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Abstract

Serpentine in modern seafloor and ophiolitic environments incorporates and often retains high concentrations of atmospheric noble gases and seawater-derived halogens. