.49	0.13	1.72	98.04
TOR0000 S6	Quebec Harbor Member altered	48.9	2.1	16.74	12.78	0.2	5.78	2.25	5.26	1.55	0.53	3.71	96.09
TOR0000 SN	Quebec Harbor Member altered	65.29	1.5	11.49	7.34	0.09	2.7	2.9	5.48	0.09	0.31	2.73	97.19
TOR0000 SJ	Quebec Harbor Member unaltered	65.98	0.81	13.6	4.92	0.12	0.79	3.53	4.23	1.36	0.16	4.27	95.5
TOR0000 SK	Quebec Harbor Member unaltered	66.45	0.78	13.63	4.69	0.11	0.68	3.22	4.4	1.93	0.15	3.71	96.04
TOR0000 SM	South Shore Member	52.94	2.55	14.13	12.27	0.33	3.57	8.19	2.72	0.45	0.53	2.12	97.68
TOR0000 SL	South Shore Member	52.74	2.47	14.05	12.62	0.22	3.54	8.33	2.72	0.41	0.64	2.08	97.74
TOR0000 SI	South Shore Member	54.8	2.44	15.86	9.11	0.1	2.05	4.44	5.34	3.01	0.41	2.23	97.56
TOR0000 SH	South Shore Member	51.1	2.06	13.32	14.16	0.39	5.01	6.93	3.04	1.31	0.29	2.23	97.61
TOR0000 S4	South Shore Member	54.77	2.2	14.01	11.07	0.15	4.23	5.09	4.12	1.82	0.32	2.05	97.78
TOR0000 S3	South Shore Member	51.86	2.14	13.51	14.55	0.23	4.37	8.12	2.95	1.13	0.33	0.7	99.19
TOR0000 S2	South Shore Member	50.3	2.38	13.29	15.12	0.23	4.44	9.1	2.77	0.41	0.27	1.54	98.31
TOR0000 S1	South Shore Member	47.49	2.46	14.05	15.82	0.32	5.23	9.47	2.57	0.38	0.28	1.8	98.07
TOR0000 S0	South Shore Member	53.1	2.39	13.59	12.65	0.23	3.64	7.93	3.23	0.57	0.67	1.86	98
TOR0000 RZ	South Shore Member	50.5	2.48	14.3	12.86	0.45	4.38	8.52	2.84	0.44	0.69	2.23	97.46
TOR0000 RY	South Shore Member	49.85	2.49	14.45	13.17	0.31	3.62	8.53	2.67	0.41	0.77	3.6	96.27
TOR0000 RX	South Shore Member	52.47	2.52	13.74	14.27	0.17	3.49	5.91	3.76	1.58	0.38	1.58	98.29
TOR0000 RW	South Shore Member	51.7	2.45	13.82	13.65	0.27	4.18	7.81	2.88	1.26	0.39	1.49	98.41
TOR0000 RV	South Shore Member	53.4	2.44	14.04	11.49	0.25	4.57	3.83	4.41	1.9	0.66	2.81	96.99
TOR0000 RU	South Shore Member	53.77	2.54	14.19	11.52	0.25	4.74	3.14	4.22	2.35	0.56	2.49	97.28
TOR0000 RT	South Shore Member	53.94	2.41	13.78	12.55	0.26	3.65	7.21	3.04	1.6	0.56	0.88	99
TOR0000 RS	South Shore Member	52.99	2.43	13.76	12.97	0.28	3.77	7.77	3.2	0.94	0.52	1.26	98.63
TOR0000 RR	South Shore Member	51.57	2.44	14.06	12.98	0.26	4.04	7.71	2.96	1.4	0.72	1.74	98.14
TOR0000 RQ	South Shore Member	52.27	2.59	13.64	13.19	0.28	3.79	7.98	3.27	1.19	0.43	1.25	98.63
TOR0000 RP	Davieaux Island Member	70.9	0.19	13.75	2.43	0.04	0.78	0.15	1.16	8.62	0.02	1.75	98.04

Sample	Unit Member	Analysis Day	Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)
TOR0000 SB	Michipicoten Island Intrusive	3	15.3	91	2.71	14.2	5.92	23.2	104.7	199
TOR0000 SD	Cuesta Lower Flow	3	25.1	155	11.64	23.5	14.85	22.4	80.7	176
TOR0000 SE	Cuesta Lower Flow	3	27.9	161	12.18	25.2	16.24	22.0	66.3	165
TOR0000 SF	Cuesta Lower Flow	3	26.4	160	12.43	24.4	15.35	21.4	67.7	189
TOR0000 SG	Cuesta Lower Flow	3	26.1	157	12.27	23.0	14.74	22.8	73.6	157
TOR0000 QQ	Cuesta Upper Flow	1	20.3	82	5.06	16.0	7.04	23.4	118.8	123
TOR0000 QR	Cuesta Upper Flow	1	19.4	78	4.82	15.2	6.84	25.5	41.6	137
TOR0000 QS	Cuesta Upper Flow	3	18.6	63	4.21	13.6	5.25	23.8	58.2	612
TOR0000 QJ	Channel Lake Member	1	10.1	7	BDL	3.4	BDL	22.2	88.1	454
TOR0000 QK	Channel Lake Member	1	10.5	7	BDL	3.2	BDL	22.3	78.4	325
TOR0000 QL	Channel Lake Member	1	10.1	7	BDL	3.2	BDL	21.1	161.3	81
TOR0000 QM	Channel Lake Member	1	11.0	11	BDL	4.2	BDL	22.2	81.6	232
TOR0000 QN	Channel Lake Member	1	10.4	14	BDL	2.8	BDL	20.5	144.1	89
TOR0000 QO	Channel Lake Member	1	10.7	11	BDL	3.8	BDL	21.7	79.9	292
TOR0000 QT	Channel Lake Member	1	11.7	17	BDL	4.8	0.92	22.5	90.8	270
TOR0000 QU	Channel Lake Member	1	11.3	14	BDL	4.3	1.04	22.6	82.8	330
TOR0000 QV	Channel Lake Member	1	11.1	14	BDL	4.2	0.97	21.6	98.6	283
TOR0000 QW	Channel Lake Member	1	11.7	21	BDL	4.9	1.02	22.9	94.6	322
TOR0000 QX	Channel Lake Member	1	10.5	7	BDL	2.2	BDL	20.6	154.9	58
TOR0000 QY	Channel Lake Member	1	13.3	38	BDL	6.9	2.05	23.1	88.5	319
TOR0000 QZ	Channel Lake Member	1	12.5	25	BDL	5.6	1.09	22.0	86.9	369
TOR0000 R1	Channel Lake Member	2	21.6	136	3.02	20.3	13.01	20.9	123.7	145
TOR0000 R3	Channel Lake Member	2	24.3	153	4.11	20.8	12.75	23.0	37.9	630
TOR0000 R4	Channel Lake Member	2	23.8	161	4.12	22.4	11.79	23.1	41.2	412
TOR0000 R5	Channel Lake Member	2	22.9	160	3.73	16.5	10.73	20.8	95.7	159
TOR0000 R6	Channel Lake Member	2	16.1	39	1.55	8.3	2.73	23.1	54.0	728
TOR0000 R7	Channel Lake Member	2	18.0	54	1.90	9.5	3.18	22.6	53.3	733

 Table 2: Trace Elements Concentrations

Trace elements analyses using a Photon-Machines Analyte G2 Excimer laser and Thermo

Scientific ICAP Q quadrupole inductively coupled plasma mass spectrometer (ICP-MS).

Deviation on replicated analyses is less than 5% except for low concentrations (< 2 ppm) of

Cr and Ni. Below detection limit (BLD) is 3 times the gas blank.

Table 2 (cont'd)

Sample	Unit Member	Analysis	Sc (ppm)	V (ppm)	Cr	Co	Ni (ppm)	Ga	Rb (nnm)	Sr (ppm)
TOR0000	Channel Lake Member	3	(ppm) 27.3	(ppm) 126	(ppiii) BDL	(ppin) 18.8	(ppm) 1.19	(ppin) 21.1	(ppili) 31.3	(ppin) 509
R8 TOR0000 R9	Channel Lake Member	2	26.5	134	BDL	19.2	1.25	22.9	30.9	592
TOR0000 RA	Channel Lake Member	1	26.1	125	BDL	18.5	1.62	22.2	30.8	569
TOR0000 RB	Channel Lake Member	2	28.6	148	BDL	21.0	1.07	22.7	35.0	175
TOR0000 RC	Channel Lake Member	2	26.8	138	0.97	20.1	1.72	22.9	28.2	515
TOR0000 RD	Channel Lake Member	2	27.7	139	BDL	20.8	1.57	23.3	28.4	522
RE	Channel Lake Member	2	27.3	146	0.93	19.5	2.04	23.4	32.3	576
RF	Channel Lake Member	2	13.6	15	1.06	5.1	1.38	23.3	57.1	564
RG	Channel Lake Member	2	14.9	22	1.07	6.3	1.63	23.5	60.0	495
RH	Channel Lake Member	2	15.5	21	1.17	6.3	1.65	23.1	57.0	395
RI	Channel Lake Member	3	12.6	8	BDL	4.5	1.07	21.0	149.9	154
RJ	Channel Lake Member	1	22.1	131	4.50	19.0	16.72	23.3	63.5	184
TOR0000 RK	Channel Lake Member	1	20.5	111	4.36	17.4	15.49	22.5	166.7	219
RL	Channel Lake Member	2	21.6	121	4.56	19.4	17.82	22.1	64.8	268
TOR0000 RM	Channel Lake Member	2	20.1	62	1.50	10.8	3.71	21.6	108.9	235
TOR0000 RN	Channel Lake Member	2	21.7	103	1.40	13.0	5.37	22.8	113.4	224
TOR0000 T1	Channel Lake Member	4	18.9	74	2.00	13.4	5.04	-	94.2	140
TOR0000 S5	Quebec Harbor Member altered	3	11.2	8	BDL	3.0	0.62	18.8	142.1	135
10R0000 S6	Quebec Harbor Member altered	3	31.5	215	6.16	26.5	18.27	23.8	37.6	154
TOR0000 SN	Quebec Harbor Member altered	4	22.8	148	3.14	16.3	9.33	-	2.0	30
TOR0000 SJ	Quebec Harbor Member unaltered	4	12.8	15	BDL	5.2	0.91	-	81.0	209
TOR0000 SK	Quebec Harbor Member	4	12.4	14	BDL	5.0	0.81	-	113.6	325
TOR0000 SM	South Shore Member	3	33.4	182	BDL	23.4	0.70	20.1	7.7	1158
TOR0000 SL	South Shore Member	3	32.9	177	BDL	22.6	2.27	22.6	7.3	774
TOR0000 SI	South Shore Member	3	44.2	315	22.68	20.1	17.21	14.9	114.6	264
TOR0000 SH	South Shore Member	3	40.1	382	9.24	41.7	21.19	22.3	25.4	191
TOR0000 S4	South Shore Member	3	29.5	253	7.98	36.3	21.32	16.3	51.2	177
TOR0000 S3	South Shore Member	3	39.6	361	BDL	42.4	19.07	19.4	34.1	174
TOR0000 S2	South Shore Member	3	41.4	440	10.92	43.7	34.59	20.1	12.0	301
10R0000 S1	South Shore Member	3	42.9	461	11.46	45.6	37.33	21.5	4.9	332
TOR0000 S0	South Shore Member	3	32.3	192	BDL	26.8	3.01	20.9	19.4	459
TOR0000 RZ	South Shore Member	3	32.3	208	1.27	27.6	3.52	21.1	7.7	2104

Table 2 (cont'd)

Sample	Unit Member	Analysis Day	Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)
TOR0000 RY	South Shore Member	3	33.0	196	BDL	26.9	4.32	21.3	6.4	457
TOR0000 RX	South Shore Member	2	37.8	329	1.10	34.1	4.26	21.1	75.9	235
TOR0000 RW	South Shore Member	2	36.2	308	BDL	35.6	3.70	23.2	40.7	172
TOR0000 RV	South Shore Member	2	31.5	194	1.02	28.6	2.61	23.3	57.2	396
TOR0000 RU	South Shore Member	2	35.5	213	0.91	27.6	1.64	21.7	76.9	409
TOR0000 RT	South Shore Member	1	32.6	198	BDL	27.8	1.18	20.9	43.7	190
TOR0000 RS	South Shore Member	1	34.3	211	BDL	29.7	1.10	21.6	20.3	285
TOR0000 RR	South Shore Member	1	33.0	215	1.40	26.8	4.19	23.9	32.8	190
TOR0000 RQ	South Shore Member	2	37.0	262	1.99	31.1	7.90	23.3	38.1	185
TOR0000 RP	Davieaux Island Member	3	3.0	6	BDL	2.4	2.52	20.6	243.2	42

Table 2	(cont'd)
---------	----------

Sample	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)
TOR0000SB	93.2	469	46.1	81.41	756	60.5	123.3	14.5	57.6
TOR0000SD	71.5	468	34.6	1.65	689	45.9	96.5	11.8	49.3
TOR0000SE	78.6	493	35.7	1.03	657	47.9	98.5	12.3	52.1
TOR0000SF	73.4	465	34.5	0.98	613	46.1	95.6	11.8	49.7
TOR0000SG	70.4	467	34.8	1.03	600	47.2	97.6	11.9	50.0
TOR0000QQ	84.8	563	43.4	3.40	1939	58.5	125.2	14.8	58.9
TOR0000QR	81.1	564	41.7	3.52	451	76.6	152.3	17.4	65.9
TOR0000QS	81.1	577	40.4	51.96	759	55.4	112.8	13.8	57.3
TOR0000QJ	76.9	688	50.2	220.48	1035	63.9	131.0	14.8	55.1
TOR0000QK	77.6	699	51.4	47.45	1008	64.7	132.1	15.1	55.9
TOR0000QL	70.9	679	47.8	1.52	774	55.9	116.0	12.9	47.4
TOR0000QM	76.9	693	50.6	34.41	983	64.3	130.0	14.9	55.7
TOR0000QN	66.9	659	46.8	1.41	870	61.4	121.3	13.8	51.4
TOR0000QO	75.6	689	50.5	34.93	1022	64.4	131.5	15.1	55.9
TOR0000QT	78.3	695	49.6	26.97	998	64.2	131.4	15.2	56.2
TOR0000QU	76.4	694	49.1	33.37	964	63.5	127.4	14.7	55.2
TOR0000QV	72.2	647	48.5	28.66	953	60.8	125.3	14.1	52.8
TOR0000QW	74.9	666	49.3	34.18	967	62.5	129.2	14.7	54.7
TOR0000QX	64.1	675	48.3	2.19	882	60.2	120.7	13.9	51.7
TOR0000QY	71.0	626	46.7	34.75	941	58.0	120.4	13.9	51.5
TOR0000QZ	75.8	659	47.6	37.48	943	61.6	124.6	14.2	53.7
TOR0000R1	66.3	535	39.0	5.74	860	45.6	104.3	12.4	50.7
TOR0000R3	62.4	470	33.2	77.61	579	44.5	92.0	11.3	46.0
TOR0000R4	61.5	458	32.9	149.20	619	41.9	90.1	10.8	44.8
TOR0000R5	55.4	428	31.5	3.40	1156	39.6	88.2	10.6	42.9
TOR0000R6	72.9	706	47.1	161.88	821	54.6	120.5	14.0	54.6
TOR0000R7	75.7	704	44.7	131.86	787	54.8	115.2	13.7	54.7
TOR0000R8	76.0	442	33.8	59.01	496	44.4	93.2	11.7	49.5
TOR0000R9	71.4	417	33.7	83.61	514	41.6	90.9	11.5	48.6
TOR0000RA	72.0	418	32.8	63.53	499	42.8	88.3	11.1	46.0
TOR0000RB	78.8	444	35.3	4.66	393	39.5	94.5	12.1	50.9
TOR0000RC	72.4	418	32.7	72.67	505	40.8	88.7	11.2	47.4
TOR0000RD	72.2	414	32.5	66.80	496	40.4	87.2	11.0	47.0
TOR0000RE	71.8	428	33.0	70.84	466	40.4	86.5	10.8	46.5
TOR0000RF	79.7	828	49.5	117.29	898	59.8	126.2	14.8	57.6
TOR0000RG	79.5	826	50.0	96.35	903	59.7	127.6	14.8	57.9
TOR0000RH	83.3	851	50.3	81.54	974	61.2	125.9	15.1	59.2
TOR0000RI	79.6	866	49.1	1.85	1174	98.8	163.4	18.1	66.0
TOR0000RJ	58.7	460	32.5	1.70	593	48.0	94.0	11.2	44.1

|--|

Sample	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)
TOR0000RK	59.0	483	33.8	18.83	655	53.4	98.7	11.6	46.1
TOR0000RL	58.8	481	34.4	2.40	567	46.5	98.8	11.9	47.5
TOR0000RM	84.1	763	48.0	4.54	923	51.8	110.7	13.4	54.3
TOR0000RN	75.4	769	48.3	6.15	795	49.3	112.0	13.2	52.5
TOR0000T1	71.1	640	42.3	4.09	618	49.0	105.6	12.5	49.6
TOR0000S5	75.4	659	49.3	2.53	1025	57.1	117.8	13.0	49.9
TOR0000S6	71.7	511	37.6	3.46	480	44.2	104.5	12.8	52.5
TOR0000SN	47.7	344	24.8	0.28	39	27.1	57.7	6.8	28.4
TOR0000SJ	78.7	680	50.0	47.14	883	61.2	124.8	14.7	57.4
TOR0000SK	79.6	691	50.6	18.92	900	62.0	126.4	14.8	57.1
TOR0000SM	63.4	285	25.1	0.45	354	31.4	67.8	8.7	37.6
TOR0000SL	63.0	285	25.8	0.42	289	35.7	74.4	9.5	40.4
TOR0000SI	62.6	360	28.5	24.89	775	37.1	80.4	10.0	41.7
TOR0000SH	49.9	262	20.5	0.50	449	28.7	60.2	7.4	31.1
TOR0000S4	32.9	195	15.5	3.00	464	20.0	43.4	5.3	22.3
TOR0000S3	49.9	242	19.3	0.59	343	26.8	56.4	7.1	29.7
TOR0000S2	50.2	208	18.3	6.97	257	22.8	47.9	6.3	27.1
TOR0000S1	51.1	210	18.7	0.51	233	23.7	50.8	6.5	28.2
TOR0000S0	63.1	279	24.5	15.75	354	33.9	71.1	9.2	40.0
TOR0000RZ	63.1	280	25.5	1.52	409	34.9	77.3	9.7	41.1
TOR0000RY	67.7	296	26.7	0.48	290	37.4	80.8	10.2	43.9
TOR0000RX	56.8	263	22.0	8.34	495	27.4	58.5	7.6	33.5
TOR0000RW	55.5	250	21.1	0.49	344	26.8	58.1	7.5	32.7
TOR0000RV	61.2	282	26.2	2.32	866	31.6	73.2	9.4	40.3
TOR0000RU	61.9	303	26.8	1.79	1180	33.3	73.2	9.5	41.0
TOR0000RT	59.4	271	24.2	1.27	405	32.3	67.9	8.7	36.4
TOR0000RS	58.8	274	23.9	4.58	362	31.9	66.4	8.5	36.0
TOR0000RR	64.3	282	25.2	0.64	391	35.3	73.3	9.4	39.8
TOR0000RQ	60.0	263	22.6	0.59	362	28.5	62.3	8.1	35.7
TOR0000RP	108.2	270	51.0	16.94	1180	42.5	88.3	9.1	32.3

Table 2	(cont'	d)
---------	--------	----

Sample	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)
TOR0000SB	13.5	2.52	14.5	2.44	15.5	3.37	9.74	1.56	10.22
TOR0000SD	11.5	3.51	12.3	1.98	12.4	2.65	7.52	1.16	7.62
TOR0000SE	12.3	3.64	13.3	2.10	13.2	2.85	7.96	1.25	8.03
TOR0000SF	11.8	3.55	12.6	2.00	12.4	2.66	7.59	1.18	7.75
TOR0000SG	11.8	3.63	12.3	2.02	12.5	2.62	7.35	1.15	7.43
TOR0000QQ	13.6	3.70	14.4	2.39	15.0	3.10	9.00	1.41	8.70
TOR0000QR	12.9	3.50	13.3	2.15	13.7	2.95	8.87	1.35	8.91
TOR0000QS	13.1	3.70	13.9	2.21	13.9	2.96	8.61	1.32	8.50
TOR0000QJ	12.1	2.26	12.1	2.04	13.0	2.78	8.33	1.30	8.59
TOR0000QK	12.2	2.32	12.2	2.09	13.1	2.80	8.42	1.35	8.69
TOR0000QL	10.6	2.32	11.1	1.91	12.4	2.66	8.00	1.25	8.40
TOR0000QM	12.1	2.33	12.4	2.09	13.2	2.81	8.48	1.35	8.85
TOR0000QN	11.2	2.12	11.1	1.87	11.7	2.47	7.29	1.16	7.47
TOR0000QO	12.3	2.36	12.3	2.06	13.1	2.81	8.43	1.31	8.81
TOR0000QT	12.5	2.43	12.5	2.10	13.3	2.84	8.52	1.33	8.81
TOR0000QU	12.0	2.36	12.2	2.07	13.2	2.80	8.33	1.33	8.57
TOR0000QV	11.5	2.27	11.5	1.94	12.4	2.59	7.75	1.26	8.06
TOR0000QW	12.1	2.41	12.0	2.03	12.8	2.71	8.16	1.26	8.43
TOR0000QX	11.1	2.11	11.0	1.85	11.7	2.46	7.40	1.21	7.87
TOR0000QY	11.3	2.32	11.4	1.94	12.3	2.59	7.70	1.25	7.89
TOR0000QZ	11.9	2.43	12.1	2.03	12.9	2.71	8.13	1.31	8.33
TOR0000R1	11.4	2.88	11.8	1.88	11.4	2.36	6.84	1.02	6.99
TOR0000R3	10.5	2.70	10.9	1.73	10.9	2.28	6.55	0.98	6.63
TOR0000R4	10.1	2.67	10.6	1.67	10.7	2.18	6.38	0.95	6.53
TOR0000R5	9.7	2.60	9.9	1.58	9.9	2.04	5.87	0.88	5.94
TOR0000R6	12.1	2.86	12.3	1.98	12.6	2.62	7.75	1.19	8.25
TOR0000R7	12.1	2.88	12.5	2.03	12.7	2.66	7.89	1.21	8.18
TOR0000R8	11.7	3.19	12.9	2.13	13.0	2.78	7.99	1.20	7.75
TOR0000R9	11.8	3.16	12.7	2.01	12.7	2.63	7.54	1.11	7.48
TOR0000RA	11.1	3.10	12.3	2.07	12.7	2.67	7.66	1.20	7.33
TOR0000RB	12.4	3.02	13.4	2.17	13.5	2.77	8.15	1.19	7.92
TOR0000RC	11.6	3.05	12.7	1.97	12.6	2.62	7.56	1.11	7.47
TOR0000RD	11.2	3.06	12.4	1.98	12.5	2.59	7.51	1.13	7.44
TOR0000RE	10.9	3.01	12.1	1.96	12.1	2.53	7.30	1.09	7.26
TOR0000RF	12.9	2.84	12.8	2.09	13.3	2.80	8.43	1.29	8.94
TOR0000RG	12.6	2.86	12.6	2.09	13.2	2.78	8.34	1.29	8.82
TOR0000RH	12.9	2.89	13.3	2.16	13.8	2.90	8.73	1.35	9.25
TOR0000RI	12.2	2.60	12.0	2.05	13.1	2.87	8.57	1.39	9.00
TOR0000RJ	9.9	2.74	10.4	1.68	10.3	2.14	6.14	0.96	5.94

Sample	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)
TOR0000RK	10.8	3.04	10.7	1.70	10.4	2.14	6.21	0.97	6.06
TOR0000RL	10.3	2.61	10.7	1.67	10.3	2.09	6.13	0.91	6.14
TOR0000RM	12.5	2.96	13.5	2.22	14.4	3.01	9.07	1.37	9.43
TOR0000RN	12.1	2.65	12.2	2.05	13.3	2.80	8.25	1.27	8.62
TOR0000T1	10.9	2.71	11.7	1.91	12.1	2.59	7.58	1.16	7.68
TOR0000S5	10.8	2.20	11.1	1.94	12.5	2.72	8.02	1.26	8.32
TOR0000S6	12.0	2.94	12.5	1.96	12.3	2.62	7.51	1.17	7.48
TOR0000SN	7.1	2.25	8.0	1.33	8.3	1.75	5.07	0.77	5.02
TOR0000SJ	12.1	2.49	12.5	2.05	12.9	2.76	8.21	1.28	8.42
TOR0000SK	12.0	2.43	12.4	2.05	13.0	2.79	8.20	1.28	8.54
TOR0000SM	9.4	2.78	10.6	1.73	10.9	2.35	6.55	1.01	6.44
TOR0000SL	10.1	2.97	11.0	1.77	10.8	2.32	6.50	1.01	6.44
TOR0000SI	9.8	2.66	10.3	1.66	10.4	2.27	6.45	0.99	6.37
TOR0000SH	7.5	2.19	8.2	1.34	8.4	1.81	5.12	0.79	5.13
TOR0000S4	5.3	1.64	5.8	0.93	5.9	1.23	3.40	0.52	3.34
TOR0000S3	7.3	2.19	8.3	1.35	8.6	1.81	5.21	0.79	5.20
TOR0000S2	7.0	2.07	8.1	1.34	8.5	1.83	5.20	0.80	5.17
TOR0000S1	7.3	2.21	8.2	1.37	8.7	1.87	5.31	0.81	5.28
TOR0000S0	9.8	2.83	11.0	1.76	10.8	2.29	6.44	0.97	6.17
TOR0000RZ	10.1	3.01	11.0	1.78	10.9	2.31	6.53	0.97	6.19
TOR0000RY	10.7	3.17	12.0	1.91	11.7	2.47	6.97	1.03	6.50
TOR0000RX	8.5	2.64	9.8	1.58	10.0	2.07	5.81	0.86	5.72
TOR0000RW	8.4	2.51	9.6	1.54	9.8	2.04	5.85	0.87	5.74
TOR0000RV	10.1	2.99	11.1	1.75	11.0	2.30	6.45	0.94	6.33
TOR0000RU	10.1	2.97	11.4	1.78	11.4	2.33	6.53	0.99	6.65
TOR0000RT	9.2	2.70	10.3	1.70	10.5	2.19	6.27	0.98	6.02
TOR0000RS	9.0	2.76	10.3	1.69	10.6	2.19	6.30	0.98	5.99
TOR0000RR	9.9	2.96	11.3	1.82	11.4	2.36	6.68	1.04	6.25
TOR0000RQ	9.1	2.77	10.5	1.65	10.6	2.17	6.20	0.91	6.07
TOR0000RP	7.7	0.86	11.1	2.38	16.4	3.63	10.70	1.65	10.30

Table 2 (cont'd)

Table 2 ((cont'd)
-----------	----------

Sample	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
TOR0000SB	1.50	12.2	3.21	18.0	14.97	3.75
TOR0000SD	1.17	10.8	2.36	11.7	9.72	2.68
TOR0000SE	1.25	11.4	2.50	10.5	10.19	2.70
TOR0000SF	1.18	10.8	2.35	10.7	9.65	2.59
TOR0000SG	1.14	10.8	2.37	12.9	9.64	2.72
TOR0000QQ	1.35	13.3	2.95	5.4	11.90	3.35
TOR0000QR	1.37	13.4	2.89	6.8	12.10	3.58
TOR0000QS	1.30	13.5	2.85	14.7	12.30	3.35
TOR0000QJ	1.34	16.5	3.41	18.7	17.36	4.76
TOR0000QK	1.36	16.5	3.45	17.6	17.24	4.42
TOR0000QL	1.30	16.2	3.31	6.8	16.92	4.53
TOR0000QM	1.35	16.6	3.48	17.9	17.14	4.28
TOR0000QN	1.17	15.6	3.20	13.2	15.87	4.13
TOR0000QO	1.33	16.6	3.44	17.4	17.31	4.51
TOR0000QT	1.35	16.6	3.44	17.7	17.18	4.54
TOR0000QU	1.35	16.5	3.36	17.2	16.71	4.34
TOR0000QV	1.26	15.4	3.24	17.3	15.97	4.46
TOR0000QW	1.28	15.8	3.32	18.3	16.38	4.39
TOR0000QX	1.22	16.1	3.37	16.0	16.60	4.20
TOR0000QY	1.24	15.0	3.11	17.7	15.28	4.39
TOR0000QZ	1.32	15.8	3.22	16.2	15.83	4.12
TOR0000R1	1.02	12.0	2.58	6.0	10.47	2.64
TOR0000R3	0.97	10.8	2.24	12.5	9.30	2.22
TOR0000R4	0.95	10.5	2.17	9.9	9.09	2.39
TOR0000R5	0.88	9.8	2.07	8.5	8.53	2.16
TOR0000R6	1.21	15.6	3.08	14.0	13.50	3.46
TOR0000R7	1.24	15.7	2.92	13.2	13.17	3.46
TOR0000R8	1.16	10.5	2.32	9.6	8.97	2.29
TOR0000R9	1.08	10.0	2.30	9.8	8.65	2.15
TOR0000RA	1.15	10.4	2.25	13.0	8.49	2.15
TOR0000RB	1.15	10.7	2.45	6.5	9.07	2.26
TOR0000RC	1.11	10.1	2.26	8.9	8.57	2.13
TOR0000RD	1.08	9.9	2.20	8.7	8.37	2.14
TOR0000RE	1.09	10.1	2.21	8.5	8.53	2.24
TOR0000RF	1.32	18.4	3.30	15.8	15.67	4.16
TOR0000RG	1.33	18.0	3.29	15.6	15.26	4.09
TOR0000RH	1.38	19.0	3.37	26.7	16.00	4.02
TOR0000RI	1.43	18.9	3.36	4.8	16.12	4.54
TOR0000RJ	0.93	10.7	2.20	9.8	9.34	2.38
Sample	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
-----------	----------	----------	----------	----------	----------	---------
TOR0000RK	0.96	11.3	2.27	11.1	9.71	2.42
TOR0000RL	0.92	10.9	2.25	10.6	9.87	2.46
TOR0000RM	1.40	17.3	3.32	4.6	14.26	3.07
TOR0000RN	1.27	17.0	3.24	5.8	14.40	3.38
TOR0000T1	1.16	14.7	2.84	5.3	12.47	3.36
TOR0000S5	1.27	15.2	3.32	12.7	15.70	4.12
TOR0000S6	1.16	11.7	2.50	5.0	10.34	2.78
TOR0000SN	0.74	8.1	1.65	4.7	6.83	1.78
TOR0000SJ	1.29	16.1	3.40	16.5	16.68	4.46
TOR0000SK	1.31	16.4	3.41	16.7	17.05	4.59
TOR0000SM	0.98	7.2	1.79	8.0	6.71	1.99
TOR0000SL	0.97	7.1	1.84	5.9	6.71	1.89
TOR0000SI	0.97	8.6	1.81	8.8	7.21	3.22
TOR0000SH	0.78	6.3	1.33	9.2	5.44	1.35
TOR0000S4	0.50	4.7	1.01	10.7	3.98	1.30
TOR0000S3	0.77	5.9	1.30	4.8	5.08	1.22
TOR0000S2	0.78	5.4	1.26	4.9	4.58	1.18
TOR0000S1	0.78	5.4	1.31	2.9	4.65	1.21
TOR0000S0	0.94	7.0	1.76	6.9	6.52	1.78
TOR0000RZ	0.93	7.1	1.81	9.1	6.69	1.93
TOR0000RY	0.98	7.4	1.92	7.3	7.03	1.97
TOR0000RX	0.84	6.7	1.62	8.3	5.77	1.56
TOR0000RW	0.86	6.4	1.55	6.9	5.51	1.53
TOR0000RV	0.91	7.2	1.89	11.6	6.78	1.87
TOR0000RU	0.98	7.8	2.00	10.9	7.29	1.87
TOR0000RT	0.95	7.0	1.73	4.5	6.35	1.81
TOR0000RS	0.93	7.1	1.75	6.6	6.35	1.70
TOR0000RR	0.98	7.3	1.82	6.8	6.61	1.89
TOR0000RQ	0.89	6.8	1.63	6.0	5.81	1.46
TOR0000RP	1.53	9.4	4.27	11.1	26.51	2.92

Table 2 (cont'd)

Table 3: Measured Isotopic Values

Name	Unit	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2se	¹⁴³ Nd/ ¹⁴⁴ Nd	2se	⁸⁷ Sr/ ⁸⁶ Sr	2se
TOR0000QR	Cuesta Upper Flow	0.282470	6E-06	0.512246	4E-06	0.713304	5E-06
TOR0000QW	Channel Lake Member	0.282453	8E-06	0.512161	3E-06	0.720782	5E-06
TOR0000RJ	Channel Lake Member	0.282433	5E-06	0.512344	5E-06	0.720515	5E-06
TOR0000RP	Davieaux Island Member	0.282576	4E-06	0.512387	2.1E-05	0.918183	7E-06
TOR0000RQ	South Shore Member	0.282577	8E-06	0.512672	8E-06	0.713099	5E-06
TOR0000S1	South Shore Member	0.282173	6E-06	0.512139	3E-06	0.729279	6E-06
TOR0000SD	Cuesta Lower Flow	0.282459	4E-06	0.512503	5E-06	0.727211	6E-06
TOR0000SJ	Quebec Harbor Member unaltered	0.282416	9E-06	0.512143	4E-06	0.720486	5E-06
Standards							
BCR-2		0.282880	6E-06	0.512633	6E-06	0.705006	8E-06
duplicate				0.512641	6E-06	0.705005	6E-06
BIR-1				0.513097	8E-06		
duplicate							
K1919 (generic	c BHVO)			0.512992	5E-06		
JMC 475		0.282155					
JMC 475		0.282157	4E-06				
JMC 475		0.282157	8E-06				
JMC 475		0.282157	4E-06				
JMC 475		0.282161	4E-06				
JMC 475		0.282152	5E-06				
JMC 475		0.282154	4E-06				
JMC 475		0.282148	3E-06				
JMC 475		0.282148	3E-06				

Samples were measured on a Nu Plasma HR multi-collector inductively coupled plasma mass

spectrometer (MC-ICPMS). Uncertainties are reported in terms of standard error (se)

Name	Unit	208Pb/204Pb	1se	²⁰⁷ Pb/ ²⁰⁴ Pb	1se	²⁰⁶ Pb/ ²⁰⁴ Pb	1se
TOR0000QR	Cuesta Upper Flow	41.0815	0.0011	15.8271	0.0003	20.6698	0.0003
TOR0000QW	Channel Lake Member	40.3183	0.0009	15.7396	0.0006	20.0029	0.0004
TOR0000RJ	Channel Lake Member	39.4122	0.0005	15.6832	0.0002	19.2491	0.0002
TOR0000RP	Davieaux Island Member	42.5978	0.0008	15.7616	0.0003	20.9796	0.0003
TOR0000RQ	South Shore Member	39.4615	0.0007	15.7054	0.0003	19.4941	0.0003
TOR0000S1	South Shore Member	43.6013	0.0008	15.9285	0.0003	22.8858	0.0003
TOR0000SD	Cuesta Lower Flow	38.6391	0.0004	15.6552	0.0002	18.7893	0.0002
TOR0000SJ	Quebec Harbor Member unaltered	43.9524	0.0010	15.9487	0.0004	23.1900	0.0005
Standards							
BCR-2		38.6569	0.0008	15.5999	0.0003	18.7375	0.0003
duplicate							
BIR-1		38.4700	0.0007	15.6535	0.0002	18.8480	0.0003
duplicate		38.4819	0.0006	15.6530	0.0003	18.8518	0.0003

Sample	Unit	⁸⁷ Rb/ ⁸⁶ Sr	(⁸⁷ Sr/ ⁸⁶ Sr) _i	¹⁴⁷ Sm/ ¹⁴⁴ Nd	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	εNdi	¹⁷⁶ Lu/ ¹⁷⁷ Hf	(¹⁷⁶ Hf/ ¹⁷⁷ Hf) _i	εHf _i
TOR00 00QR	Cuesta Upper Flow	0.8808	0.699665	0.1186	0.511389	3.41	0.0146	0.282168	2.83
TOR00 00QW	Channel Lake Member	0.8507	0.707611	0.1335	0.511197	-0.35	0.0116	0.282212	4.41
TOR00 00RJ	Channel Lake Member	0.9977	0.705066	0.1362	0.511361	2.86	0.0124	0.282176	3.14
TOR00 00RP	Davieaux Island Member	16.8382	0.657469	0.1453	0.511338	2.40	0.0230	0.282098	0.36
TOR00 00RQ	South Shore Member	0.5964	0.703865	0.1542	0.511559	6.72	0.0188	0.282186	3.49
TOR00 00S1	South Shore Member	0.0423	0.728624	0.1555	0.511016	-3.89	0.0207	0.281744	- 12.1 8
TOR00 00SD	Cuesta Lower Flow	1.7263	0.700482	0.1652	0.511310	1.86	0.0198	0.282048	- 1.42
TOR00 00SJ	Quebec Harbor Member unaltered	1.1243	0.703078	0.1270	0.511227	0.23	0.0114	0.282179	3.23

Table 4: Calculated Isotopic Values

Sample	²³⁸ U/ ²⁰⁴ Pb	²³² Th/ ²⁰⁴ Pb	²³⁵ U/ ²⁰⁴ Pb	(²⁰⁶ Pb/ ²⁰⁴ Pb) _i	(²⁰⁷ Pb/ ²⁰⁴ Pb) _i	(²⁰⁸ Pb/ ²⁰⁴ Pb) _i
TOR0000QR	35.48	123.98	0.26	14.0693	15.3243	34.1474
TOR0000QW	16.00	61.69	0.12	17.0266	15.5128	36.8679
TOR0000RJ	15.85	64.33	0.11	16.3006	15.4585	35.8142
TOR0000RP	18.21	170.96	0.13	17.5920	15.5035	33.0358
TOR0000RQ	15.79	64.90	0.11	16.5554	15.4815	35.8315
TOR0000S1	29.81	118.65	0.22	17.3393	15.5059	36.9649
TOR0000SD	13.31	54.95	0.10	16.3127	15.4665	35.5657
TOR0000SJ	19.68	76.03	0.14	19.5291	15.6698	39.7000

APPENDIX C

STANDARDS

Table 5: Major Element Standards

Sample	SiO2 (%)	TiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MnO (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	P2O5 (%)	LOI (%)	Sum (%)
std JB1a	52.65	1.27	14.46	8.98	0.15	7.82	9.34	2.78	1.43	0.26	0.66	99.14
STD JB1A	52.51	1.28	14.47	8.99	0.15	7.81	9.34	2.77	1.43	0.26	0.81	99.01
STD JB1A	52.46	1.27	14.48	9.02	0.15	7.83	9.34	2.77	1.43	0.26	0.79	99.01
Jb-1a GIVEN	52.41	1.28	14.45	9.02	0.148	7.83	9.31	2.73	1.4	0.26	-	98.838
std BHVO-1	49.59	2.73	13.64	12.18	0.17	7.18	11.33	2.2	0.52	0.27	0.05	99.81
STD BHVO-1	49.61	2.73	13.64	12.21	0.17	7.19	11.34	2.2	0.52	0.27	0	99.88
STD BHVO-1	49.53	2.73	13.62	12.24	0.17	7.17	11.33	2.19	0.52	0.27	0.1	99.77
BHVO-1 GIVEN	49.94	2.71	13.8	12.23	0.168	7.23	11.4	2.26	0.52	0.273	-	100.531
STD RGM-2	73.77	0.27	13.84	1.86	0.04	0.28	1.16	4.07	4.33	0.05	0.2	99.67
STD RGM-2	73.74	0.27	13.81	1.86	0.04	0.28	1.16	4.09	4.32	0.05	0.25	99.62
STD RGM-2	73.55	0.27	13.81	1.87	0.04	0.28	1.16	4.07	4.32	0.05	0.45	99.42
RGM-2 GIVEN	73.45	0.27	13.72	1.86	0.036	0.27	1.15	4.07	4.3	0.048	-	99.174

Major elements concentrations were analyzed at Michigan State University on a Bruker S4 Pioneer X-Ray Fluorescence

Spectrometer (XRF).

Table 6: Trace Element Standards

Day 1	Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	Pr (ppm)	Nd (ppm)
JB1-a STANDARD RUN AS UNKNOWN, D	RIFT CORRECTE	ED, INTERSPER	SED BETWEEN S	AMPLES (ppm)											
JB1a 3	27.859	198.805	415.194	38.162	142.145	18.834	36.583	445.049	22.107	138.209	28.266	1.122	504.176	7.151	25.373
JB1a cal 4	28.283	195.274	416.527	37.634	140.693	18.528	38.202	443.080	22.567	139.026	28.155	1.198	505.976	7.149	26.151
JB1a 5	27.786	195.269	415.141	37.799	142.872	19.021	38.148	446.388	22.696	138.554	28.331	1.175	512.652	7.230	26.127
JB1a 6	27.723	199.065	420.933	38.076	143.465	19.609	38.568	441.019	22.313	137.774	28.322	1.195	502.945	7.052	25.638
JB1a 7	28.122	196.801	413.127	37.927	140.834	18.338	36.592	446.090	22.270	138.823	28.191	1.126	506.141	7.202	25.672
JB1a 10	27.639	198.595	412.799	37.841	142.748	19.110	36.763	443.913	21.842	135.876	28.317	1.196	505.931	7.142	25.602
JB1a 11	28.157	195.188	420.495	37.956	142.838	18.942	38.526	440.023	22.899	140.474	27.839	1.148	501.992	7.083	25.867
JB1a 12	28.092	196.597	419.617	37.880	139.776	18.225	38.028	448.929	22.361	140.124	28.587	1.108	508.937	7.246	25.835
JB1a 13	28.435	196.818	410.722	38.224	140.598	18.912	37.582	449.831	23.242	140.275	28.555	1.186	516.208	7.261	26.294
JB1a 14	27.449	198.016	417.287	37.696	144.057	19.140	37.195	438.930	21.608	135.636	27.966	1.179	498.820	7.051	25.364
AVERAGE	27.954	197.043	416.184	37.920	142.003	18.866	37.619	444.325	22.390	138.477	28.253	1.163	506.378	7.157	25.792
RSD	0.0111	0.0077	0.0083	0.0051	0.0101	0.0218	0.0209	0.0082	0.0217	0.0122	0.0082	0.0295	0.0101	0.0108	0.0125
GEOREM	28.3	197	414	38.7	140	18.4	38.4	441	23.2	140	28.1	1.2	495	7.19	26.3
ACCURACY (average)	-0.01221	0.00022	0.00528	-0.02017	0.01430	0.02531	-0.02035	0.00754	-0.03489	-0.01088	0.00544	-0.03064	0.02299	-0.00462	-0.01931
DRIFTCORRECTED															
					m)										
BHVO-2 STAINDARD ROM AS UNRINOWIN	, DRIFT CORREC	IED, INTERSF	ERGED BETWEEN	SAINFLES (ppi	11)										
BHVO-2.3	30.2	319.3	292.1	45.8	122.4	21.7	9.2	390.0	24.1	164.4	18.5	0.1	129.8	53	23.7
BHVO-2 cal 4	30.6	313.0	289.6	44.8	110.0	21.7	9.2	397.6	25.2	169.8	18.6	0.1	132.6	5.3	24.1
BHVO-2.5	31.0	310.7	293.0	43.8	118.4	21.2	9.2	391.5	24.8	164.8	18.2	0.1	132.0	5.4	23.6
BHVO-2.6	31.9	308.6	292.6	44.3	122.6	22.0	9.0	397.7	25.7	172.8	18.3	0.1	132.2	5.4	24.2
BHVO-2 7	31.6	312.2	293.5	43.8	123.7	21.9	9.0	396.2	25.2	170.1	18.1	0.1	131.6	5.3	24.2
BHVO-2 10	31.3	307.8	284.7	44.5	120.1	21.1	9.2	389.4	24.7	167.6	18.5	0.1	131.8	5.2	23.8
BHVO-2 11	31.1	311.6	290.5	44.2	119.0	21.4	9.3	390.3	24.4	168.5	18.3	0.1	131.2	5.3	23.1
BHVO-2 12	30.4	308.0	284.4	43.9	118.4	21.6	9.2	384.9	24.3	165.8	18.0	0.1	131.3	5.1	23.2
BHVO-2 13	30.1	312.6	284.2	44.2	117.6	22.2	9.1	393.8	24.2	168.0	18.5	0.1	132.3	5.2	23.4
BHVO-2 14	30.5	311.0	285.1	44.1	120.9	21.3	9.2	391.7	24.3	166.5	18.1	0.1	128.0	5.1	23.2
AVERAGE	30.9	311.6	289.0	44.3	120.3	21.6	9.2	392.3	24.7	167.8	18.3	0.1	131.3	5.3	23.6
STDEV	0.0196	0.0109	0.0136	0.0134	0.0170	0.0168	0.0131	0.0104	0.0219	0.0155	0.0108	0.1013	0.0107	0.0212	0.0174
GEOREM	34.0	308.0	292.0	44.0	119.0	22.0	8.9	396.0	24.6	164.0	17.9	0.1	131.0	5.4	24.5
400/01/01/	0.0000		c	0.0101-	0.00.00	0.00075	0.0000-	0.00.00		0.0107	0.0400-	0.0500-	0.0005-	0.0105-	0.0055
ACCURACY (average)	-0.02984	-0.02084	0.00620	-0.01216	0.00420	0.00973	-0.00986	-0.00454	-0.04664	-0.01971	0.01205	-0.05629	0.00288	-0.01257	-0.02593
detection limits (based on gas blanks 2)	otondord doviet	ion on goo bio	k monouromente	dono oftor cash	comple) or	acced in ==	-								
detection limits (based on gas blank: 3)	standard deviat	ion on gas blar	ik measurements	uone alter each	sample) expr	esseu in pp	0.00	0.00	0.04	0.04	0.000	0.01		0.000	0.00
	0.2	0.07	0.4	0.04	0.3	0.05	0.09	0.06	0.01	0.04	0.008	0.01	0.1	0.003	0.02

Trace elements analyses using a Photon-Machines Analyte G2 Excimer laser and Thermo Scientific ICAP Q quadrupole inductively coupled plasma mass spectrometer (ICP-MS).

Day 1		Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
JB1-a STANDA	RD RUN AS UNKNOWN, D	RIFT CORRECT	ED, INTERSPE	RSED BETWE	EN SAMPLES (opm)										
	JB1a 3	5.146	1.522	4.760	0.718	4.171	0.818	2.261	0.337	2.113	0.318	3.550	1.746	6.514	9.024	1.544
	JB1a cal 4	5.154	1.507	4.907	0.725	4.270	0.814	2.289	0.345	2.173	0.319	3.708	1.779	6.485	9.258	1.573
	JB1a 5	5.240	1.540	4.960	0.736	4.241	0.852	2.331	0.334	2.131	0.321	3.623	1.822	6.633	9.340	1.644
	JB1a 6	5.185	1.482	4.737	0.720	4.183	0.816	2.261	0.330	2.037	0.312	3.646	1.807	6.544	9.175	1.622
	JB1a 7	5.139	1.534	4.853	0.722	4.217	0.819	2.279	0.344	2.178	0.322	3.586	1.737	6.497	9.086	1.532
	JB1a 10	5.128	1.514	4.793	0.723	4.174	0.826	2.279	0.337	2.104	0.312	3.598	1.793	6.547	9.129	1.550
	JB1a 11	5.141	1.510	4.806	0.722	4.206	0.809	2.294	0.334	2.122	0.320	3.614	1.756	6.540	9.132	1.606
	JB1a 12	5.272	1.513	4.959	0.726	4.250	0.836	2.260	0.343	2.158	0.329	3.647	1.769	6.544	9.254	1.617
	JB1a 13	5.260	1.558	4.939	0.733	4.360	0.831	2.324	0.347	2.169	0.318	3.700	1.799	6.449	9.356	1.577
	JB1a 14	5.064	1.490	4.722	0.717	4.093	0.815	2.263	0.330	2.078	0.312	3.552	1.773	6.592	9.013	1.564
	AVERAGE	5.173	1.517	4.844	0.724	4.217	0.824	2.284	0.338	2.126	0.318	3.622	1.778	6.535	9.177	1.583
	RSD	0.0128	0.0150	0.0191	0.0085	0.0169	0.0157	0.0114	0.0185	0.0214	0.0168	0.0150	0.0154	0.0081	0.0133	0.0236
	GEOREM	5.1	1.48	4.93	0.717	4.08	0.796	2.19	0.319	2.13	0.309	3.6	1.8	6.25	9.17	1.55
	ACCURACY (average)	0.01429	0.02498	-0.01754	0.00972	0.03348	0.03457	0.04296	0.05970	-0.00169	0.03049	0.00623	-0.01224	0.04554	0.00072	0.02121
DRIFTCORREC	JED															
						(
BHV0-2 STAIL	ARD RON AS UNKNOWN	, DRIFT CORRE	CIED, INTERSF	EKSED BEIW	EEN SAWFLES	s (ppili)										
	BHVO-2.3	6.0	2.0	6.0	0.9	5.0	0.9	24	0.3	2.0	0.3	41	11	17	12	0.4
	BHVO-2 cal 4	6.1	2.0	6.2	0.9	5.3	1.0	2.4	0.3	2.0	0.3	4.1	1.1	1.7	1.2	0.4
	BHVO-2.5	61	2.0	6.3	0.9	5.2	1.0	25	0.3	2.0	0.3	4.4	12	17	12	0.4
	BHVO-2.6	6.3	2.0	6.4	1.0	5.5	1.0	2.6	0.3	2.1	0.3	4.6	1.2	1.8	1.2	0.4
	BHVO-2 7	6.1	2.0	6.2	0.9	5.4	1.0	2.5	0.3	2.1	0.3	4.5	1.2	1.8	1.1	0.4
	BHVO-2 10	6.2	2.0	6.2	0.9	5.3	1.0	2.4	0.3	2.1	0.3	4.5	1.3	1.7	1.2	0.4
	BHVO-2 11	6.1	2.0	6.0	0.9	5.1	1.0	2.4	0.3	2.1	0.3	4.4	1.2	1.8	1.1	0.4
	BHVO-2 12	6.0	2.0	6.0	0.9	5.1	1.0	2.4	0.3	2.1	0.3	4.4	1.2	1.8	1.1	0.4
	BHVO-2 13	6.2	2.0	6.0	0.9	5.2	1.0	2.5	0.3	2.0	0.3	4.4	1.2	1.9	1.1	0.4
	BHVO-2 14	6.1	2.0	5.9	0.9	5.1	0.9	2.4	0.3	2.0	0.3	4.4	1.2	1.9	1.1	0.4
	AVERAGE	6.1	2.0	6.1	0.9	5.2	1.0	2.5	0.3	2.0	0.3	4.4	1.2	1.8	1.1	0.4
	STDEV	0.0132	0.0158	0.0270	0.0200	0.0301	0.0239	0.0271	0.0243	0.0252	0.0309	0.0274	0.0271	0.0432	0.0362	0.0489
	GEOREM	6.1	2.1	6.2	0.9	5.2	1.0	2.6	0.3	2.0	0.3	4.3	1.2	1.7	1.2	0.4
	ACCURACY (average)	0.01618	-0.01064	-0.01571	-0.02079	-0.01221	-0.02767	-0.01616	-0.02984	0.02249	-0.00710	-0.01250	0.03311	0.06407	-0.06070	0.00921
detection limits	(based on gas blank: 3x	standard devia	tion on gas bla	nk measureme	ents done after	each sample) e	xpressed in pp	m								
		0.009	0.003	0.008	0.002	0.005	0.001	0.003	0.001	0.004	0.002	0.004	0.002	0.02	0.001	0.002

