

Constraints on Early Paleozoic deep-ocean oxygen concentrations from the iron geochemistry of the Bay of Islands ophiolite

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Abstract: The deep ocean is generally considered to have changed from anoxic in the Precambrian to oxygenated by the Late Paleozoic (~420-400 Ma) due to changes in atmospheric oxygen concentrations. When the transition occurred, i.e., in the Early Paleozoic or not until the Late Paleozoic, is less well constrained. To address this, we measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ of volcanic rocks, sheeted dykes, gabbros, and ultramafic rocks from the Early Paleozoic (~485 Ma) Bay of Islands ophiolite as a proxy for hydrothermal alteration in the presence or absence of O_2 derived from deep marine fluids. Combining this data with previously published data from the Bay of Islands indicates that volcanic rocks are oxidized relative to intrusive crustal rocks (0.35 ± 0.02 vs. 0.19 ± 0.01 , 1 standard error), which we interpret to indicate that the volcanic section was altered by marine-derived fluids that contained some dissolved O_2 . We compare our results directly to the Macquarie Island and Troodos ophiolites, drilled oceanic crust, previously compiled data for ophiolitic volcanic rocks, and newly compiled data for ophiolitic intrusive rocks. These comparisons show that the Bay of Islands volcanic (but not intrusive) rocks are oxidized relative to Precambrian equivalents, but are less oxidized relative to Late Paleozoic to modern equivalents. We interpret these results to indicate that the Early Paleozoic ocean contained dissolved O_2 , but at concentrations ~2.4x lower than for the Late Paleozoic to today.

Key Points

- We report $\text{Fe}^{3+}/\Sigma\text{Fe}$ in volcanic and intrusive crustal rocks and ultramafic rocks from the Early Paleozoic Bay of Islands ophiolite.
- $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the Bay of Islands volcanic rocks are elevated compared to Precambrian systems but lower than Late Paleozoic to modern systems.
- This difference indicates deep-ocean O_2 levels in the Early Paleozoic were elevated compared to the Precambrian but lower than today.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1029/2021GC010196](https://doi.org/10.1029/2021GC010196).

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1. Introduction

The circulation of seawater through newly formed igneous oceanic crust represents one of the primary means by which the fluid and solid Earth interact and exchange both heat and chemical components (as reviewed in Coogan & Gillis, 2018 and Elderfield & Schultz, 1996). This circulation is generally divided into low- and high-temperature systems. High-temperature hydrothermal systems occur near spreading centers in young oceanic crust (<1 million years) where fluids penetrate and react with rocks at depths of multiple kilometers (Elderfield & Schultz, 1996). In contrast, low-temperature hydrothermal systems (<100°C) occur throughout shallower volcanic sections for tens of millions of years post crystallization (Coogan et al., 2016; Coogan & Gillis, 2018; Elderfield & Schultz, 1996; Hart & Staudigel, 1978).

Low-temperature circulation of seawater through volcanic sections of oceanic crust results in changes in the chemical composition of these rocks (e.g., Alt et al., 1996; Coggon et al., 2016; Staudigel et al., 1996; Kelley et al., 2003). Specifically, as cold seawater circulates through a volcanic section, igneous minerals are replaced by secondary minerals (as reviewed in Coogan & Gillis, 2018). In the modern ocean, this alteration includes redox reactions in which O₂ dissolved in seawater reacts with and oxidizes reduced sulfur (S²⁻) to S⁶⁺ in sulfate and reduced iron as Fe²⁺ to Fe³⁺ (Bach & Edwards, 2003). At the low temperatures at which this alteration occurs (<100°C), sulfate is soluble and is removed from the section lowering the total sulfur content (Bach & Edwards, 2003). In contrast, Fe³⁺ is insoluble and precipitates as secondary iron oxide minerals (primarily Fe-oxyhydroxides). Because the modern deep ocean is oxygenated, low-temperature hydrothermal alteration of volcanic rocks in oceanic crust causes sulfur contents to decrease and the ratio of Fe³⁺/(Fe²⁺+Fe³⁺) (here given as Fe³⁺/ΣFe) to increase (Bach & Edwards, 2003; Johnson & Semyan, 1994) relative to their value at crystallization (i.e., the original igneous value). In contrast, deeper sections in oceanic crust (e.g., the sheeted dykes and gabbros) are not as extensively altered by oxygenated low-temperature fluids (Bach & Edwards, 2003). Instead they are dominantly altered by higher-temperature anoxic fluids that lost their dissolved O₂ earlier in the hydrothermal system via reactions with other igneous rocks. As a consequence, the Fe³⁺/ΣFe of altered modern sheeted dykes and gabbros are generally lower and closer to the values expected for pristine oceanic crust as compared to hydrothermally altered modern mid-ocean ridge basalts (MORB; Bach & Edwards, 2003). A general review of the processes controlling how iron-bearing igneous minerals become oxidized in oceanic crust during modern hydrothermal circulation is given in Bach and Edwards (2003).

Although the atmosphere and oceans are oxygenated today, this has not always been the case. The Archean atmosphere and oceans are typically thought to have been anoxic (e.g., Canfield, 2005; Farquhar et al., 2000; Lyons et al., 2014; Pavlov & Kasting, 2002). The Paleoproterozoic and Mesoproterozoic are generally modeled to have had atmospheric O₂ contents of order 1% vs. modern such that the deep ocean remained anoxic (e.g., Lyons et al., 2014; Planavsky et al., 2018). Sometime in the Neoproterozoic to Early Phanerozoic, it is generally thought that atmospheric O₂ concentrations rose to levels sufficient to oxygenate the deep ocean. Recent studies based on, for example, sedimentary Mo concentrations and Mo isotopic ratios (Dahl et al., 2010), sedimentary Fe speciation (Sperling et al., 2015, 2021), and sedimentary Ce anomalies (Wallace et al., 2017) have been used to argue that the transition to an oxygenated deep ocean occurred in the Paleozoic and potentially not until the late Paleozoic (~420-400 Ma). However, other studies have argued that O₂ concentrations began increasing in the Neoproterozoic (e.g.,

Blamey et al., 2016; Och & Shields-Zhou, 2012; Sahoo et al., 2012). Such increases in the Neoproterozoic are sometimes interpreted as transient events as opposed to a stepwise oxygenation event such that marine O₂ concentrations varied spatially and temporally in the Neoproterozoic and Early Paleozoic (e.g., Kendall et al., 2015; Reinhard & Planavsky, 2022; Sahoo et al., 2016; Tostevin & Mills, 2020). If, as is usually assumed, deep-ocean oxygen concentrations are largely controlled by atmospheric O₂ concentrations (Canfield, 1998; Lyons et al., 2014), this timeline would require a delay of hundreds of millions of years between the processes that caused atmospheric oxygen levels to begin increasing (once or multiple times if dynamic) over background Paleoproterozoic and Mesoproterozoic levels until the final increase in atmospheric O₂ concentrations to levels sufficient to oxygenate the deep ocean. Why such a delay may have occurred is not known, but various ideas include that the oxygenation of the deep ocean was caused by the rise of land plants (Lenton et al., 2016; Wallace et al., 2017), changes in internal feedbacks in global biogeochemical cycles (Alcott et al., 2019), or changes in the size of igneous O₂ sinks (Stolper et al., 2021). These ideas are generally predicated on a positive dependence on atmospheric and deep ocean O₂ concentrations. Finally, we note that there remains debate on the fidelity of some of the geochemical records used to reconstruct past marine and atmospheric O₂ (Planavsky et al., 2020; Slotznick et al., 2018, 2019; Yeung, 2017).

Given this history of deep-ocean O₂ concentrations, Stolper and Keller (2018) proposed that the Fe³⁺/ΣFe of altered submarine volcanic rocks should be lower when the deep ocean was anoxic vs. in an oxygenated deep ocean as there would be no dissolved O₂ to oxidize the igneous rocks during hydrothermal alteration. On this basis, they proposed that the Fe³⁺/ΣFe of ancient altered submarine volcanic rocks could be a proxy for deep-ocean O₂ concentrations. To explore this, they compiled Fe³⁺/ΣFe ratios of submarine volcanic rocks preserved in previously identified ophiolite sequences from the Archean to today. They found that in the Precambrian, when the deep ocean is thought to have been anoxic, Fe³⁺/ΣFe of submarine volcanic rocks are low, and similar to the average value of modern day unaltered mid-ocean ridge basalts. In contrast, in the Phanerozoic when the deep ocean is thought to have been oxygenated, Fe³⁺/ΣFe of submarine volcanic rocks are elevated. Stolper and Keller (2018) proposed that this change was due to the increase in deep-ocean O₂ concentrations between the Proterozoic and Phanerozoic (and thus consistent with the studies discussed above) that then allowed O₂ to begin flowing into the volcanic section of oceanic crust during hydrothermal alteration. This, in turn, caused the oxidation of iron in the relatively reduced igneous rocks on the ocean floor.

In that study, Stolper and Keller (2018) also examined differences in volcanic rocks from the Early Paleozoic (541-420 Ma) vs older and younger rocks. They found that volcanic rocks from the Late Paleozoic (and also the Mesozoic-Cenozoic) showed clear elevation in Fe³⁺/ΣFe vs. Precambrian equivalents. However, the volcanic rocks from the Early Paleozoic, though somewhat elevated in Fe³⁺/ΣFe, had mean Fe³⁺/ΣFe values and distributions that were not demonstrably different from the Precambrian rocks with lower Fe³⁺/ΣFe. On this basis, Stolper and Keller (2018) proposed that it was ‘probably’ not until the Late Paleozoic that O₂ concentrations reached sufficient levels to clearly oxidize volcanic rocks — i.e., there may have been a shift in the Early Paleozoic in terms of volcanic Fe³⁺/ΣFe, but it was not until the Late Paleozoic to modern that this shift is readily apparent. This was consistent with the prior work described above that indicated that the deep ocean did not become oxygenated until the Late

Paleozoic (Dahl et al., 2010; Sperling et al., 2015) and thus provided independent evidence that the deep ocean did not become oxygenated until the Late Paleozoic.

Understanding precisely when the deep ocean became oxygenated is important to a variety of problems ranging from the evolution and diversification of animals (see review in Wood et al., 2020) to changes in the composition of subducted components to the mantle and the origin of porphyry copper deposits and oxidized island-arc rocks (Evans, 2012; Richards, 2015; Stolper & Bucholz, 2019). An approach that many of the studies above have used to conclude that the deep ocean did not become oxygenated until the Late Paleozoic are based on data compilations from a variety of settings that allow one to observe changes in mean trends over time (Dahl et al., 2010; Sperling et al., 2015; Stolper & Keller, 2018; Tostevin & Mills, 2020; Wallace et al., 2017). This approach has the advantage of removing potential biases associated with the palaeoceanographic conditions and potentially later alteration that may have occurred at a specific study site and thus provide, hopefully, a better estimate of the mean state of the Earth. An alternative approach is to examine one geologic formation in detail and test whether, at the individual level, conclusions drawn from a mean trend are consistent with a specific system. This has the disadvantage that conclusions are fundamentally local. But it allows for a careful examination of systematics of a given proxy when holding the study location constant. Such a detailed study has not been done for the $\text{Fe}^{3+}/\Sigma\text{Fe}$ as a proxy for marine O_2 concentrations in the Paleozoic or in older rocks. To address this, we present $\text{Fe}^{3+}/\Sigma\text{Fe}$ of hydrothermally altered ophiolitic igneous rocks from the Early Phanerozoic (~485 Ma) Bay of Islands ophiolite to examine whether, at this time, oxidative alteration of volcanic rocks was as intense as seen in Late Paleozoic to modern rocks, more similar to the Precambrian, or intermediate. As such, this system serves as a test of whether in the Early Paleozoic deep-ocean O_2 levels were or were not sufficiently high to allow for measurable oxidation of submarine basalts during hydrothermal alteration.

2. The Bay of Islands Ophiolite

2.1 Geologic background

The Bay of Islands (BOI) ophiolite complex (Newfoundland) is a ‘Penrose’ style ophiolite with some massifs (North Arm Mountain and Blow-Me-Down Mountain) containing complete sections that include peridotites, gabbros, sheeted dykes, and volcanic rocks (Cawood & Suhr, 1992; Church & Stevens, 1971; Dewey & Casey, 2013; Williams, 1973). It is commonly used as a model for the formation and obduction of ophiolites (Cawood & Suhr, 1992), low-temperature alteration of igneous rocks (Jacobsen & Wasserburg, 1979; Parendo et al., 2017), as well as a proxy for the properties of oceanic crust (e.g., Christensen & Salisbury, 1982).

BOI igneous rocks formed in a subduction setting at ~485 Ma (Cawood & Suhr, 1992; Dewey & Casey, 2013). Assignment to a subduction setting is based on the geochemistry of the igneous rocks (Elthon, 1991; Jenner et al., 1991). The generally quoted formation age of ~485 Ma is based on U/Pb zircon ages from a trondhjemite ($486_{-1.2}^{+1.9}$ Ma; 2σ) (Dunning & Krogh, 1985) as well as 484 ± 5 Ma based on U/Pb dating of zircon and baddeleyite from a gabbro (Jenner et al., 1991). Here we follow Dewey and Casey (2013) and use an age of ~485 Ma for the formation of the igneous rocks. Yan and Casey (2020) recently revisited these ages using laser ablation inductively coupled plasma U-Pb dating of zircons from trondhjemites and derived an age of 488.3 ± 1.5 (2σ) and thus within uncertainty of prior estimates. We note that there is not a

singular age for the various igneous rocks in the ophiolite as they will have formed over millions of years when spreading was active.

The BOI igneous rocks obducted onto Laurentia during the Taconic Orogeny (Cawood & Suhr, 1992). The age of obduction is generally given as ~470 Ma and, as summarized in Cawood & Suhr (1992) and Yan and Casey (2020), is based on hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages (Dallmeyer & Williams, 1975) from the metamorphic sole and amphibolite K-Ar ages (Archibald & Farrar, 1976).

The paleolatitude of the BOI igneous rocks at the time of formation is not, to our knowledge, known. General paleogeographical constraints as follows. At the time of obduction (~470 Ma) onto Newfoundland, Newfoundland's paleolatitude (as part of Laurentia) was between 0 to 10° S with the Iapetus Ocean to the south (Swanson-Hysell & Macdonald, 2017). The various accreted terranes that form the Taconic orogeny (which includes the BOI) are derived from the collision of arcs generated in the Iapetus Ocean (and thus in the southerly direction) (Mac Niocaill et al., 1997; Swanson-Hysell & Macdonald, 2017). On this basis, we can place the likely formational location of the BOI southward of the equator and in the Iapetus Ocean.

The palaeoceanographic context of the BOI formational environment is also not well constrained. Casey et al. (1985) suggested the igneous rocks may have formed in an open-ocean setting based on the presence of radiolarian cherts interstratified in pillow basalts. However, we are unaware of any quantitative constraints on water depth or further details of the paleoenvironment.

Finally, the system is known to have experienced hydrothermal alteration by seawater down to the gabbroic section based on mineral assemblages (Williams & Malpas, 1972), presence of volcanogenic massive sulfides (Duke & Hutchinson, 1974), and the strontium (Jacobsen & Wasserburg, 1979) and potassium (Parendo et al., 2017) isotope systematics of the igneous rocks.

2.2 Samples

We measured the same samples ($n = 41$) as described in Christensen and Salisbury (1982) from the North Arm Massif of the BOI. All samples were from cored material (~2 cm in diameter and 6 cm in length) subsampled from larger hand samples taken from outcrops and stored since their original collection. Lithologies include volcanic rocks, sheeted dykes, gabbros, and serpentized peridotites that, together, span ~9 km of depth into the crust and upper mantle lithosphere (Figure 1). Samples and the basis for emplacement depth assignments are described in detail in and taken from Christensen and Salisbury (1982). Christensen and Salisbury (1982) give depths relative to the sediment-basalt contact and interpret sediments as conformably overlying the pillow basalts (as also interpreted in the original mapping of Williams, 1973; as well as the work of Malpas, 1977). In contrast, Casey and Kidd (1981) interpreted most of the overlying sediments as forming on top of an erosion surface and thus unrelated to the initial formation of the ophiolite — Casey et al. (1981) note that conformable sediments do overlie the volcanic sequence in the North Arm massif in one area. We have preserved the original depth assignments of Christensen and Salisbury (1982).

3. Methods

As samples had been in storage in air for ~40 years, exteriors were removed to eliminate any potential surface oxidation (which was not observed to be visually present). Specifically, at UC Berkeley, outer surfaces were shaved with a diamond-coated abrasion saw, then remaining cores were rinsed in flowing water and dried with compressed air. For $\text{Fe}^{3+}/\Sigma\text{Fe}$ determinations, samples were manually crushed with 5–8 taps in a tungsten carbide-lined percussion mortar and mm-sized grains collected. This was done to avoid the oxidation of iron that can occur during automated rock crushing and milling (Fitton & Gill, 1970). For major and trace element analyses, a separate split of the sample was powdered in an agate grinding vessel in a planetary ball mill at Caltech.

Fe^{2+} concentrations (as FeO) in the 41 samples were analyzed at the University of Michigan over five analytical sessions following the titration method of Wilson (1960). A subset ($n = 19$) was analyzed in duplicate or triplicate and yielded a pooled standard deviation for FeO analyses of 0.15 wt. % (1σ). Accuracy and reproducibility were verified by analyzing two US Geological Survey standards, BIR-1 and W-2a, in duplicate in each analytical session (12 and 8 replicates, respectively). The resulting averages were 8.40 (± 0.17 ; 1σ) and 8.38 (± 0.18) wt. % FeO respectively and match the certified concentration of 8.30 wt. % FeO for both standards. We note that one sample (129-Ba) exhibited a worse reproducibility than typical (standard deviation of 0.7 wt. % FeO on two replicates). This sample is a serpentinite and this elevated uncertainty does not impact any interpretations presented below.

We measured the major and trace element geochemistry of splits from the same samples measured for FeO contents at Caltech using a 4 kW Zetium Panalytical X-ray fluorescence spectrometer following the methods of Bucholz and Spencer (2019). One sample was not measured for major and trace element geochemistry at Caltech (31-116, a wehrlite from 5.9 km depth) due to insufficient sample. We additionally report major and trace element geochemistry where available on some samples made by the X-Ray Assay Laboratories at the University of Washington (though from different sample splits vs. those studied here) — these measurements were made in the 1980s as part of the initial characterization of these rocks, but were never published.

4. Results

4.1 Bay of Islands samples measured in this study

The geochemistry of the individual samples is given in Supplementary Data Set S1. We generally have calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ using the total Fe measured at Caltech. For sample 31-116, we use the University of Washington total Fe determination as this sample was not measured at Caltech for major element geochemistry (see Methods). Additionally, for three gabbroic rocks, using the Caltech major element determinations yields Fe^{2+} concentrations that are larger than the total Fe concentration. These samples contain the lowest measured total iron contents ($\leq 3\%$ as determined at Caltech). For two of these samples, XRF measurements made at the University of Washington yielded total Fe greater than Fe^{2+} and were used to calculate $\text{Fe}^{3+}/\Sigma\text{Fe}$ for these instances. However, for one sample (34-114), Fe^{2+} contents are still larger than total Fe measurements regardless of where the total Fe was measured and this sample is not discussed further.

We do not believe that these specific results, i.e. Fe^{2+} greater than total Fe, are due to analytical issues. For example, FeO determinations on USGS standards are within 0.1 wt. % of accepted values and sample FeO determinations are generally reproducible (1σ of 0.15 wt. %). Additionally total iron contents measured on different aliquots of samples in different labs ~40 years apart are in general agreement. Specifically, total Fe measured on different aliquots of hand samples at the University of Washington and Caltech differ, on average, by 0.05 wt. % Fe (with the University of Washington higher) and yield a slope of 0.88 (x =Caltech, y =University of Washington) with an uncertainty of ± 0.06 (1 s.e.) and thus within ± 2 s.e. of a slope of 1 (Figure S1). However, there is variability in total Fe determinations between labs with a standard deviation of the difference between the two of 0.76 wt. % Fe. Our interpretation of this is that these differences are real and reflect heterogeneity in total iron contents that exist on the scale of some hand samples. Based on this, we propose that we may have generated variability between the geochemistry of samples lightly crushed for Fe^{2+} analyses vs. the samples ground for XRF analyses — different aliquots were taken for these different analyses (see Methods). Such variability could create the potential for measured Fe^{2+} contents greater than the total Fe when samples have both low $\text{Fe}^{3+}/\Sigma\text{Fe}$ and have low total Fe as was the case for the three gabbroic samples discussed above.

In Figure 2 we plot the variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ as a function of depth below the sediment-basalt interface. Before examining the structure of the data vs. depth, we first compare mean values of the various lithologies. Mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the volcanic rocks is 0.29 ± 0.05 (1 s.e., $n = 9$) vs. 0.21 ± 0.02 ($n = 24$) for the intrusive rocks (i.e., dykes, amphibolites, and gabbros). The amphibolites examined here are found in the gabbroic section. They have been interpreted to have formed when seawater flowed along fractures and shear zones at this depth (Christensen & Salisbury, 1982). For the intrusive rocks more specifically: the dyke $\text{Fe}^{3+}/\Sigma\text{Fe}$ mean is 0.19 ± 0.03 (1 s.e., $n = 8$), the gabbro mean is 0.22 ± 0.03 ($n = 13$), and the amphibolite mean is 0.23 ± 0.05 ($n = 3$). Finally, the ultramafic rocks yield a mean value of 0.46 ± 0.06 (1 s.e., $n = 7$). For comparison, typical mid-ocean ridge, back-arc basin, and forearc glasses show a range of ~0.14 to 0.20 (Brounce et al., 2014, 2015; Cottrell & Kelley, 2011).

The high (>0.4) $\text{Fe}^{3+}/\Sigma\text{Fe}$ of altered ultramafic rocks is common in ophiolites (e.g., Evans, 2012) and is thought to be caused by fluid-mediated oxidative serpentinization reactions during initial hydrothermal circulation near the spreading center, during hydrothermal processes associated with obduction, and/or by meteoric alteration. This oxidation is disconnected from marine O_2 levels and occurs in anoxic fluids (e.g., Neal & Stanger, 1983; Stevens & McKinley, 2000; Bach & Edwards, 2003). As such, the high $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the ultramafic rocks is not discussed further as, based on this, their $\text{Fe}^{3+}/\Sigma\text{Fe}$ does not provide a constraint on the presence of absence of O_2 in the altering fluids.

In identifying whether ophiolite volcanic rocks were oxidized by dissolved O_2 during hydrothermal alteration on the seafloor, we consider it useful to compare such rocks to intrusive rocks from the same system as opposed to modern basalts or glasses. This is because ophiolite rocks may have experienced oxidation following hydrothermal alteration due to, for example, oxidation on Earth's surface by atmospheric O_2 or some amount of oxidation via serpentinization of the igneous minerals. We propose that looking at relative differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ between volcanic and the intrusive rocks from the same setting (and exposed at the surface today) can act

to normalize for any of this later oxidative alteration. Implicit in doing this comparison is the assumption that the intrusive sections are not strongly oxidized by O_2 during hydrothermal alteration, which appears to commonly be the case (Bach & Edwards, 2003).

At BOI, we observe a slight elevation in the average $Fe^{3+}/\Sigma Fe$ of the volcanic vs. intrusive rocks with a difference of 0.09 ± 0.06 (± 1 s.e.; with volcanic rocks elevated). This difference is not distinguishable from zero at the ± 2 s.e. level and thus it is not clear if, on average, the studied BOI volcanic rocks are meaningfully oxidized as compared to the intrusive rocks. However, the depth distribution of $Fe^{3+}/\Sigma Fe$ indicates that this difference may be meaningful. Specifically, five of the volcanic rocks have $Fe^{3+}/\Sigma Fe$ of 0.1 to 0.2 and are found in the top 320 meters and bottom 720-800 meters of the volcanic section. These values scatter around that for modern MORB (Cottrell & Kelley, 2011; Zhang et al., 2018) and, as such, we consider these samples to be relatively unaltered in terms of $Fe^{3+}/\Sigma Fe$ from the original values at crystallization. In contrast, from 390 to 650 meters depth, $Fe^{3+}/\Sigma Fe$ of the volcanic rocks range from 0.41 to 0.51 which, other than the ultramafic rocks, are the highest values in the BOI ophiolite measured here (the next highest sample is a gabbro at 0.38). As such, these samples are indicative of oxidative alteration post crystallization focused as this depth range (discussed in detail below).

We also provide in Figure 3 K_2O contents vs. depth. We use K_2O as a proxy for low-temperature alteration that is independent of the O_2 content of the deep. During low-temperature hydrothermal alteration of oceanic crust, seawater-derived potassium can be taken up in secondary minerals, increasing total K_2O concentrations over initial igneous values set at crystallization (Hart & Staudigel, 1982). For this study, it is important to know if samples have been hydrothermally altered as, if a sample displays low $Fe^{3+}/\Sigma Fe$, it could be caused either because samples were not altered by hydrothermal flow or were altered but the fluid was anoxic. As seen in Figure 3, samples from the shallow section (top 320 meters), all have elevated K_2O (0.55-0.91 wt.%) vs. mean values of various forms of mid-ocean ridge basalts (MORB) with average N-MORB=0.14%, D-MORB=0.096%, and E-MORB=0.394% and back-arc basin basalts=0.236% (Gale et al., 2013) indicating hydrothermal alteration by seawater occurred that did not cause oxidation of iron in these samples.

4.2 Bay of Islands samples measured in this study vs. presented in prior work.

As part of this work, we also compiled an additional 99 BOI $Fe^{3+}/\Sigma Fe$ measurements (24 volcanic and 75 intrusive rocks; data given in Supplementary Data Set S2) (data from Coish, 1977; Duke & Hutchinson, 1974; Malpas, 1976; Williams & Malpas, 1972). Emplacement depths for these samples are not available, but the rock types are. As such, we can compare $Fe^{3+}/\Sigma Fe$ of volcanic vs. intrusive rocks (Figure 4). Mean $Fe^{3+}/\Sigma Fe$ of intrusive rocks of the two datasets do not differ beyond ± 2 s.e.: 0.21 ± 0.02 (1 s.e., $n = 24$) as measured here vs. 0.19 ± 0.01 ($n = 75$) for the compilation. Histograms of the intrusive data (Figure 4C and D) are also similar with peak $Fe^{3+}/\Sigma Fe$ distributions between 0.1 to 0.3. Means for the volcanic rocks also do not differ at the ± 2 s.e. level — 0.29 ± 0.05 (± 1 s.e., $n = 9$) as measured here vs. 0.37 ± 0.03 ($n = 24$) in the compilation. Although the means do not differ beyond ± 2 s.e., the compiled data demonstrates an important point — the relatively oxidized samples measured here ($Fe^{3+}/\Sigma Fe > 0.3$) are not anomalous compared to other volcanic samples from the BOI. Rather, in the newly compiled data most (79%) of the volcanic rocks are similarly oxidized ($Fe^{3+}/\Sigma Fe > 0.3$) — this skew to somewhat elevated $Fe^{3+}/\Sigma Fe (> 0.3)$ is also seen in the histograms (Figure 4A and B).

5. Comparison of BOI data to other ophiolites and oceanic crust

5.1 Comparison of $Fe^{3+}/\Sigma Fe$ vs. depth for BOI with Mesozoic and Cenozoic ophiolites and drilled oceanic crust

Before interpreting the BOI results in terms of their connection to Early Paleozoic ocean chemistry, we first place these results into a wider context. In this subsection, we compare the variations in $Fe^{3+}/\Sigma Fe$ vs. depth at BOI to equivalent data from Mesozoic and Cenozoic ophiolites and drilled oceanic crust. We do this as it is generally understood that atmospheric O_2 levels were sufficiently high in the Mesozoic and Cenozoic to keep the deep ocean oxygenated (e.g., Lyons et al., 2014). As such, these systems provide a comparison point for BOI samples to a boundary condition of approximately modern concentrations of O_2 in the deep ocean — we note that we are unaware of data sets for older time frames that allow for such a comparison vs. depth, which is why only a comparison to Mesozoic and younger systems is made. Following this and in the next subsection, we compare the BOI data to compiled data from ophiolites without depth assignments but as a function of rock type (intrusive vs. extrusive) with ages going back to ~3.5 billion years.

We compare the BOI $Fe^{3+}/\Sigma Fe$ vs. depth data to equivalent data from three younger systems: the Cenozoic Macquarie Island ophiolite, the Cretaceous Troodos ophiolite, and Mesozoic to Cenozoic volcanic rocks from drilled ocean cores as well as the Site 504B drill core that sampled both volcanic rocks and sheeted dykes of 5.9 million year old oceanic crust — these systems are described in more detail below. These ophiolites and oceanic crust have $Fe^{3+}/\Sigma Fe$ that can be plotted as a function of depth below the sediment-basalt contact. In doing this comparison, we only include and discuss in this subsection BOI samples measured in this study as work from other studies do not have known depths. These comparisons are made in Figure 5 and depth is provided both on a linear and logarithmic scale. We do not include ultramafic rocks in this comparison. In all cases, we lump rocks from the transition zone where pillows and sheeted dykes co-occur (i.e., between the base of the volcanic section and top of the sheeted dyke complex) with rocks from the sheeted dyke complex for simplicity.

We first compare the BOI to the Macquarie Island ophiolite (Figure 5A and B). The Macquarie Island ophiolite is ~10 million years old and is considered to represent obducted oceanic crust formed at a mid-ocean ridge (as opposed to a subduction zone setting as is the case for BOI) (Varne et al., 2000). Based on major and trace element geochemistry as well as $^{87}Sr/^{86}Sr$ and $\delta^{18}O$, the system was hydrothermally altered by seawater through to the gabbroic layer (Coggon, 2006; Coggon et al., 2016). $Fe^{3+}/\Sigma Fe$ data for the Macquarie Island ophiolite are taken from Rutter (2015). $Fe^{3+}/\Sigma Fe$ of intrusive rocks from both ophiolites overlap within ± 2 s.e.— 0.21 ± 0.02 (1 s.e., $n = 24$) for BOI vs. 0.19 ± 0.01 ($n = 22$) for Macquarie Island. In contrast, the mean BOI volcanic rocks are lower in $Fe^{3+}/\Sigma Fe$ as compared to those at Macquarie Island and do not overlap at the ± 2 s.e. level: 0.29 ± 0.05 (1 s.e., $n = 9$) for BOI vs. 0.47 ± 0.03 ($n = 15$) for Macquarie Island. These values yield calculated mean differences in $Fe^{3+}/\Sigma Fe$ for volcanic vs. intrusive sections at Macquarie Island of 0.28 ± 0.03 (1 s.e.) as compared to 0.09 ± 0.06 at BOI. As such, although the two intrusive sections are similar in $Fe^{3+}/\Sigma Fe$, the Macquarie Island volcanic rocks are, on average, significantly more oxidized than those from BOI as measured here.

The BOI and Macquarie Island ophiolites also differ in how $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the volcanic section varies as a function of depth. Specifically, all volcanic rocks at Macquarie Island over the top 800 meters have elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ (>0.37) — only the deepest measured Macquarie Island volcanic rock (850 m) has a lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ (0.25). In contrast, as discussed above, BOI volcanic rocks do not show a uniform elevation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs. the intrusive section, but instead the oxidation is concentrated in the middle of the volcanic section.

We next compare our BOI data to the Troodos ophiolite (Figure 5C and D). The Troodos ophiolite is Cretaceous in age (~90 Ma) and formed in a suprasubduction zone setting (Osozawa et al., 2012) and is thus comparable in formational setting to the BOI. Measurements are derived from the reports of the Cyprus Crustal Study Project (Gibson et al., 1989, 1991; Robinson et al., 1987). Unlike the Macquarie Island ophiolite, the intrusive mafic rocks from Troodos are elevated in $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to those from BOI: 0.34 ± 0.01 (1 s.e., $n = 218$) at Troodos vs. 0.21 ± 0.02 ($n = 24$) at BOI. This difference is dominantly due to more oxidation in the sheeted dyke complex at Troodos, which yields a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.36 ± 0.01 (1 s.e., $n = 188$) vs. 0.23 ± 0.01 ($n = 30$) for the gabbros. This indicates that at Troodos as compared to both BOI and Macquarie Island, oxidizing fluids penetrated to depths greater than 1 km and that oxidation can occur at depths below the volcanic section. This oxidation could be due to O_2 reaching this section or, alternatively, as the sheeted dyke complex is generally altered at elevated temperatures ($>200^\circ\text{C}$; e.g., Alt et al., 1996), could be due the oxidation of iron by sulfate, which is known to occur (based on experiments) at temperatures above 200°C (Shanks III et al., 1981).

Troodos volcanic rocks are significantly more oxidized than Troodos intrusive rocks and are more oxidized than volcanic and intrusive rocks from BOI (as visually apparent in Figure 5C and D). Specifically, volcanic rocks from Troodos have an average $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.62 ± 0.01 (1 s.e., $n = 277$) vs. 0.29 ± 0.05 ($n = 9$) from BOI. Differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ at Troodos vs. BOI for volcanic vs. intrusive rocks are 0.28 ± 0.01 vs. 0.09 ± 0.06 respectively. The difference of 0.28 at Troodos is the same as that at Macquarie Island.

The differences at Troodos vs. BOI are also apparent in examinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs. depth. At Troodos, $\text{Fe}^{3+}/\Sigma\text{Fe}$ decreases with increasing depth in the volcanic section. This change is likely caused by hydrothermal fluids being able to more easily penetrate the top of the volcanic section (and thus see fluid flow for longer) than deeper sections due to differences in porosity and permeability as well as access to fresh seawater (Coogan & Gillis, 2018). The volcanic rocks from the top 320 meters of the BOI are visually lower in $\text{Fe}^{3+}/\Sigma\text{Fe}$ than equivalent depths at Troodos, but the more oxidized Bay of Island volcanic rocks at depths of 390-650 meters are similar to those at Troodos at an equivalent depth (Figure 5C and D).

Finally in Figure 5E and F, we compare our BOI data to volcanic rocks from various Deep Sea Drilling Project (and later iterations) drill cores of oceanic crust. Data are the same as those compiled in Stolper and Keller (2018) ($n = 1121$ — note 30 samples from Stolper and Keller (2018) were not included as we could not calculate depths in terms of depth to sediment-basalt interface). We also include data from Site 504B, which is from Alt et al. (1996). The compiled data given in Stolper and Keller (2018) are only from oceanic crust older than 10 million years. This age cutoff was used to ensure most of the alteration that would occur on the seafloor had occurred in samples — previous work indicates that it takes at least 10 million years for most of

the oxidation of the volcanic section to occur (Bach & Edwards, 2003; Johnson & Semyan, 1994). Igneous rocks from Site 504B are only 6 million years old. As such, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the volcanic rocks may represent a minimum value as oxidative alteration may not yet be finished — for example, Alt et al. (1996) note that hydrothermal flow through the volcanic section is still occurring. However, we include this system for comparison as it also has measurements of intrusive rocks.

The mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of cored >10 million year old marine volcanic rocks (as calculated in Stolper and Keller (2018)) is 0.41 (± 0.01 , 1 s.e.), which is elevated but within ± 2 s.e. of the BOI volcanic samples. As discussed in Stolper and Keller (2018), the oceanic crust values are potentially biased due to incomplete recovery of the altered igneous rocks from cores. Corrections that take these potential sampling issues into account arrive at a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the volcanic section of oceanic crust of 0.56 (Staudigel et al., 1996) and thus similar to the values seen for the volcanic section at Macquarie Island (0.47) and Troodos (0.62). Based on this, we interpret the BOI volcanic $\text{Fe}^{3+}/\Sigma\text{Fe}$ to be lower than that of modern cored altered oceanic crust. This difference is also seen in the depth distribution. The three BOI volcanic rocks from the top 320 meters of section are low in $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to typical Mesozoic and Cenozoic volcanic rocks from oceanic crust. However, the more oxidized volcanic rocks from BOI (390–650 meters depth) overlap with oceanic volcanic rocks recovered from that depth range. We note that the cored samples compiled in Stolper and Keller (2018) are from systems where cores did not recover intrusive rocks and so a comparison to such rocks cannot be made.

Finally, Site 504B volcanic rocks yield a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.35 ± 0.006 (1 s.e., $n = 157$) vs. 0.24 ± 0.003 ($n = 261$) in the intrusive section, equivalent to a difference of 0.11 ± 0.01 (1 s.e.). These rocks are thus more similar in $\text{Fe}^{3+}/\Sigma\text{Fe}$ to values we measured at BOI (0.29 for the volcanic rocks and 0.21 for the intrusive rocks with a difference of 0.09). However, as noted above, this system is sufficiently young that, if left for longer on the seafloor, $\text{Fe}^{3+}/\Sigma\text{Fe}$ of volcanic rocks would likely increase. Regardless, as was the case for the other ophiolites and drill cores, BOI volcanic rocks from the top 320 meters are still not as oxidized as the site 504B volcanic rocks from a similar depth range, despite the latter likely not having seen its potential full integrated history of oxidative alteration by low-temperature fluids.

5.2 Bay of Islands vs. ophiolites from the past 3.5 billion years

Here we compare the measured and compiled BOI data to a compilation of both extrusive and intrusive igneous rocks from other ophiolites formed over the past 3.5 billion years of Earth history. For the volcanic rocks, we use the already compiled data from Stolper and Keller (2018) and also include the Macquarie Island data and newly measured and compiled BOI data (which were not included in that work). This compilation did not include intrusive data and so, to address this, we newly compiled for this study intrusive data from the same ophiolites as those in Stolper and Keller (2018) (when intrusive data was available) and Macquarie Island.

Specifically, we compiled 700 measurements of intrusive rocks from 36 localities (see Supplementary Data Set S3) (724 points when the newly measured BOI data are included) — note that 73 ophiolites were included in the compilation of Stolper and Keller (2018), but not all had data for intrusive rocks.

To make this comparison, we bin data into the following time periods: the Precambrian (>541 Ma), Early Paleozoic (541-420 Ma), and Late Paleozoic-modern (<420 Ma). We note that in Stolper and Keller (2018) the Precambrian was further subdivided into time periods for the Archean, Paleo-Mesoproterozoic, and Neoproterozoic. They found no statistical differences between the various subdivisions for the Precambrian for volcanic rocks. As such we combine them into one period. We additionally combine the Late Paleozoic (420-252 Ma) with the Mesozoic-Cenozoic (<252 Ma). These were also treated as separate in Stolper and Keller (2018) and did show differences in both mean and distributions $\text{Fe}^{3+}/\Sigma\text{Fe}$. We make these combinations as we are interested in differences between Early Paleozoic systems (like the BOI) vs. older and younger rocks.

Histograms of $\text{Fe}^{3+}/\Sigma\text{Fe}$ are presented in Figure 6. We first calculate mean values for the different age ranges. To do this, we followed the approach of Stolper and Keller (2018) and calculate the mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of rocks of a specific type (volcanic or intrusive) from a given ophiolite and take the average of those means (only using ophiolites with at least 2 samples). This is done in order to avoid excess weighting of systems with more extensive sampling. Additionally, for the Late Paleozoic-modern systems, the Troodos ophiolite represents a significant amount of the compiled data (68% of the intrusive and 52% of the volcanic rocks). We show in Figure S2 that the volcanic and intrusive distributions for Troodos are similar to the equivalent distributions for the Late Paleozoic-modern without Troodos and thus that inclusion of the Troodos data does not obviously bias the shape of the histograms.

Although the focus here is on the BOI, we begin this comparison by looking at the Precambrian vs. Late Paleozoic-Mesozoic in order to establish what the endmembers look like in a world generally thought to have had anoxic deep oceans (the Precambrian) vs. a world thought to have oxygenated deep oceans (the Late Paleozoic-modern). Once we establish the differences between these systems (or lack thereof), we compare them to the BOI.

For the Precambrian, locality $\text{Fe}^{3+}/\Sigma\text{Fe}$ averages of the volcanic and intrusive rocks are 0.23 ± 0.01 (± 1 s.e., $n = 42$) and $0.22 (\pm 0.03, n = 14)$ respectively — note here n is the number of ophiolites. Thus, Precambrian intrusive and volcanic rocks are indistinguishable in terms of mean $\text{Fe}^{3+}/\Sigma\text{Fe}$. This overlap is also apparent in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ distributions (Figure 6A and B) with peak values for both being between 0.1 to 0.3. The Precambrian contrasts with the Late Paleozoic to modern ophiolites where volcanic rocks yield a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.53 ± 0.04 (± 1 s.e., $n = 16$) vs. 0.33 ± 0.04 ($n = 8$) for the intrusive rocks. Thus, unlike in the Precambrian, volcanic rocks from ophiolites are significantly (beyond ± 2 s.e.) more oxidized than the deeper crustal sections. These differences are also seen in the histograms (Figure 6G and H) in which the volcanic rocks are skewed to higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ than the intrusive rocks and show a bimodal distribution. We interpret this bimodal distribution as follows: during oxidizing hydrothermal alteration, igneous rocks that are altered are generally moved from low $\text{Fe}^{3+}/\Sigma\text{Fe}$ (≈ 0.15) to high $\text{Fe}^{3+}/\Sigma\text{Fe}$ (>0.5) whereas those that are not altered are left with their original values. This can be understood as the result fluid flow through fracture systems in the volcanic section. Such unevenly distributed flow allows alteration to go to completion in the vicinity of the fracture (in this case oxidative alteration) but leaves distant mineral assemblages unaltered (Coogan & Gillis, 2018).

The elevation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ of Late Paleozoic to modern volcanic ophiolitic rocks vs. Precambrian equivalents was demonstrated in Stolper and Keller (2018) and interpreted to be due to the oxygenation of the deep ocean in the Phanerozoic, which then allowed for the delivery of O_2 to these rocks during low-temperature hydrothermal alteration. The addition of the intrusive rocks supports this interpretation. In the Precambrian no differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ between intrusive and extrusive rocks exist (and $\text{Fe}^{3+}/\Sigma\text{Fe}$ are low) while following 420 Ma $\text{Fe}^{3+}/\Sigma\text{Fe}$ of volcanic rocks is elevated vs. intrusive rocks and shows a different distribution. That the Phanerozoic intrusive rocks are relatively less oxidized can be understood by the fact that the volcanic rocks see far more fluid (~100 to 1000x) than deeper intrusive rocks (Coogan & Gillis, 2018; Elderfield & Schultz, 1996) and thus volcanic rocks will see a larger integrated flux of O_2 (if present in seawater) during their history on the seafloor. Although the intrusive rocks from <420 Ma are more oxidized on average than the Precambrian equivalents (0.33 ± 0.04 vs. 0.22 ± 0.03 , 1 s.e.) these differences overlap at the ± 2 s.e. level. However, the elevation $\text{Fe}^{3+}/\Sigma\text{Fe}$ between the Precambrian and <420 Ma rocks (Figure 6B vs. H) may also relate to changes in ocean chemistry. For example, such an elevation in Phanerozoic intrusive rocks could be due to the oxygenation of the deep ocean at this time if some dissolved O_2 reaches the intrusive rocks during hydrothermal alteration. Alternatively, such an increase may be related to changes in marine sulfate concentrations. Specifically, as discussed for the Troodos ophiolite, sulfate can oxidize iron at elevated ($>200^\circ\text{C}$) temperatures (Shanks III et al., 1981) – such temperatures characterize the hydrothermal alteration of intrusive rocks from oceanic crust. Marine sulfate concentrations have been proposed to have increased at the end of the Neoproterozoic (Algeo et al., 2015; Blättler et al., 2020; Kah et al., 2004) and, as such, this sulfate may have caused the oxidation of the deeper crustal sections in the Phanerozoic. Regardless, the intrusive data compiled here support the hypothesis of Stolper and Keller (2018) that significant increases in deep ocean O_2 concentrations from the Precambrian to Late Paleozoic changed the amount of oxidation occurring in the volcanic section while, as shown here, left the intrusive sections less disturbed in terms of the redox state of iron.

With the characteristics of these endmembers established, we now compare the Early Paleozoic data to them. We begin by examining all of the compiled and measured Late Paleozoic data before turning to the BOI specifically. The compilation of the Early Paleozoic (541 to 420 Ma) rocks (which includes BOI samples) yields a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the volcanic rocks of 0.33 ± 0.03 (1 s.e., $n = 15$) vs. 0.30 ± 0.04 ($n = 11$) for the intrusive rocks. Thus, the two do not differ at the ± 2 s.e. level. Additionally, the Early Paleozoic intrusive rocks do not differ from the Precambrian equivalents beyond 2 s.e. while the volcanic rocks do and are elevated in $\text{Fe}^{3+}/\Sigma\text{Fe}$ (0.33) vs. the Precambrian (0.23). However, these differences in terms of the means are subtle. This is seen in the histograms where, for the intrusive rocks, the Precambrian and Early Paleozoic rocks are similar (peak in distributions of 0.2 to 0.3), while for the volcanic rocks, the Early Paleozoic rocks show a slight skew towards higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ (peak distribution of 0.3 to 0.4 vs 0.2 to 0.3 in the Precambrian). The Early Paleozoic volcanic rocks do not show the bimodal distributions in $\text{Fe}^{3+}/\Sigma\text{Fe}$ seen in the more recent ophiolites. Thus, the Early Paleozoic $\text{Fe}^{3+}/\Sigma\text{Fe}$ distribution for volcanic rocks differs from the Late Paleozoic and younger rocks in two ways: (1) $\text{Fe}^{3+}/\Sigma\text{Fe}$ of Early Paleozoic volcanic rocks are typically lower than Late Paleozoic and younger rocks; And (2) the Early Paleozoic volcanic rocks do not show the bimodality in $\text{Fe}^{3+}/\Sigma\text{Fe}$ seen in in the Late Paleozoic and younger rocks.

Unlike for the compilation that includes all ophiolites, the Early Paleozoic BOI volcanic and intrusive rocks are, on average, measurably different in $\text{Fe}^{3+}/\Sigma\text{Fe}$: 0.35 ± 0.02 (± 1 s.e., $n = 33$) vs. 0.19 ± 0.01 ($n = 99$). The volcanic value is indistinguishable at ± 2 s.e., from the mean Early Paleozoic rocks for all ophiolites examined (0.33 ± 0.02), while the intrusive rocks are lower (0.19 ± 0.01 vs. 0.30 ± 0.04) and more similar to the Precambrian values (0.22 ± 0.03). The histograms also show this difference with BOI volcanic rocks $\text{Fe}^{3+}/\Sigma\text{Fe}$ skewed to higher values (most >0.3) compared to the intrusive rocks and the compilation of Early Paleozoic and Precambrian values. However, this oxidation is significantly less both in mean and peak distribution compared to the Late Paleozoic-modern examples. For example, in Late Paleozoic-modern ophiolites, most volcanic $\text{Fe}^{3+}/\Sigma\text{Fe}$ are >0.6 (53% of the data), whereas such elevated values are rare for BOI (3% of the data). This indicates that for BOI: (1) oxidation in the volcanic rocks does seem to have occurred preferentially relative to the intrusive section; But (2) the oxidation in the volcanic rocks occurred to less of an extent as is generally seen in the Late Paleozoic-modern systems.

6. Discussion

6.1 Bay of Islands $\text{Fe}^{3+}/\Sigma\text{Fe}$

The question motivating this study is whether or not the hydrothermal alteration of BOI igneous rocks was associated with oxidative alteration by O_2 and if so, to what degree. Based on the results described above, BOI samples show some degree of elevation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the volcanic rocks vs. the intrusive sections — when all BOI data are combined (measured here and compiled), we observe that the mean Paleozoic BOI volcanic and intrusive rocks are, on average, measurably different in $\text{Fe}^{3+}/\Sigma\text{Fe}$: 0.35 ± 0.02 (± 1 s.e., $n = 33$) vs. 0.19 ± 0.01 ($n = 99$). These values are elevated compared to Precambrian volcanic and intrusive rock $\text{Fe}^{3+}/\Sigma\text{Fe}$ averages: 0.23 ± 0.01 (± 1 s.e., $n = 42$) and 0.22 (± 0.03 , $n = 14$). But they are lower than values seen in the Late Paleozoic to modern, with a mean for volcanic rocks of 0.53 ± 0.04 (± 1 s.e., $n = 16$) vs. 0.33 ± 0.04 ($n = 8$) for the intrusive rocks.

Thus, as compared to the Precambrian, the BOI volcanic samples are somewhat oxidized, but both share similar values for the intrusive sections. We propose that this elevated oxidation in the BOI volcanic section is not due to later metamorphism (e.g., during obduction) or during subaerial exposure, but instead occurred while in place on the seafloor by oxidizing hydrothermal fluids. Our basis in stating this is that we would expect that if such later oxidation had occurred, it would have affected the volcanic rocks and intrusive rocks equally as opposed to being concentrated in the extrusive rocks. As such, we propose that the volcanic rocks show evidence for some degree of oxidation by O_2 during seawater alteration and thus provide evidence for the presence of O_2 in the water masses that fed the hydrothermal systems in the BOI formational environment.

We note that this differs from the proposal of Stolper and Keller (2018). Specifically, they proposed that it was ‘probably’ not until the Late Paleozoic that O_2 concentrations reached sufficient levels to clearly oxidize volcanic rocks — i.e., there may be a shift in the Early Paleozoic in terms of volcanic $\text{Fe}^{3+}/\Sigma\text{Fe}$, but it is not until the Late Paleozoic-Modern that this shift is readily apparent. This proposal was based on the general similarity of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the Early Paleozoic and Precambrian volcanic rocks and differences between Early Paleozoic and younger rocks (Figure 6).

If our interpretation of the BOI dataset is correct, it would indicate that this prior interpretation based on the compiled data, though apparently supported when looking at time-bin averages, is not the complete story. Instead, by focusing on a specific location, at least for this specific system, O₂ was present in the source waters feeding the hydrothermal systems in the Late Paleozoic.

However, it also appears that these O₂ levels were less than what was typical in ophiolites from the Late Paleozoic to today. This is observed both in the mean values discussed above and in the depth distributions of Fe³⁺/ΣFe. Specifically, the comparison of the BOI data measured as a function depth vs. the Troodos and Macquarie Island as well as drilled oceanic crust indicates that the BOI samples do not show the same degree of iron oxidation as these younger systems (Figure 5). Volcanic rocks from above 320 meters and below 720 meters have Fe³⁺/ΣFe of 0.1 to 0.2 and thus scatter around the values expected for modern MORB. We can rule out for the shallowest samples (<320 m) that no hydrothermal alteration occurred as these samples have elevated K₂O contents, which is indicative of low-temperature hydrothermal alteration (Figure 3). As such, for these samples, we interpret that the lower Fe³⁺/ΣFe are due to alteration in fluids that contained less O₂ as compared to younger ophiolites. Although K₂O levels are generally within the range expected for unaltered igneous rocks below this depth (320 m), both potassium isotopes (Parengo et al., 2017) and strontium isotopes (Jacobsen & Wasserburg, 1979) indicate that hydrothermal alteration of seawater occurred down to the gabbroic section — note that these studies were on rocks from the Blow-Me-Down Massif (as opposed to the North Arm Mountain massif studied here). Regardless, we expect that hydrothermal fluids penetrated to the gabbros for the samples measured here as well. Additionally, we note that the volcanic samples with elevated Fe³⁺/ΣFe (>0.4) do not show enhancements in K₂O content (<0.25 wt. %) indicating that oxidation of these rocks did not co-occur with extensive potassium uptake. This is not unusual in modern marine hydrothermal systems: in a cross plot of Fe³⁺/ΣFe vs. K₂O, the volcanic rocks at BOI with elevated Fe³⁺/ΣFe but low K₂O contents overlap data for volcanic rocks from Site 504B, Troodos, and other BOI samples (Figure S3).

In contrast the samples from 390 to 650 meters depth yield elevated Fe³⁺/ΣFe: 0.41 to 0.51. We interpret the grouping of elevated volcanic Fe³⁺/ΣFe over 250 meters of depth to indicate that the flow of oxidizing fluids was focused over this depth interval, whereas fluids that flowed above and below this section were not sufficiently oxidizing to measurably increase volcanic Fe³⁺/ΣFe. Put another way, we propose that fluids that altered the measured volcanic rocks above 390 meters and below 650 meters were anoxic while those between 390-650 meters contained some dissolved O₂ during low temperature alteration that oxidized the iron.

A question is why, if this interpretation is correct, is the oxidation apparently focused in the middle of the volcanic section as opposed to throughout or the top of the section which, in general, sees more fluid flow than deeper sections (Coogan & Gillis, 2018)? We propose the following explanation: during hydrothermal flow through the volcanic section, water enters and exits the system at different points and flows along fractures. As that water flows, O₂ dissolved in the water can react with and oxidize igneous minerals adjacent to the fracture. However, if all of the O₂ in fluid is consumed before it exits the hydrothermal system back to the ocean, rocks altered at the end of the flow path will instead react in anoxic fluids and thus not become

oxidized, despite being hydrothermally altered. Thus it is the combination of the integrated water flux, concentration of O₂ in the starting fluid, and proximity to the inlet of seawater to the volcanic aquifer that controls the amount of oxidation at a given position in the volcanic section. An explanation for the observed oxidation in the mid-depth volcanic section samples is that they happened to have been closer to a fluid entrance point into the volcanic aquifers vs. the other samples and thus, during alteration, the fluid still had O₂ present vs. the other samples that were altered in fluids that had gone anoxic earlier in the flow path. This is consistent with the oxidized samples (4, 5, 6, and 7 in Figure 1), all being collected in the same vicinity.

Based on the above discussion, we propose that the BOI volcanic section did experience alteration in oxidizing conditions and that this was done by O₂ dissolved in seawater. This is distinct from the Precambrian equivalents that do not show evidence for this. However, the degree of oxidation appears less than what is typical in volcanic rocks from the Late Paleozoic to modern indicating that O₂ concentrations were, on average, lower in the seawater that fed the hydrothermal systems of the BOI as compared to typical Late Paleozoic and younger equivalents.

6.2 Implications of the Bay of Islands for Early Paleozoic deep-ocean O₂ concentrations

Based on the above discussion, we interpret the Fe³⁺/ΣFe of the BOI to indicate that the seawater that altered the BOI volcanic rocks contained some dissolved O₂, but that this concentration was lower than calculated previously for Mesozoic and Cenozoic O₂ concentrations. The question we take up here is what bearing this has on the history of deep-ocean O₂ concentrations.

Our discussion of the history of deep-ocean O₂ above has implicitly followed a simplifying conceptual framework introduced by others (e.g., Canfield, 1998; Laakso & Schrag, 2014; Lyons et al., 2014; Sarmiento et al., 1988) in which the ocean is effectively separated into various boxes that includes, at a minimum, (i) a shallow box in contact with the atmosphere with O₂ concentrations in equilibrium with atmospheric O₂ and (ii) a deeper box that is not in contact with the atmosphere and whose O₂ is set by the downwelling water from the shallower box(es) into the deep box and the amount of respiration in the deep ocean box. In this framework, there is effectively one deep-ocean O₂ concentration. However, in the modern world, O₂ concentrations vary both in and between ocean basins as a function of water mass age, source region, and overlying productivity. For example, deep water (>2000 m) in the Atlantic vs. the Pacific can differ by ~100 μmol/kg seawater as compared to the average deep-ocean O₂ concentration of ~180 μmol/kg seawater (Sarmiento & Gruber, 2006). Additionally, marine water masses can go anoxic at some depths (so-called oxygen minimum zones). We raise this because, ultimately, the O₂ concentrations in the water masses that fed the hydrothermal systems of the BOI igneous rocks are fundamentally local and likely different from any hypothetical mean deep ocean O₂ concentration that existed at this time.

As discussed in Section 2, the BOI igneous rocks formed in the Iapetus Ocean. Although palaeoceanographic constraints are limited, based on sediments intercalated in the pillow basalts (radiolarian cherts), the formational environment appears to have been a deep-water open-ocean setting. The lack of terrigenous sediment also indicates formation in an open ocean setting. Typical water depths for modern mid-ocean ridges are generally >2000 meters. Similar water depths are observed for spreading systems associated with subduction-zone settings such as

back-arc basins (e.g., Taylor & Martinez, 2003). Today, these depths are below typical modern oxygen minimum zone depths and are at depths typically taken to represent deep water masses sourced from high latitudes that represent the majority of the ocean's volume (Sarmiento & Gruber, 2006). Given this, we assume that the source of fluids to the BOI hydrothermal systems was below the wind mixed layer and likely below any potential local oxygen minimum zones. On this basis, we assume the fluid sources approximate average deep-ocean water chemistry in the Iapetus Ocean.

As such, we propose that some deep-water masses in the Early Paleozoic did have sufficient O₂ (order tens of micromoles/kg seawater) to cause some oxidation of basalts during hydrothermal circulation. However, this oxygen concentration was less than that of the Later Paleozoic, Mesozoic, and Cenozoic. A question is if this condition was common throughout the Early Paleozoic both in time and space? The BOI data cannot answer this as it is in a specific location. However, in looking at the data available for Early Paleozoic rocks, the BOI does not stand out as particularly distinct. Its mean value for the Fe³⁺/ΣFe of the volcanic rocks (0.35) is similar to the mean for all 15 localities (0.33), which span an age range of 530 to 440 million years old. Additionally, the histograms indicate that although the Late Paleozoic volcanic rocks show some small degree of iron oxidation compared to Precambrian equivalents, higher degrees of oxidation do not occur until after the Late Paleozoic.

On this basis, we propose that in the Early Paleozoic (~485 million years ago) there were moderate amounts of O₂ in the deep ocean, but at concentrations significantly lower than found today. This oxygen was able to oxidize portions of the volcanic section of the BOI ophiolite, but not to the levels seen after the Late Paleozoic and that it was not until this later time frame that deep-ocean O₂ concentrations were sufficient for clear and significant oxidation of marine volcanic rocks during low-temperature hydrothermal alteration. An explanation for these changes is that any increases in O₂ concentrations that did occur in the late Neoproterozoic to Early Paleozoic above previously lower values in the Proterozoic were insufficient to oxygenate the deep ocean to modern levels and were then followed by an additional increase in O₂ levels to near modern levels in the Late Paleozoic. This interpretation is broadly consistent with a variety of recent studies of the evolution of atmospheric and marine O₂ concentrations from the Proterozoic to Phanerozoic (see review in Tostevin & Mills, 2020). However, other explanations including changes in O₂ solubility (due to temperature changes), ocean circulation, and biological productivity are also possible as these also control deep-ocean oxygen concentrations.

Finally, the calculated O₂ concentrations in the deep ocean based on the BOI volcanic vs. intrusive data are sufficiently low that small changes in either atmospheric O₂ concentrations or oceanographic conditions (e.g., solubility of O₂ due to temperature changes, circulation changes, and/or the strength of the biological pump) could have driven parts of the ocean to anoxia more readily than can occur today. Such could allow for more oscillations in the redox chemistry of the deep ocean in time and space. This supports the proposal for variable O₂ contents of Paleozoic marine waters with swings towards higher and lower O₂ concentration over relatively short time periods (e.g., order millions of years), sometimes termed ocean oxygenation events (e.g., Kendall et al., 2015; Reinhard & Planavsky, 2022; Sahoo et al., 2016; Tostevin & Mills, 2020). Such oscillations would also explain why, when all Early Paleozoic Fe³⁺/ΣFe of volcanic rocks from ophiolites are combined into one bin, they are not as obviously oxidized vs. their

Precambrian counterparts as compared to Late Paleozoic and younger rocks. This may be because some are indeed not oxidized – i.e., they formed in a region of the ocean or time in the Early Paleozoic when the deep ocean was anoxic – while others formed and were altered by waters with finite but low O₂ concentrations (<50 μmol O₂/kg seawater). This could be tested by conducting a similar study as this on a range of Early Paleozoic ophiolites looking at Fe³⁺/ΣFe of both intrusive and extrusive rocks.

7. Summary and Conclusions

This study shows that for the Bay of Islands ophiolite, Fe³⁺/ΣFe values of the volcanic section are elevated compared to Precambrian ophiolites, but lower than those of the Late Paleozoic to modern. The Bay of Islands intrusive section does not show this elevation. These differences are seen both via comparisons of Fe³⁺/ΣFe as a function of depth in the Bay of Islands vs. Mesozoic and Cenozoic Ophiolites and oceanic crust as well as in a comparison to a larger data compilation of Fe³⁺/ΣFe values for volcanic and intrusive rocks from ophiolites ranging in age from the Archean to Cenozoic. Based on this, we propose that the Bay of Islands volcanic section was altered at low temperatures in fluids that contained some, but lower (~2.4×) O₂ concentrations as compared to today. Thus, the Early Paleozoic, at least at the time of the Bay of Islands formation (485 Ma), was a time of low, but not negligible oxygen concentrations in the deep ocean. These O₂ concentrations may have been sufficiently low to allow for the deep ocean to be spatially heterogenous in terms of O₂ concentration (e.g., anoxic in some places but oxic in others) as well as to oscillate between oxygenated and anoxic conditions on relatively short geologic timescales (e.g., order millions of years). The data also support previous work that proposed that it was not until the Late Paleozoic (~420 Ma) that the deep ocean appears to have become persistently oxygenated.

Acknowledgements: DAS acknowledges support from an Esper Larsen Jr. Research Grant. MKL acknowledges support from the Agouron Institute Geobiology Postdoctoral Fellowship. XP and RAL acknowledge support from University of Michigan discretionary research funds. DAS thanks N Swanson-Hysell for helpful discussions on the paleogeography of Early Paleozoic landmasses.

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Data Availability Statement: The newly produced and compiled data for this paper are contained in the text, figures and Supporting Information and are also archived externally at <https://doi.org/10.5281/zenodo.6262559>. Data associated with Stolper and Keller (2018) are available from <https://doi.org/10.1038/nature25009>.

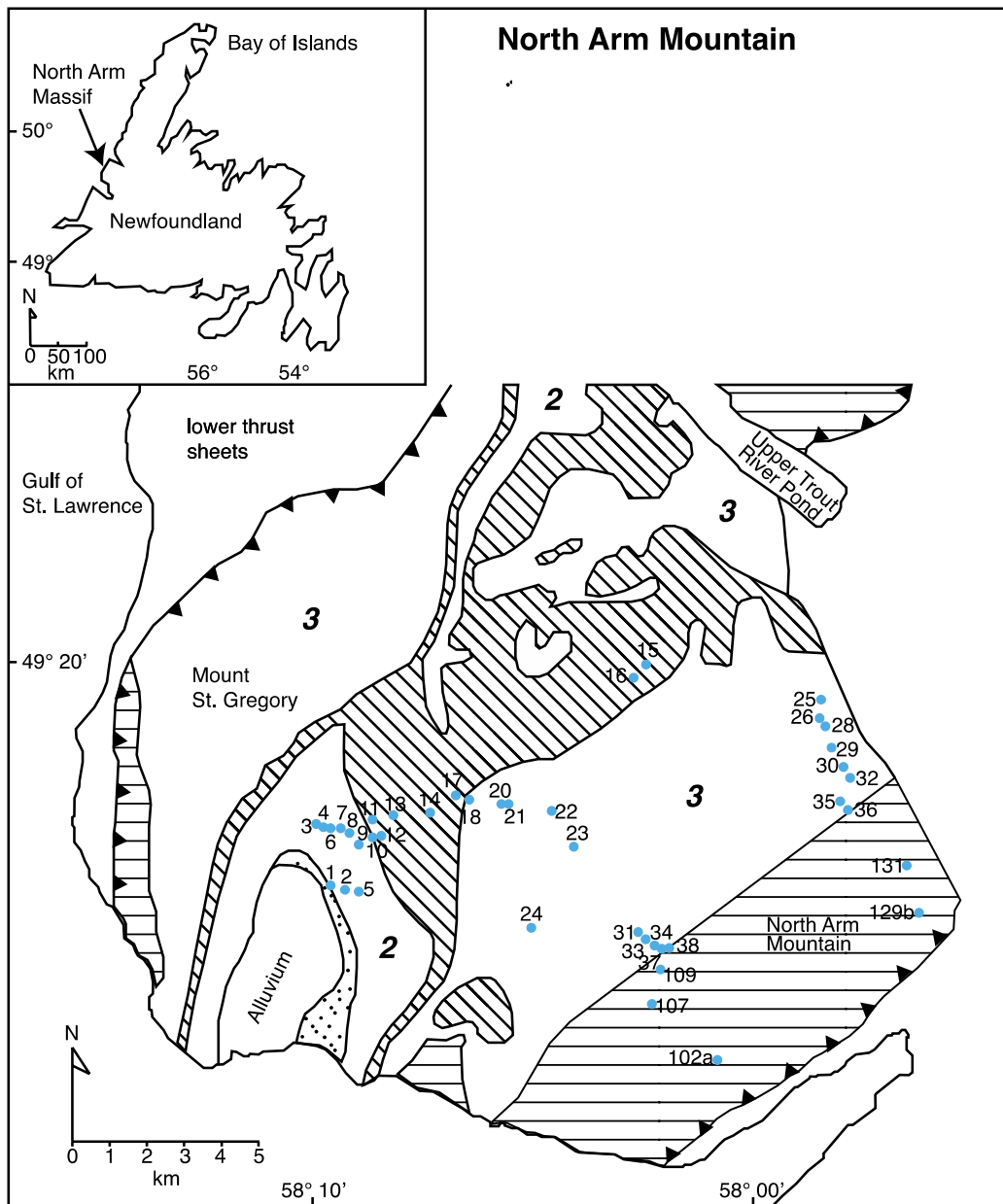


Figure 1. Map of the North Arm Massif of the Bay of Islands ophiolite. Blue circles are the samples measured here as originally described in Christensen and Salisbury (1982) and the map is modified from that study.