Day 2		Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	Pr (ppm)	Nd (ppm)
JB1-a STANDAF	D RUN AS UNKNOWN, E	ORIFT CORRECT	ED, INTERSPER	SED BETWEEN S	AMPLES (ppm)											
	JB1a 3	27.61	211.50	426.13	38.88	149.01	18.91	37.86	444.66	21.00	131.26	28.69	1.27	501.18	7.31	26.26
	JB1a cal 4	26.77	202.89	423.87	38.30	143.76	19.20	38.95	438.49	21.76	136.29	27.73	1.20	493.74	7.14	26.01
	JB1a 5	28.38	209.79	419.01	37.20	138.49	19.63	38.45	460.25	23.02	139.82	29.16	1.21	520.02	7.45	27.01
	JB1a 6	28.78	204.36	417.73	37.85	137.58	20.34	39.01	450.34	23.34	140.13	28.86	1.18	503.25	7.19	26.80
	JB1a 7	27.31	200.59	416.27	37.82	136.37	20.21	39.90	444.27	21.98	134.62	28.07	1.21	495.85	7.02	26.11
	JB1a 10	26.86	201.34	421.15	37.00	147.06	19.56	35.99	433.08	21.58	132.47	28.21	1.16	483.37	7.01	26.02
	JB1a 11	28.72	210.35	414.54	38.19	140.84	19.26	37.85	446.41	22.21	136.20	28.61	1.27	501.16	7.24	26.28
	JB1a 12	27.06	201.90	419.30	38.99	146.32	19.75	38.70	436.18	21.81	135.86	28.28	1.19	499.97	7.22	26.41
	JB1a 13	27.92	210.00	431.85	37.57	140.26	19.31	39.09	449.30	21.86	135.74	28.29	1.20	503.12	7.21	26.39
	JB1a 14	27.57	207.79	419.49	38.30	144.04	19.35	38.55	453.11	22.18	135.94	28.84	1.25	507.70	7.36	26.53
	AVERAGE	27.70	206.05	420.93	38.01	142.37	19.55	38.43	445.61	22.07	135.83	28.48	1.21	500.94	7.21	26.38
	Relative std deviation	0.03	0.02	0.01	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.01
	GEOREM	27.81	200.30	408.00	38.53	139.50	18.13	38.15	443.40	22.91	140.10	27.57	1.22	495.10	7.10	26.15
	ACCURACY (average)	-0.00405	0.02871	0.03170	-0.01356	0.02060	0.07840	0.00745	0.00498	-0.03650	-0.03045	0.03284	-0.00178	0.01179	0.01609	0.00884
DRIFT CORREC	TED															
	BHVO-23	31.546	331.091	293.346	45.795	123.592	21.482	9.079	392.647	24.710	165.756	18.949	0.099	126.106	5.405	24.208
	BHVO-2 cal 4	30.822	317.023	290.838	44.861	117.908	21.635	9.330	391.143	24.842	165.338	18.519	0.107	129.822	5.418	24.314
	BHVO-2 5	31.259	329.322	297.768	45.001	120.129	22.220	9.810	392.041	24.989	168.815	18.473	0.106	132.050	5.389	24.690
	BHVO-2 6	32.263	312.866	293.090	44.324	114.868	21.314	9.555	392.222	25.083	170.020	18.548	0.086	129.503	5.307	24.489
	BHVO-27	31.584	323.125	294.951	45.299	117.998	22.202	9.359	391.453	25.224	170.101	18.626	0.096	129.321	5.395	24.325
	BHVO-2 10	32.302	333.503	294.264	44.350	125.010	21.281	8.867	401.011	24.746	171.322	18.784	0.107	129.964	5.526	25.046
	BHVO-2 11	30.663	324.623	288.868	44.671	120.473	21.515	9.014	386.807	24.617	163.703	18.396	0.106	129.770	5.309	23.791
	BHVO-2 12	30.997	322.681	293.979	45.224	117.528	21.972	9.262	385.048	24.615	166.210	18.325	0.096	128.854	5.345	24.511
	BHVO-2 13	30.089	332.892	295.131	43.981	119.231	21.742	9.689	394.949	24.307	167.346	18.385	0.098	133.088	5.401	24.608
	BHVO-2 14	29.951	326.598	291.698	45.034	115.126	22.086	9.506	386.724	23.593	161.272	18.111	0.088	130.631	5.326	24.196
	AVERAGE	31.147	325.372	293.393	44.854	119.186	21.745	9.347	391.404	24.673	166.988	18.512	0.099	129.911	5.382	24.418
	Relative std deviation	0.02589	0.02078	0.00848	0.01200	0.02752	0.01636	0.03231	0.01177	0.01869	0.01888	0.01281	0.07757	0.01436	0.01219	0.01381
Georem preferre	GEOREM	31.83	318.20	287.20	44.89	119.80	21.37	9.26	394.10	25.91	171.20	18.10	0.10	130.90	5.34	24.27
	ACCURACY (average)	-0.0214	0.0225	0.0216	-0.0008	-0.0051	0.0175	0.0093	-0.0068	-0.0478	-0.0246	0.0227	-0.0077	-0.0076	0.0081	0.0061
detection limits	(based on gas blank: 3x	standard devia	tion on gas blar	k measurements	done after each	n sample) expr	essed in p	om								
		0.2	0.07	0.3	0.04	0.2	0.05	0.09	0.06	0.01	0.04	0.008	0.01		0.01	0.003

Day 2		Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
JB1-a STANDAR	RD RUN AS UNKNOWN,	DRIFT CORREC	TED, INTERSPE	RSED BETWE	EN SAMPLES (ppm)										
	JB1a 3	5.29	1.48	4.74	0.70	4.03	0.78	2.12	0.32	2.06	0.31	3.37	1.78	6.65	8.97	1.62
	JB1a cal 4	4.99	1.48	4.83	0.67	4.01	0.78	2.13	0.31	2.00	0.30	3.50	1.77	6.54	9.13	1.63
	JB1a 5	5.42	1.57	4.88	0.71	4.13	0.81	2.25	0.33	2.21	0.32	3.63	1.83	6.49	9.41	1.60
	JB1a 6	5.20	1.51	4.83	0.71	4.19	0.83	2.22	0.33	2.25	0.31	3.63	1.76	6.50	9.26	1.58
	JB1a 7	5.12	1.45	4.74	0.69	4.04	0.78	2.14	0.31	2.01	0.31	3.52	1.73	6.39	8.94	1.66
	JB1a 10	5.13	1.47	4.66	0.67	3.96	0.76	2.12	0.31	2.03	0.30	3.41	1.74	6.13	8.69	1.45
	JB1a 11	5.24	1.56	4.85	0.70	4.07	0.80	2.19	0.31	2.04	0.30	3.52	1.78	6.38	9.09	1.54
	JB1a 12	5.18	1.50	4.69	0.71	3.94	0.79	2.19	0.32	2.12	0.31	3.48	1.76	6.55	9.05	1.62
	JB1a 13	5.17	1.49	4.84	0.68	4.03	0.78	2.17	0.33	2.05	0.32	3.44	1.79	6.48	9.18	1.61
	JB1a 14	5.26	1.50	4.84	0.70	4.19	0.80	2.14	0.32	2.15	0.31	3.56	1.79	6.72	9.24	1.66
	AVERAGE	5.20	1.50	4.79	0.69	4.06	0.79	2.17	0.32	2.09	0.31	3.51	1.77	6.49	9.10	1.60
	Relative std deviation	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.02	0.02	0.02	0.02	0.02	0.04
	GEOREM	5.10	1.48	4.70	0.70	4.07	0.81	2.23	0.32	2.10	0.31	3.47	1.74	6.44	8.97	1.62
	ACCURACY (average)	0.01976	0.01149	0.01920	-0.00609	-0.00255	-0.01703	-0.02966	-0.00209	-0.00267	-0.02170	0.01029	0.02051	0.00708	0.01399	-0.01077
DRIFT CORREC	TED															
	BHVO-2 3	6.151	2.028	6.079	0.888	5.062	0.918	2.379	0.319	1.955	0.260	4.267	1.147	1.638	1.189	0.384
	BHVO-2 cal 4	6.200	2.045	6.234	0.905	5.139	0.921	2.399	0.322	1.976	0.278	4.360	1.156	1.692	1.213	0.408
	BHVO-2 5	6.227	2.053	6.304	0.905	5.161	0.923	2.478	0.325	2.044	0.280	4.470	1.178	1.756	1.190	0.414
	BHVO-2 6	6.163	2.043	6.192	0.924	5.075	0.934	2.420	0.320	1.885	0.279	4.334	1.164	1.685	1.176	0.432
	BHVO-2 7	6.114	2.040	6.127	0.905	5.103	0.956	2.434	0.318	1.970	0.273	4.253	1.135	1.718	1.160	0.417
	BHVO-2 10	6.202	2.103	6.239	0.934	5.124	0.965	2.546	0.333	2.025	0.269	4.343	1.181	1.674	1.170	0.390
	BHVO-2 11	6.092	2.060	5.950	0.911	4.862	0.908	2.337	0.326	1.902	0.272	4.180	1.145	1.712	1.109	0.409
	BHVO-2 12	6.291	2.033	6.088	0.922	5.022	0.935	2.429	0.307	1.986	0.262	4.217	1.111	1.754	1.127	0.421
	BHVO-2 13	6.107	2.065	6.003	0.907	4.958	0.913	2.353	0.316	1.913	0.266	4.216	1.147	1.792	1.141	0.447
	BHVO-2 14	6.007	2.047	5.841	0.910	5.015	0.892	2.396	0.311	1.801	0.272	4.171	1.122	1.897	1.121	0.428
	AVERAGE	6.156	2.052	6.106	0.911	5.052	0.926	2.417	0.320	1.946	0.271	4.281	1.149	1.732	1.160	0.415
	Relative std deviation	0.01304	0.01036	0.02365	0.01400	0.01806	0.02371	0.02523	0.02310	0.03705	0.02573	0.02203	0.01955	0.04241	0.02943	0.04534
Georem preferre	GEOREM	6.02	2.04	6.21	0.94	5.28	0.99	2.51	0.33	1.99	0.28	4.47	1.15	1.65	1.22	0.41
	ACCURACY (average)	0.0220	0.0042	-0.0163	-0.0298	-0.0431	-0.0630	-0.0374	-0.0452	-0.0242	-0.0156	-0.0423	-0.0047	0.0477	-0.0525	0.0074
detection limits	(based on gas blank: 3	x standard devia	ation on gas bl	ank measurem	ents done after	each sample) e	expressed in pr	om								
		0.02	0.009	0.003	0.008	0.002	0.005	0.001	0.003	0.001	0.004	0.002	0.004	0.002	0.02	0.001

Day 3		Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	Pr (ppm)	Nd (ppm)
DRIFT CORRE	CTED															
	JB1a 3	26.969	199.093	419.432	38.914	148.241	18.730	36.957	438.884	21.807	137.250	28.066	1.177	490.208	7.039	25.762
	JB1a cal 4	28.299	199.066	417.741	38.336	139.041	18.400	39.001	440.111	22.531	137.304	28.089	1.187	507.276	6.999	25.998
	JB1a 5	28.872	193.877	416.032	38.035	138.694	18.035	39.026	447.583	23.062	142.132	28.601	1.163	513.011	7.327	27.391
	JB1a 6	28.341	194.554	414.754	37.785	137.227	17.676	39.876	449.374	23.046	137.654	28.613	1.167	519.457	7.159	26.609
	JB1a 7	28.394	196.388	422.800	38.463	137.021	18.326	40.365	447.499	23.201	140.836	28.259	1.240	516.985	7.280	26.125
	JB1a 10	28.584	205.155	421.249	38.926	153.269	18.470	36.093	448.235	22.406	137.266	28.522	1.158	495.162	7.176	25.816
	JB1a 11	28.341	198.438	418.263	39.332	143.093	17.849	38.717	447.636	22.557	139.557	28.384	1.224	505.737	7.128	26.026
	JB1a 12	28.508	196.743	422.579	38.743	143.771	18.348	38.594	446.893	22.992	143.137	28.232	1.177	509.222	7.243	26.724
	JB1a 13	27.873	197.998	416.509	38.229	140.653	18.370	38.900	440.591	22.666	137.484	28.096	1.161	500.250	7.068	26.200
	JB1a 14	27.563	195.513	415.627	37.953	139.366	18.440	38.438	440.100	22.092	136.557	28.340	1.180	506.859	7.071	26.285
	AVERAGE	28.174	197.683	418.499	38.472	142.037	18.264	38.597	444.691	22.636	138.918	28.320	1.183	506.417	7.149	26.294
	Relative std deviation	0.01980	0.01617	0.00697	0.01292	0.03683	0.01734	0.03254	0.00939	0.02004	0.01689	0.00735	0.02309	0.01817	0.01519	0.01880
	GEOREM	27.81	200.3	408	38.53	139.5	18.13	38.15	443.4	22.91	140.1	27.57	1.216	495.1	7.1	26.15
	ACCURACY (average)	0.0131	-0.0131	0.0257	-0.0015	0.0182	0.0074	0.0117	0.0029	-0.0120	-0.0084	0.0272	-0.0269	0.0229	0.0069	0.0055
DRIFT CORRE	CTED															
	BHVO-2 3	30.207	320.376	291.902	46.243	123.491	20.761	8.948	394.832	24.566	163.962	18.105	0.097	128.887	5.217	23.504
	BHVO-2 cal 4	30.015	312.582	288.935	45.386	119.481	21.613	9.141	387.874	24.521	165.068	17.970	0.102	128.444	5.227	23.610
	BHVO-2 5	31.129	316.401	290.344	45.131	118.704	19.764	9.634	398.487	25.315	173.000	18.609	0.098	132.413	5.522	24.851
	BHVO-2 6	30.024	311.281	284.120	45.169	119.758	21.451	9.176	387.283	24.027	164.212	18.062	0.088	128.573	5.253	23.726
	BHVO-2 7	29.708	315.908	285.058	43.915	120.607	21.261	9.151	374.930	23.073	158.147	17.808	0.096	123.862	5.128	22.580
	BHVO-2 10	29.951	305.429	287.521	44.208	121.328	20.097	9.268	378.878	22.842	158.115	18.077	0.095	125.755	5.146	22.606
	BHVO-2 11	29.744	306.716	289.736	44.499	117.928	20.112	9.387	381.248	23.946	161.591	18.000	0.100	129.188	5.226	23.116
	BHVO-2 12	30.883	311.021	288.381	44.949	117.899	19.937	9.573	387.768	24.462	167.401	18.294	0.088	134.064	5.363	23.903
	BHVO-2 13	31.010	311.338	289.709	44.936	120.182	20.172	9.476	388.160	24.551	166.160	18.334	0.093	131.813	5.364	23.861
	BHVO-2 14	30.773	313.679	290.735	45.024	120.962	21.270	9.403	390.378	24.208	163.577	18.540	0.098	131.001	5.189	23.717
AVERAGE		30.344	312.473	288.644	44.946	120.034	20.644	9.316	386.984	24.151	164.123	18.180	0.096	129.400	5.264	23.547
Relative std de	eviation	0.01799	0.01426	0.00856	0.01441	0.01415	0.03408	0.02322	0.01832	0.03042	0.02672	0.01414	0.04924	0.02376	0.02282	0.02831
GEOREM		34	308	292	44	119	22	8.9	396	24.6	164	17.9	0.106	131	5.35	24.5
ACCURACY (averagé)	-0.10752	0.01452	-0.01149	0.02150	0.00869	-0.06165	0.04672	-0.02277	-0.01825	0.00075	0.01564	-0.09878	-0.01221	-0.01616	-0.03888
aetection limi	ts (based on gas blank: 3x	standard devia	tion on gas blan	ik measurements	done atter eacl	n sample) expre	essed in pp	o	0.00		0.01	0.000	0.01		0.04	0.000
		0.2	0.07	0.3	0.04	0.2	0.05	0.09	0.06	0.01	0.04	0.008	0.01		0.01	0.003

Day 3		Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	Pr (ppm)	Nd (ppm)
DRIFT CORRE	CTED															
	JB1a 3	26.969	199.093	419.432	38.914	148.241	18.730	36.957	438.884	21.807	137.250	28.066	1.177	490.208	7.039	25.762
	JB1a cal 4	28.299	199.066	417.741	38.336	139.041	18.400	39.001	440.111	22.531	137.304	28.089	1.187	507.276	6.999	25.998
	JB1a 5	28.872	193.877	416.032	38.035	138.694	18.035	39.026	447.583	23.062	142.132	28.601	1.163	513.011	7.327	27.391
	JB1a 6	28.341	194.554	414.754	37.785	137.227	17.676	39.876	449.374	23.046	137.654	28.613	1.167	519.457	7.159	26.609
	JB1a 7	28.394	196.388	422.800	38.463	137.021	18.326	40.365	447.499	23.201	140.836	28.259	1.240	516.985	7.280	26.125
	JB1a 10	28.584	205.155	421.249	38.926	153.269	18.470	36.093	448.235	22.406	137.266	28.522	1.158	495.162	7.176	25.816
	JB1a 11	28.341	198.438	418.263	39.332	143.093	17.849	38.717	447.636	22.557	139.557	28.384	1.224	505.737	7.128	26.026
	JB1a 12	28.508	196.743	422.579	38.743	143.771	18.348	38.594	446.893	22.992	143.137	28.232	1.177	509.222	7.243	26.724
	JB1a 13	27.873	197.998	416.509	38.229	140.653	18.370	38.900	440.591	22.666	137.484	28.096	1.161	500.250	7.068	26.200
	JB1a 14	27.563	195.513	415.627	37.953	139.366	18.440	38.438	440.100	22.092	136.557	28.340	1.180	506.859	7.071	26.285
	AVERAGE	28.174	197.683	418.499	38.472	142.037	18.264	38.597	444.691	22.636	138.918	28.320	1.183	506.417	7.149	26.294
	Relative std deviation	0.01980	0.01617	0.00697	0.01292	0.03683	0.01734	0.03254	0.00939	0.02004	0.01689	0.00735	0.02309	0.01817	0.01519	0.01880
	GEOREM	27.81	200.3	408	38.53	139.5	18.13	38.15	443.4	22.91	140.1	27.57	1.216	495.1	7.1	26.15
	ACCURACY (average)	0.0131	-0.0131	0.0257	-0.0015	0.0182	0.0074	0.0117	0.0029	-0.0120	-0.0084	0.0272	-0.0269	0.0229	0.0069	0.0055
DRIFT CORRE	CTED															
	BHVO-2 3	30.207	320.376	291.902	46.243	123.491	20.761	8.948	394.832	24.566	163.962	18.105	0.097	128.887	5.217	23.504
	BHVO-2 cal 4	30.015	312.582	288.935	45.386	119.481	21.613	9.141	387.874	24.521	165.068	17.970	0.102	128.444	5.227	23.610
	BHVO-2 5	31.129	316.401	290.344	45.131	118.704	19.764	9.634	398.487	25.315	173.000	18.609	0.098	132.413	5.522	24.851
	BHVO-2 6	30.024	311.281	284.120	45.169	119.758	21.451	9.176	387.283	24.027	164.212	18.062	0.088	128.573	5.253	23.726
	BHVO-2 7	29.708	315.908	285.058	43.915	120.607	21.261	9.151	374.930	23.073	158.147	17.808	0.096	123.862	5.128	22.580
	BHVO-2 10	29.951	305.429	287.521	44.208	121.328	20.097	9.268	378.878	22.842	158.115	18.077	0.095	125.755	5.146	22.606
	BHVO-2 11	29.744	306.716	289.736	44.499	117.928	20.112	9.387	381.248	23.946	161.591	18.000	0.100	129.188	5.226	23.116
	BHVO-2 12	30.883	311.021	288.381	44.949	117.899	19.937	9.573	387.768	24.462	167.401	18.294	0.088	134.064	5.363	23.903
	BHVO-2 13	31.010	311.338	289.709	44.936	120.182	20.172	9.476	388.160	24.551	166.160	18.334	0.093	131.813	5.364	23.861
	BHVO-2 14	30.773	313.679	290.735	45.024	120.962	21.270	9.403	390.378	24.208	163.577	18.540	0.098	131.001	5.189	23.717
AVERAGE		30.344	312.473	288.644	44.946	120.034	20.644	9.316	386.984	24.151	164.123	18.180	0.096	129.400	5.264	23.547
Relative std de	viation	0.01799	0.01426	0.00856	0.01441	0.01415	0.03408	0.02322	0.01832	0.03042	0.02672	0.01414	0.04924	0.02376	0.02282	0.02831
GEOREM		34	308	292	44	119	22	8.9	396	24.6	164	17.9	0.106	131	5.35	24.5
ACCURACY (average)	-0.10752	0.01452	-0.01149	0.02150	0.00869	-0.06165	0.04672	-0.02277	-0.01825	0.00075	0.01564	-0.09878	-0.01221	-0.01616	-0.03888
detection limi	ts (based on gas blank: 3x	standard devia	tion on gas blan	k measurements	done after each	n sample) expre	essed in p	om								
		0.2	0.07	0.3	0.04	0.2	0.05	0.09	0.06	0.01	0.04	0.008	0.01		0.01	0.003

Day 3		Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
DRIFT CORRECTED																
	JB1a 3	5.089	1.464	4.620	0.692	4.021	0.798	2.106	0.319	2.052	0.301	3.397	1.701	6.313	8.676	1.479
	JB1a cal 4	5.128	1.480	4.701	0.691	4.021	0.790	2.214	0.326	2.113	0.301	3.496	1.763	6.523	9.106	1.618
	JB1a 5	5.319	1.536	4.863	0.731	4.225	0.837	2.299	0.348	2.198	0.327	3.609	1.837	6.663	9.650	1.624
	JB1a 6	5.225	1.529	4.836	0.723	4.135	0.809	2.220	0.338	2.112	0.315	3.562	1.776	6.720	9.176	1.693
	JB1a 7	5.249	1.519	4.733	0.728	4.089	0.827	2.137	0.331	2.091	0.312	3.445	1.738	6.699	9.135	1.655
	JB1a 10	5.285	1.503	4.638	0.694	3.948	0.799	2.138	0.325	2.066	0.307	3.364	1.741	6.025	8.834	1.411
	JB1a 11	5.261	1.499	4.763	0.720	4.101	0.798	2.165	0.342	2.055	0.298	3.532	1.771	6.432	9.061	1.551
	JB1a 12	5.251	1.503	4.864	0.719	4.228	0.832	2.283	0.345	2.192	0.321	3.520	1.782	6.500	9.258	1.616
	JB1a 13	5.147	1.471	4.601	0.709	4.094	0.795	2.210	0.329	2.118	0.313	3.574	1.733	6.589	9.047	1.579
	JB1a 14	5.101	1.506	4.744	0.692	3.999	0.806	2.143	0.319	2.078	0.302	3.413	1.760	6.564	9.052	1.606
	AVERAGE	5.205	1.501	4.736	0.710	4.086	0.809	2.192	0.332	2.107	0.310	3.491	1.760	6.503	9.099	1.583
	Relative std deviation	0.01577	0.01586	0.02062	0.02299	0.02265	0.02098	0.02965	0.03158	0.02459	0.03118	0.02374	0.02062	0.03209	0.02818	0.05295
	GEOREM	5.099	1.484	4.7	0.699	4.07	0.805	2.232	0.3197	2.1	0.3147	3.47	1.738	6.44	8.97	1.615
	ACCURACY (average)	0.0209	0.0115	0.0077	0.0156	0.0040	0.0050	-0.0181	0.0391	0.0035	-0.0160	0.0061	0.0128	0.0098	0.0144	-0.0198
DRIFT CORRE	CTED															
	BHVO-23	5.724	1.968	5.843	0.872	4.946	0.919	2.333	0.310	1.914	0.246	4.115	1.125	1.642	1.133	0.374
	BHVO-2 cal 4	5.885	1.977	5.955	0.899	5.024	0.932	2.350	0.324	1.900	0.258	4.243	1.147	1.718	1.157	0.403
	BHVO-2 5	6.450	2.082	6.281	0.929	5.292	0.982	2.496	0.344	2.004	0.281	4.513	1.192	1.752	1.212	0.409
	BHVO-26	5.993	2.022	5.979	0.896	4.958	0.919	2.343	0.326	1.941	0.277	4.159	1.135	1.764	1.166	0.398
	BHVO-27	5.716	1.917	5.635	0.852	4.650	0.893	2.225	0.304	1.803	0.260	3.935	1.099	1.685	1.060	0.403
	BHVO-2 10	5.825	1.925	5.739	0.853	4.601	0.885	2.239	0.298	1.783	0.254	3.881	1.116	1.659	1.104	0.373
	BHVO-2 11	5.863	1.973	5.772	0.902	4.848	0.910	2.382	0.318	1.867	0.257	4.176	1.105	1.730	1.115	0.408
	BHVO-2 12	6.035	2.016	6.082	0.923	5.037	0.926	2.366	0.322	1.908	0.285	4.293	1.144	1.831	1.156	0.420
	BHVO-2 13	5.852	2.002	6.013	0.912	4.921	0.949	2.395	0.320	1.907	0.283	4.206	1.109	1.814	1.102	0.443
	BHVO-2 14	5.880	2.055	5.988	0.915	4.812	0.901	2.362	0.318	1.893	0.269	4.192	1.121	1.892	1.060	0.438
AVERAGE		5.922	1.994	5.929	0.895	4.909	0.922	2.349	0.318	1.892	0.267	4.171	1.129	1.749	1.126	0.407
Relative std der	viation	0.03558	0.02639	0.03160	0.03087	0.04048	0.03093	0.03274	0.04029	0.03364	0.05240	0.04246	0.02409	0.04537	0.04264	0.05721
GEOREM		6.1	2.07	6.16	0.92	5.22	0.98	2.56	0.34	2.01	0.279	4.32	1.15	1.7	1.23	0.403
ACCURACY (average)		-0.02913	-0.03691	-0.03752	-0.02687	-0.05958	-0.05963	-0.08241	-0.06337	-0.05872	-0.04332	-0.03441	-0.01807	0.02864	-0.08422	0.00952
detection limit	s (based on gas blank: 3	x standard devia	ation on gas bl	ank measurem	ents done afte	r each sample) e	expressed in pr	om								
		0.02	0.009	0.003	0.008	0.002	0.005	0.001	0.003	0.001	0.004	0.002	0.004	0.002	0.02	0.001