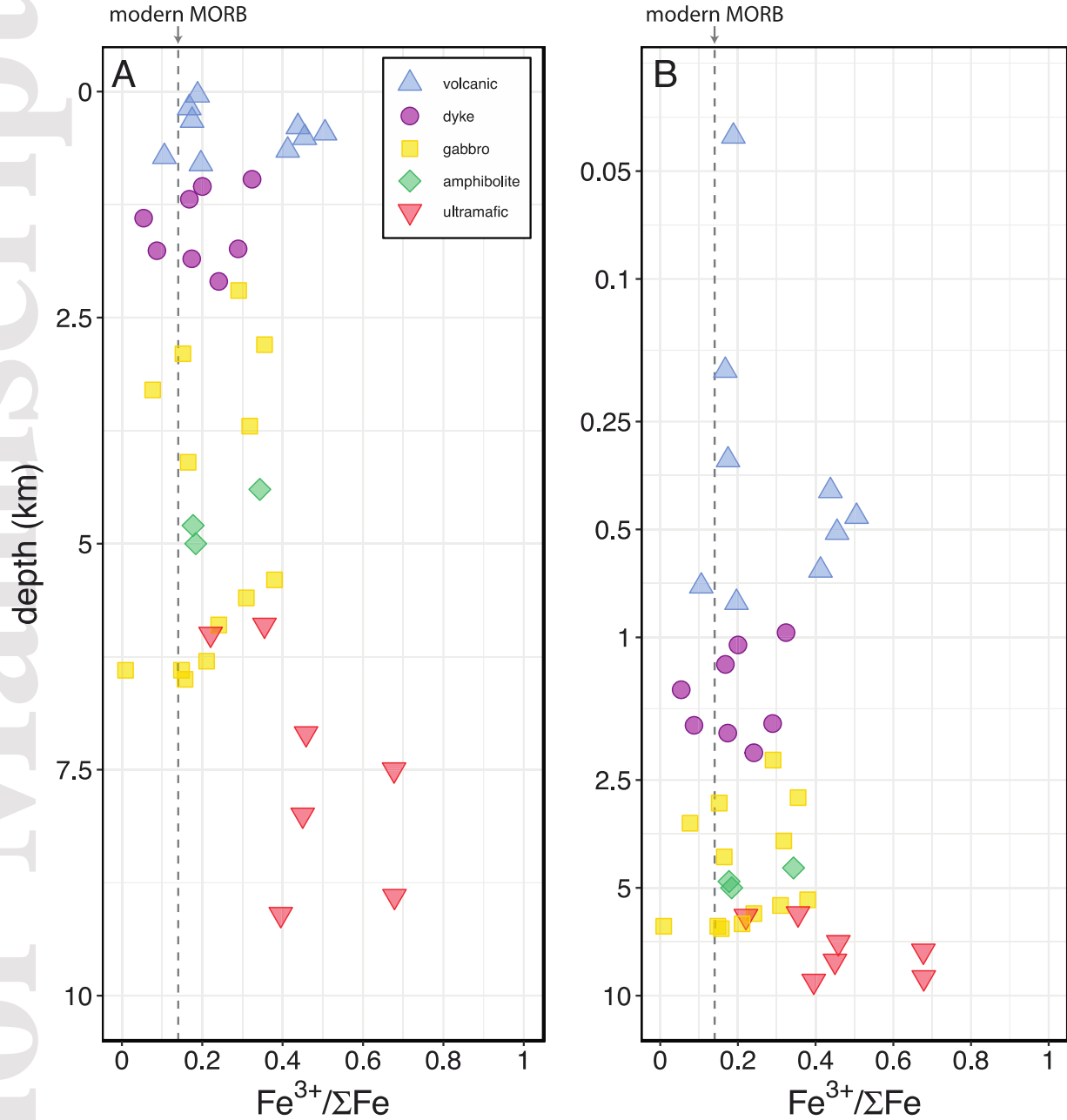


Figure 2. $Fe^{3+}/\Sigma Fe$ of various rock types from the Bay of Islands vs. depth below the sediment-basalt interface. The vertical dotted line is the average $Fe^{3+}/\Sigma Fe$ of MORB glasses from Zhang et al. (2018).

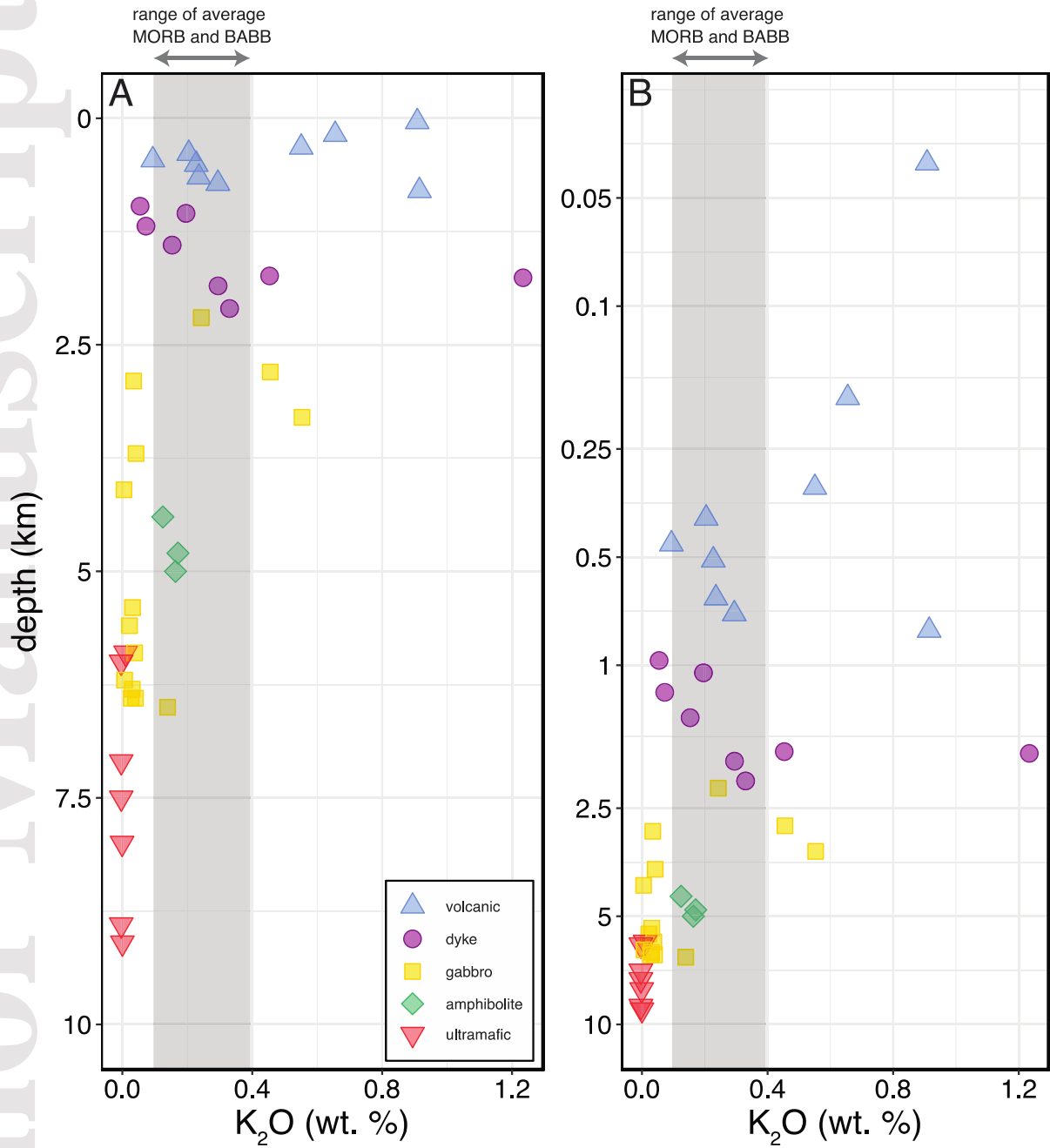


Figure 3. K_2O of various rock types from the Bay of Islands vs. depth below the sediment-basalt interface. The grey rectangle is the range of primary K_2O contents of MORB and back-arc basin basalts (BABB) from Gale et al. (2013).