Day 4		Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Ga (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Cs (ppm)	Ba (ppm)	Pr (ppm)	Nd (ppm)
JB1-a STANDARD RUN AS UNKNOWN, DRIFT CORRECTED, INTERSPERSED BETWEEN SAMPLES (ppm)																
	JB1-a	27.663	200.805	417.652	38.957	146.028		37.829	441.705	21.597	132.705	27.875	1.265	498.173	7.130	26.463
	JB1-a	27.867	194.999	415.000	38.169	140.754		38.299	445.266	22.283	135.722	27.949	1.241	495.526	7.262	26.640
	JB1-a	27.820	196.076	415.508	37.065	138.520		38.839	450.979	23.812	140.996	28.211	1.200	499.360	7.403	27.553
	JB1-a	28.649	195.905	417.258	38.370	141.312		39.185	446.288	23.654	141.610	28.311	1.225	499.818	7.311	27.501
	JB1-a	29.827	194.453	417.715	37.867	141.177		39.183	452.193	23.847	143.051	28.516	1.218	503.175	7.363	27.456
	JB1-a	27.344	200.861	419.044	38.683	145.269		37.566	450.809	23.029	139.324	28.541	1.300	500.984	7.393	27.374
	JB1-a	28.304	197.107	416.335	38.036	142.742		38.386	445.108	22.432	134.634	28.075	1.246	507.007	7.267	26.728
	JB1-a	28.460	197.805	417.514	38.266	142.135		38.591	448.908	23.297	139.558	28.252	1.275	502.733	7.288	27.418
	JB1-a	27.759	195.329	414.668	38.064	140.475		38.695	441.903	22.072	135.387	27.714	1.176	488.320	7.177	26.475
Average		28.188	197.038	416.744	38.164	142.046		38.508	447.018	22.892	138.110	28.160	1.239	499.455	7.288	27.068
Relative std devi	ation	0.026	0.012	0.003	0.014	0.017		0.014	0.009	0.036	0.026	0.010	0.031	0.011	0.013	0.018
compiled from G	eorem database	28.3	197	414	38.7	140		38.4	441	23.2	140	28.1	1.19	495	7.19	26.3
AVERAGE ACC	URACY	-0.00395	0.00019	0.00663	-0.01385	0.01461		0.00282	0.01365	-0.01329	-0.01350	0.00215	0.04080	0.00900	0.01366	0.02919
BHVO-2 STAND	ARD RUN AS UNKNOWN	I, DRIFT CORREC	CTED, INTERSPE	RSED BETWEEN	N SAMPLES (pp	m)										
	BHVO-2	30.430	322.098	289.772	45.116	122.166		8.974	390.070	24.456	160.247	18.202	0.114	129.933	5.211	24.023
	BHVO-2	32.605	310.815	287.506	43.780	119.078		9.286	395.696	25.453	169.329	18.263	0.109	132.032	5.305	24.797
	BHVO-2	32.235	310.432	287.572	45.237	117.814		9.460	391.706	25.118	166.759	18.282	0.092	130.699	5.256	24.654
	BHVO-2	31.017	306.128	288.485	43.906	118.720		9.405	391.472	25.420	169.102	18.015	0.100	128.225	5.308	24.586
	BHVO-2	32.154	307.529	285.844	45.214	115.780		9.575	392.636	26.022	168.851	18.249	0.098	128.427	5.339	24.688
	BHVO-2	30.118	309.846	289.183	45.233	122.422		9.226	387.593	24.806	165.748	18.387	0.091	129.866	5.236	24.576
	BHVO-2	30.770	311.747	285.890	44.440	120.017		9.244	390.053	24.835	166.157	18.320	0.100	131.308	5.269	24.542
	BHVO-2	31.595	306.956	283.993	44.436	118.612		9.326	392.156	25.681	170.537	18.612	0.096	130.053	5.239	24.687
	BHVO-2	31.112	309.745	290.301	43.786	118.216		9.639	388.677	25.523	168.490	18.113	0.102	129.875	5.251	24.126
Average		31.337	310.588	287.616	44.572	119.203		9.348	391.118	25.257	167.247	18.271	0.100	130.046	5.268	24.520
Relative std devi	ation	0.027477561	0.015169689	0.007202439	0.014438108	0.017551511		0.02145329	0.006092967	0.019515052	0.018356076	0.009241175	0.077226978	0.009407655	0.007829415	0.010804076
compiled from Georem database		31.83	318.2	287.2	44.89	119.8		9.261	394.1	25.91	171.2	18.1	0.0996	130.9	5.339	24.27
AVERAGE ACC	URACY	-0.015477827	-0.023920595	0.001448907	-0.007086589	-0.004985485		0.009420223	-0.007567467	-0.025197789	-0.023091956	0.009463173	0.006868627	-0.006521325	-0.01326846	0.010295672
detection limits	(based on gas blank: 3	k standard devia	tion on gas blan	k measurements	done after each	n sample) expr	essed in p	pm								
	_	0.2	- 0.2	0.6	0.07	0.2		0.1	0.1	0.02	0.2	0.02	0.02	0.2	0.008	0.04

Day 4		Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
JB1-a STANDARD RUN AS UNKNOWN, DRIFT CORRECTED, INTERSPERSED BETWEEN SAMPLES (ppm)					(ppm)											
	JB1-a	4.908	1.475	4.624	0.687	3.932	0.772	2.120	0.313	2.026	0.303	3.438	1.740	6.339	8.991	1.536
	JB1-a	5.278	1.508	4.916	0.712	4.096	0.792	2.271	0.326	2.111	0.299	3.588	1.776	6.466	9.338	1.584
	JB1-a	5.220	1.510	4.982	0.717	4.231	0.845	2.322	0.328	2.140	0.305	3.551	1.798	6.511	9.541	1.607
	JB1-a	5.413	1.559	4.761	0.736	4.201	0.849	2.319	0.334	2.174	0.323	3.694	1.793	6.495	9.460	1.599
	JB1-a	5.273	1.519	5.071	0.712	4.269	0.844	2.353	0.341	2.203	0.317	3.676	1.784	6.539	9.583	1.629
	JB1-a	5.229	1.495	4.933	0.726	4.091	0.832	2.287	0.328	2.136	0.313	3.632	1.791	6.498	9.413	1.549
	JB1-a	5.188	1.545	4.757	0.703	4.151	0.800	2.195	0.324	2.111	0.301	3.434	1.763	6.536	9.272	1.608
	JB1-a	5.290	1.535	4.848	0.729	4.209	0.832	2.312	0.336	2.178	0.312	3.646	1.802	6.551	9.475	1.589
	JB1-a	5.004	1.460	4.787	0.686	3.959	0.780	2.193	0.313	2.019	0.300	3.505	1.743	6.277	9.103	1.562
Average		5.200	1.512	4.853	0.712	4.127	0.816	2.264	0.327	2.122	0.308	3.574	1.777	6.468	9.353	1.585
Relative std devia	ation	0.030	0.021	0.028	0.025	0.029	0.037	0.034	0.029	0.030	0.028	0.027	0.013	0.015	0.021	0.019
compiled from G	eorem database	5.1	1.48	4.93	0.717	4.08	0.796	2.19	0.319	2.13	0.309	3.6	1.8	6.25	9.17	1.55
AVERAGE ACC	URACY	0.01967	0.02145	-0.01555	-0.00699	0.01140	0.02532	0.03360	0.02535	-0.00371	-0.00323	-0.00727	-0.01292	0.03490	0.01994	0.02252
BHVO-2 STAND	ARD RUN AS UNKNOW	/N, DRIFT CORRE	CTED, INTERS	PERSED BETV	VEEN SAMPLE	S (ppm)										
	BHVO-2	5.937	2.024	6.008	0.879	4.909	0.922	2.379	0.313	1.915	0.261	4.186	1.165	1.627	1.170	0.397
	BHVO-2	6.028	2.076	6.312	0.933	5.259	0.986	2.454	0.342	1.993	0.285	4.471	1.175	1.702	1.224	0.413
	BHVO-2	5.897	2.034	6.215	0.924	5.152	0.959	2.477	0.330	1.931	0.267	4.330	1.163	1.725	1.190	0.403
	BHVO-2	6.001	2.058	6.094	0.908	5.057	0.969	2.497	0.331	1.952	0.282	4.455	1.195	1.739	1.200	0.433
	BHVO-2	6.279	2.136	6.230	0.909	5.152	0.961	2.514	0.337	2.006	0.285	4.392	1.194	1.734	1.181	0.432
	BHVO-2	6.002	2.112	5.933	0.898	5.052	0.943	2.444	0.327	1.949	0.255	4.291	1.190	1.787	1.132	0.433
	BHVO-2	6.124	2.146	5.879	0.892	5.091	0.970	2.457	0.332	1.924	0.279	4.312	1.193	1.840	1.116	0.450
	BHVO-2	6.261	2.144	6.112	0.933	5.071	0.955	2.482	0.339	1.945	0.271	4.374	1.198	1.811	1.121	0.446
	BHVO-2	6.278	2.137	5.757	0.921	5.114	0.942	2.377	0.328	1.880	0.266	4.301	1.177	1.866	1.086	0.456
Average		6.090	2.096	6.060	0.911	5.095	0.956	2.453	0.331	1.944	0.272	4.346	1.183	1.759	1.158	0.429
Relative std devia	ation	0.024765635	0.023344869	0.029950492	0.020495921	0.018639656	0.019643298	0.019572618	0.025518245	0.019758259	0.040846662	0.020342273	0.011501588	0.042376243	0.039595554	0.048316525
compiled from Georem database		6.023	2.043	6.207	0.9392	5.28	0.9887	2.511	0.3349	1.994	0.2754	4.47	1.154	1.653	1.224	0.412
AVERAGE ACCURACY		0.011074289	0.026083129	-0.02367955	-0.03023053	-0.035016232	-0.032722373	-0.022908154	-0.011811566	-0.025236259	-0.011301083	-0.027780725	0.025466879	0.064087651	-0.054026439	0.042085422
detection limits (based on gas blank: 3x standard deviation on gas blank measurements done after each sample)					expressed in p	om										
		0.02	0.005	0.02	0.002	0.007	0.002	0.005	0.002	0.007	0.002	0.006	0.003	0.02	0.01	0.003

REFERENCES

REFERENCES

- Annells, R.N., 1974, Keweenawan Volcanic Rocks of Michipicoten Island, Lake Superior, Ontario: An Eruptive Centre of Proterozoic Age, 41N: Department of Energy, Mines and Resources.
- Annells, 1973, Proterozic Flood Basalt of eastern Lake Superior: The Keweenawan Volcanic Rocks of the Mamainse Point Area, Ontario: Department of Energy, Mines and Resources Calgary, Alberta, Canada, v. 5.
- Bachmann, O., and Bergantz, G.W., 2004, On the origin of crystal-poor rhyolites: extracted from batholithic crystal mushes: Journal of Petrology, v. 45, p. 1565–1582.
- Baragar, W.R.A., 1978, Michipicoten Island, Ontario: Rubidium-strontium isotopic age studies, Report, v. 2, p. 77–14.
- Beard, J.S., and Lofgren, G.E., 1989, Effect of water on the composition of partial melts of greenstone and amphibolite: Science, v. 244, p. 195–197.
- Bell, K., and Blenkinsop, J., 1987, Archean depleted mantle: evidence from Nd and Sr initial isotopic ratios of carbonatites: Geochimica et Cosmochimica Acta, v. 51, p. 291–298.
- Bennett, V.C., 2003, Compositional evolution of the mantle: Treatise on geochemistry, v. 2, p. 568.
- Blichert-Toft, J., Chauvel, C., and Albarède, F., 1997, Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS: Contributions to Mineralogy and Petrology, v. 127, p. 248–260.
- Bouvier, A., Vervoort, J.D., and Patchett, P.J., 2008, The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets: Earth and Planetary Science Letters, v. 273, p. 48–57.
- Bryan, S.E., and Ernst, R.E., 2008, Revised definition of large igneous provinces (LIPs): Earth-Science Reviews, v. 86, p. 175–202.
- Buck, W.R., and Karner, G.D., 2004, Consequences of asthenospheric variability on continental rifting: Rheology and deformation of the lithosphere at continental margins, v. 62, p. 1–30.
- Cannon, W.F., 1994, Closing of the Midcontinent rift-A far—field effect of Grenvillian compression: Geology, v. 22, p. 155–158.
- Cannon, W.F., 1992, The Midcontinent rift in the Lake Superior region with emphasis on its geodynamic evolution: Tectonophysics, v. 213, p. 41–48.
- Cannon, W.F., and Hinze, W.J., 1992, Speculations on the origin of the North American Midcontinent rift: Tectonophysics, v. 213, p. 49–55.

- Chaudhuri, S., and Faure, G., 1967, Geochronology of the Keweenawan rocks, White Pine, Michigan: Economic Geology, v. 62, p. 1011–1033.
- Chauvel, C., Lewin, E., Carpentier, M., Arndt, N.T., and Marini, J.-C., 2008, Role of recycled oceanic basalt and sediment in generating the Hf–Nd mantle array: Nature geoscience, v. 1, p. 64.
- Chiarenzelli, J.R., and McLelland, J.M., 1991, Age and regional relationships of granitoid rocks of the Adirondack Highlands: The Journal of Geology, v. 99, p. 571–590.
- Connelly, J.N., Ulfbeck, D.G., Thrane, K., Bizzarro, M., and Housh, T., 2006, A method for purifying Lu and Hf for analyses by MC-ICP-MS using TODGA resin: Chemical Geology, v. 233, p. 126–136.
- Courtillot, V., Jaupart, C., Manighetti, I., Tapponnier, P., and Besse, J., 1999, On causal links between flood basalts and continental breakup: Earth and Planetary Science Letters, v. 166, p. 177–195.
- Davis, D.W., and Green, J.C., 1997, rift in western Lake Superior and implications for: Earth, v. 488, p. 476–488.
- Davis, D.W., and Paces, J.B., 1990, Time resolution of geologic events on the Keweenaw Peninsula and implications for development of the Midcontinent Rift system: Earth and Planetary Science Letters, v. 97, p. 54–64.
- Deering, C.D., and Bachmann, O., 2010, Trace element indicators of crystal accumulation in silicic igneous rocks: Earth and Planetary Science Letters, v. 297, p. 324–331.
- Dixon, S., and Rutherford, M.J., 1979, Plagiogranites as late-stage immiscible liquids in ophiolite and mid-ocean ridge suites: an experimental study: Earth and Planetary Science Letters, v. 45, p. 45–60.
- Dosso, L., 1984, The nature of the Precambrian subcontinental mantle: Isotopic study (Sr, Pb, Nd) of the Keweenawan volcanism of the North Shore of Lake Superior: University of Minnesota.
- Ernst, R.E., 2014, Large igneous provinces: Cambridge University Press.
- Fairchild, L.M., Swanson-Hysell, N.L., Ramezani, J., Sprain, C.J., and Bowring, S.A., 2017, The end of Midcontinent Rift magmatism and the paleogeography of Laurentia: Lithosphere, v. 9, p. 117–133.
- Faure, G., 1986, Principles of isotope geology, 2nd edn: Wiley. New York.
- Finlayson, V.A., Konter, J.G., Konrad, K., Koppers, A.A.P., Jackson, M.G., and Rooney, T.O., 2018, Sr–Pb–Nd–Hf isotopes and 40Ar/39Ar ages reveal a Hawaii–Emperor-style bend in the Rurutu hotspot: Earth and Planetary Science Letters, v. 500, p. 168–179.
- Good, D., and Lightfoot, P.C., 2019, Significance of Metasomatized Lithospheric Mantle in the Formation of Early Basalts and Cu-PGE Sulfide Mineralization in the Coldwell Complex, Midcontinent Rift, Canada: Canadian Journal of Earth Sciences,.

- Grant, J.A., 2005, Isocon analysis: A brief review of the method and applications: Physics and Chemistry of the Earth, Parts A/B/C, v. 30, p. 997–1004.
- Gualda, G.A., Ghiorso, M.S., Lemons, R.V., and Carley, T.L., 2012, Rhyolite-MELTS: a modified calibration of MELTS optimized for silica-rich, fluid-bearing magmatic systems: Journal of Petrology, v. 53, p. 875–890.
- Heaman, L.M., Easton, R.M., Hart, T.R., MacDonald, C.A., Hollings, P., and Smyk, M., 2007, Further refinement to the timing of Mesoproterozoic magmatism, Lake Nipigon region, Ontario: Canadian Journal of Earth Sciences, v. 44, p. 1055–1086.
- Helz, R.T., 1976, Phase relations of basalts in their melting ranges at P H2O= 5 kb. Part II. Melt compositions: Journal of Petrology, v. 17, p. 139–193.
- Hess, P.C., 1971, Polymer model of silicate melts: Geochimica et Cosmochimica Acta, v. 35, p. 289–306.
- Hildreth, W., 2004, Volcanological perspectives on Long Valley, Mammoth Mountain, and Mono Craters: several contiguous but discrete systems: Journal of Volcanology and Geothermal Research, v. 136, p. 169–198.
- Hollings, P., Hart, T., Richardson, A., and MacDonald, C.A., 2007, Geochemistry of the Mesoproterozoic intrusive rocks of the Nipigon Embayment, northwestern Ontario; evaluating the earliest phases of rift development: Canadian Journal of Earth Sciences = Revue Canadienne des Sciences de la Terre, v. 44, p. 1087–1110, doi:http://dx.doi.org/10.1139/E06-127.
- Irvine, T.N.J., and Baragar, W.R.A., 1971, A guide to the chemical classification of the common volcanic rocks: Canadian journal of earth sciences, v. 8, p. 523–548.
- Janoušek, V., Moyen, J.-F., Martin, H., Erban, V., and Farrow, C., 2016, Geochemical Modelling of Igneous Processes – Principles And Recipes in R Language: Bringing the Power of R to a Geochemical Community: Berlin Heidelberg, Springer-Verlag, Springer Geochemistry, https://www.springer.com/us/book/9783662467916 (accessed April 2019).
- Klewin, K.W., and Berg, J.H., 1990, Geochemistry of the Mamainse Point volcanics, Ontario, and implications for the Keweenawan paleomagnetic record: Canadian Journal of Earth Sciences, v. 27, p. 1194–1199.
- Klewin, K.W., and Berg, J.H., 1991, Petrology of the Keweenawan Mamainse Point lavas, Ontario: Petrogenesis and continental rift evolution: Journal of Geophysical Research: Solid Earth, v. 96, p. 457–474.
- Konter, J.G., and Storm, L.P., 2014, High precision 87Sr/86Sr measurements by MC-ICP-MS, simultaneously solving for Kr interferences and mass-based fractionation: Chemical Geology, v. 385, p. 26–34, doi:10.1016/j.chemgeo.2014.07.009.
- Krans, S.R., Rooney, T.O., Kappelman, J., Yirgu, G., and Ayalew, D., 2018, From initiation to termination: a petrostratigraphic tour of the Ethiopian Low-Ti Flood Basalt Province: Contributions to Mineralogy and Petrology, v. 173, p. 37.

- de Laeter, J.R., Böhlke, J.K., De Bièvre, P., Hidaka, H., Peiser, H.S., Rosman, K.J., and Taylor, P.D., 2003, Atomic weights of the elements. Review 2000 (IUPAC Technical Report): Pure and applied chemistry, v. 75, p. 683–800.
- Le Bas, M.J., Le Maitre, R.W., Streckeisen, A., Zanettin, B., and Rocks, I.S. on the S. of I., 1986, A chemical classification of volcanic rocks based on the total alkali-silica diagram: Journal of petrology, v. 27, p. 745–750.
- Lee, C.-T.A., Lee, T.C., and Wu, C.-T., 2014, Modeling the compositional evolution of recharging, evacuating, and fractionating (REFC) magma chambers: Implications for differentiation of arc magmas: Geochimica et Cosmochimica Acta, v. 143, p. 8–22.
- Marshall, L., 1996, Geochemistry and paleomagnetism of Keweenawan basalt in the subsurface of Nebraska: Precambrian Research, v. 76, p. 47–65, doi:10.1016/0301-9268(95)00027-5.
- Matthews, T.P., and Rooney, T.O., 2009, Deducing Rhyolite Origins in Keweenawan Magmas-Geochemical Correlations With Flood Basalts, Mamainse Point, ON, *in* AGU Fall Meeting Abstracts,.
- McBirney, A.R., 1996, The Skaergaard intrusion, *in* Developments in Petrology, Elsevier, v. 15, p. 147–180.
- McDonough, W.F., and Sun, S.-S., 1995, The composition of the Earth: Chemical geology, v. 120, p. 223–253.
- McLelland, J., Hamilton, M., Selleck, B., McLelland, J., Walker, D., and Orrell, S., 2001, Zircon U-Pb geochronology of the Ottawan orogeny, Adirondack highlands, New York: regional and tectonic implications: Precambrian Research, v. 109, p. 39–72.
- Miller, C.F., and Mittlefehldt, D.W., 1982, Depletion of light rare-earth elements in felsic magmas: Geology, v. 10, p. 129–133.
- Miller, J., and Nicholson, S.W., 2013, Geology and mineral deposits of the 1.1 Ga Midcontinent Rift in the Lake Superior region–an overview: Field guide to the copper-nickel-platinum group element deposits of the Lake Superior Region. Edited by Miller, J. Precambrian Research Center Guidebook, v. 13, p. 1–49.
- Nicholson, S.W., 1990, Portage Lake rhyolites of the midcontinent rift system, Keweenaw Peninsula, Michigan: geology, petrogenesis and implications for rift magmatism and mineralization: University of Minnesota Minneapolis.
- Nicholson, S.W., Schulz, K.J., Shirey, S.B., and Green, J.C., 1997, Rift-wide correlation of 1.1 Ga Midcontinent rift system basalts: implications for multiple mantle sources during rift development: Canadian Journal of Earth Sciences, v. 34, p. 504–520.
- Nicholson, S.W., and Shirey, S.B., 1990, Midcontinent rift volcanism in the Lake Superior region: Sr, Nd, and Pb isotopic evidence for a mantle plume origin: Journal of Geophysical Research: Solid Earth, v. 95, p. 10851–10868.

Paces, J.B., 1988, Magmatic processes, evolution and mantle source characteristics ...:

- Paces, J.B., and Bell, K., 1989a, Non-depleted sub-continental mantle beneath the Superior Province of the Canadian Shield: Nd-Sr isotopic and trace element evidence from Midcontinent Rift basalts: Geochimica et Cosmochimica Acta, v. 53, p. 2023–2035.
- Paces, J.B., and Bell, K., 1989b, Non-depleted sub-continental mantle beneath the Superior Province of the Canadian Shield: Nd-Sr isotopic and trace element evidence from Midcontinent Rift basalts: Geochimica et Cosmochimica Acta, v. 53, p. 2023–2035, doi:10.1016/0016-7037(89)90322-0.
- Palmer, H.C., and Davis, D.W., 1987, Paleomagnetism and U-Pb geochronology of volcanic rocks from michipicoten island, lake superior, canada: precise calibration of the keweenawan polar wander track: Precambrian Research, v. 37, p. 157–171, doi:10.1016/0301-9268(87)90077-5.
- Philpotts, A.R., 1982, Compositions of immiscible liquids in volcanic rocks: Contributions to Mineralogy and Petrology, v. 80, p. 201–218.
- Polat, A., and Kerrich, R., 2000, Archean greenstone belt magmatism and the continental growth–mantle evolution connection: constraints from Th–U–Nb–LREE systematics of the 2.7 Ga Wawa subprovince, Superior Province, Canada: Earth and Planetary Science Letters, v. 175, p. 41–54.
- Polat, A., and Münker, C., 2004, Hf–Nd isotope evidence for contemporaneous subduction processes in the source of late Archean arc lavas from the Superior Province, Canada: Chemical Geology, v. 213, p. 403–429.
- Rivers, T., 2008, Assembly and preservation of lower, mid, and upper orogenic crust in the Grenville Province—Implications for the evolution of large hot long-duration orogens: Precambrian Research, v. 167, p. 237–259.
- Rivers, T., 1997, Lithotectonic elements of the Grenville Province: review and tectonic implications: Precambrian Research, v. 86, p. 117–154, doi:10.1016/S0301-9268(97)00038-7.
- Rivers, T., Ketchum, J., Indares, A., and Hynes, A., 2002, The High Pressure belt in the Grenville Province: architecture, timing, and exhumation: Canadian Journal of Earth Sciences, v. 39, p. 867–893.
- Rooney, T.O., LaVigne, A., Konter, J., Eric, B., Stein, S., Moucha, R., and Stein, C., 2018, CONSTRAINING THE GEOCHEMICAL RESERVOIRS CONTRIBUTING TO VOLCANISM IN THE KEWEENAW LIP, *in* GSA, https://gsa.confex.com/gsa/2018AM/webprogram/Paper323279.html (accessed June 2019).
- Saunders, A.D., England, R.W., Reichow, M.K., and White, R.V., 2005, A mantle plume origin for the Siberian traps: uplift and extension in the West Siberian Basin, Russia: Lithos, v. 79, p. 407–424.
- Shirey, S.B., 1997, Re-Os isotopic compositions of Midcontinent rift system picrites: implications for plume–lithosphere interaction and enriched mantle sources: Canadian Journal of Earth Sciences, v. 34, p. 489–503.

- Shirey, S.B., Berg, J.H., and Carlson, R.W., 1994, Temporal changes in the sources of flood basalts: isotopic and trace element evidence from the 1100 Ma old Keweenawan Mamainse Point Formation, Ontario, Canada: Geochimica et Cosmochimica Acta, v. 58, p. 4475–4490.
- Spulber, S.D., and Rutherford, M.J., 1983, The origin of rhyolite and plagiogranite in oceanic crust: an experimental study: Journal of Petrology, v. 24, p. 1–25.
- Stein, C.A., Kley, J., Stein, S., Hindle, D., and Keller, G.R., 2015, North America's Midcontinent Rift: when rift met LIP: Geosphere, v. 11, p. 1607–1616.
- Stein, S., Stein, C.A., Elling, R., Kley, J., Keller, R., Wysession, M., Rooney, T., Frederiksen, A., and Moucha, R., 2018, Insights from North America's failed Midcontinent Rift into the evolution of continental rifts and passive continental margins: Tectonophysics,.
- Stein, C.A., Stein, S., Merino, M., Randy Keller, G., Flesch, L.M., and Jurdy, D.M., 2014, Was the Midcontinent Rift part of a successful seafloor-spreading episode? Geophysical Research Letters, v. 41, p. 1465–1470.
- Swanson-Hysell, N.L., Burgess, S.D., Maloof, A.C., and Bowring, S.A., 2014, Magmatic activity and plate motion during the latent stage of Midcontinent Rift development: Geology, v. 42, p. 475–478.
- Swanson-Hysell, N.L., Ramezani, J., Fairchild, L.M., and Rose, I.R., 2019, Failed rifting and fast drifting: Midcontinent rift development, Laurentia's rapid motion and the driver of Grenvillian orogenesis: Geological Society of America Bulletin,.
- Thy, P., Beard, J.S., and Lofgren, G.E., 1990, Experimental Constraints on the Origin of Icelandic Rhyolites: The Journal of Geology, v. 98, p. 417–421.
- Turek, A., Smith, P.E., and Schmus, W.V., 1982, Rb–Sr and U–Pb ages of volcanism and granite emplacement in the Michipicoten belt—Wawa, Ontario: Canadian Journal of Earth Sciences, v. 19, p. 1608–1626.
- Vervoort, J.D., and Green, J.C., 1997, Origin of evolved magmas in the Midcontinent rift system, northeast Minnesota: Nd-isotope evidence for melting of Archean crust: Canadian Journal of Earth Sciences, v. 34, p. 521–535.
- Vervoort, J.D., Wirth, K., Kennedy, B., Sandland, T., and Harpp, K.S., 2007, The magmatic evolution of the Midcontinent rift: New geochronologic and geochemical evidence from felsic magmatism: Precambrian Research, v. 157, p. 235–268.
- White, R., and McKenzie, D., 1989, Magmatism at rift zones: the generation of volcanic continental margins and flood basalts: Journal of Geophysical Research: Solid Earth, v. 94, p. 7685–7729.
- Wirth, K.R., Naiman, Z.J., and Vervoort, J.D., 1997, The Chengwatana Volcanics, Wisconsin and Minnesota: petrogenesis of the southernmost volcanic rocks exposed in the Midcontinent rift: Canadian Journal of Earth Sciences, v. 34, p. 536–548.

Workman, R.K., and Hart, S.R., 2005, Major and trace element composition of the depleted MORB mantle (DMM): Earth and Planetary Science Letters, v. 231, p. 53–72.

Zindler, A., and Hart, S., 1986, Chemical Geodynamics: Annual Review of Earth and Planetary Sciences, v. 14, p. 493–571, doi:10.1146/annurev.ea.14.050186.002425.