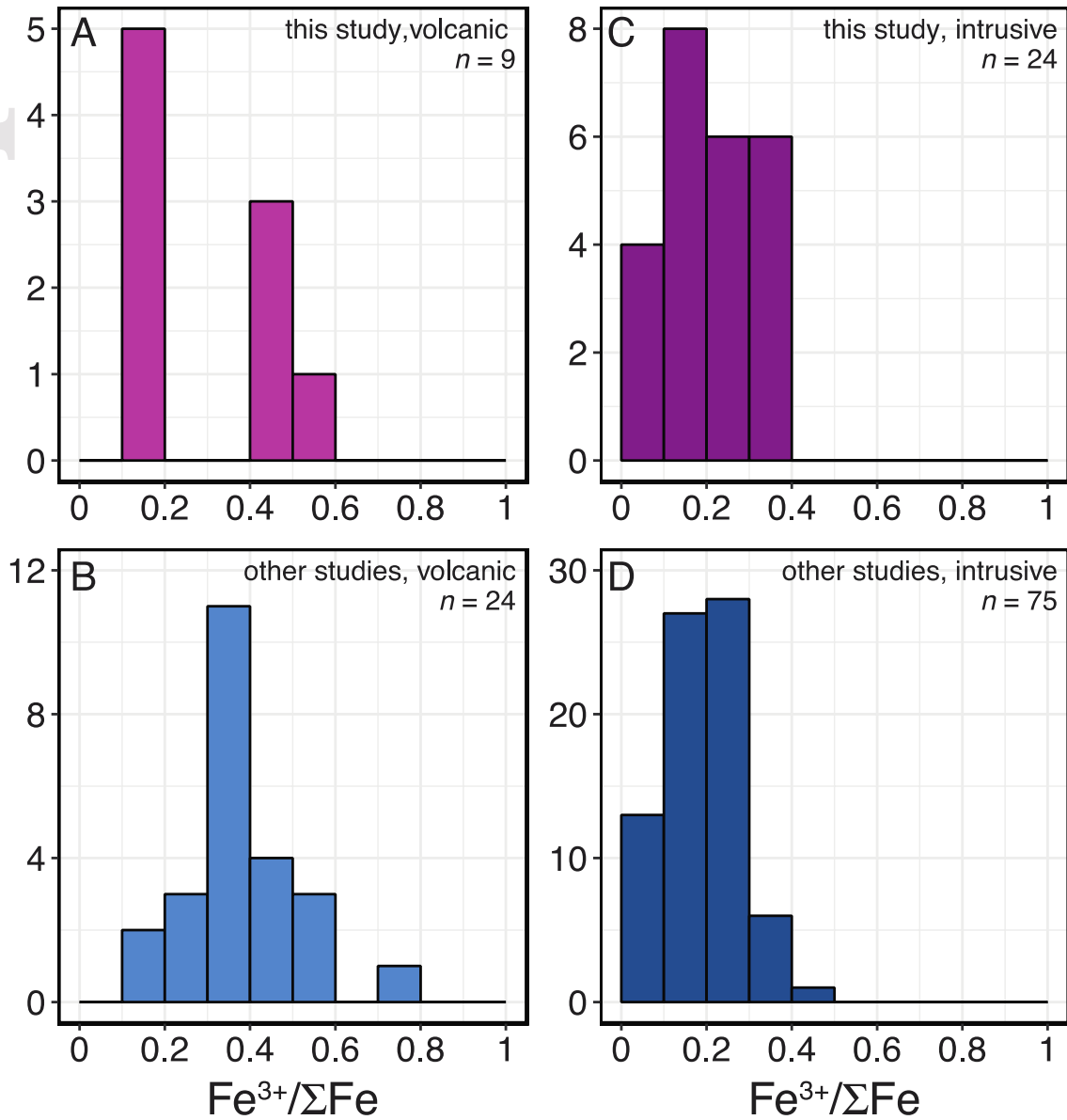


Figure 4. Comparison of $Fe^{3+}/\Sigma Fe$ from volcanic (A) and intrusive (C) rocks from this study vs. our compilation of data from other studies (B and D).

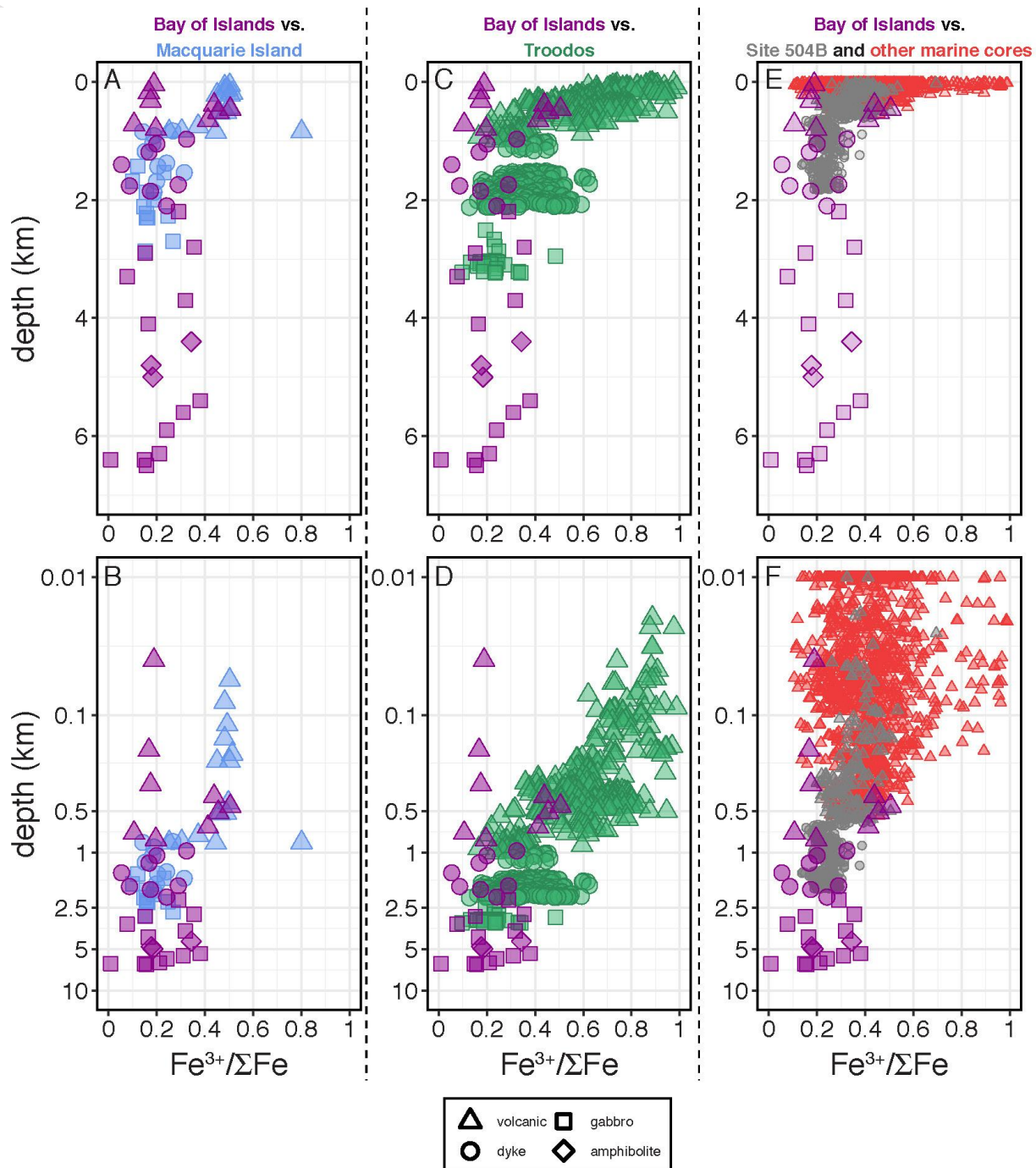


Figure 5. Comparison of Bay of Islands $Fe^{3+}/\Sigma Fe$ as a function of depth below the sediment-basalt interface vs. in A and B the Macquarie Island ophiolite (Rutter, 2015); C and D the Troodos Ophiolite (Gibson et al., 1989, 1991; Robinson et al., 1987); and E and F cored volcanic rocks from the seafloor (data from compilation given in Stolper & Keller, 2018) and cored volcanic and intrusive rocks from Site 504B (Alt et al., 1996). Symbols are the same as in Figures 2 and 3 and given in the legend. Colors correspond to the location of the sample and are given by the text color of the location at the top of the figures.

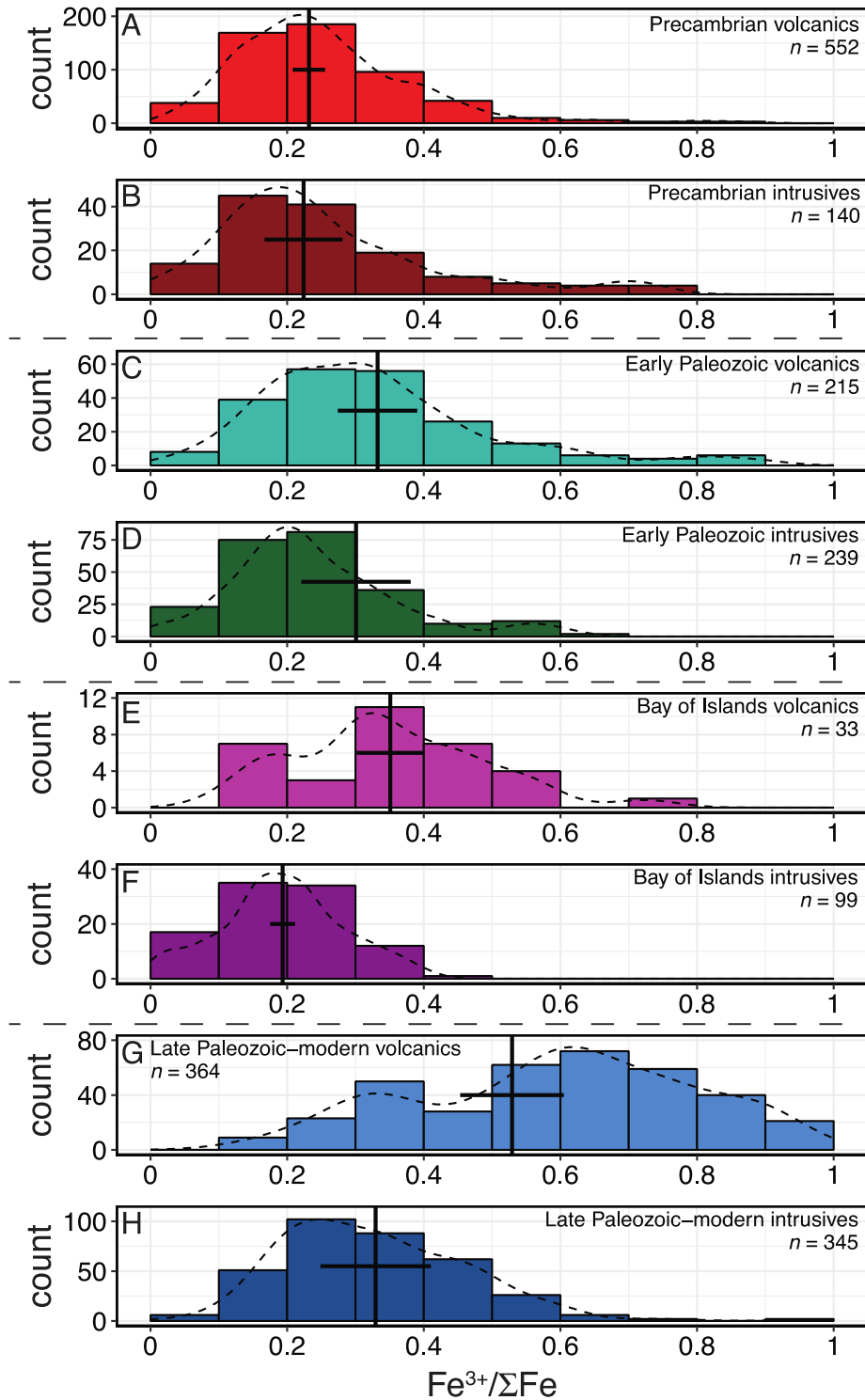


Figure 6. Comparison of $Fe^{3+}/\Sigma Fe$ from ophiolites of different ages. Solid black vertical lines are the mean values of each ophiolite for a specific time period (see main text), with horizontal 2 s.e. error bars. n is the number of data points. Dotted lines are smoothed distributions calculated using the default parameters of the `stat_smooth` function in the R statistical software package.

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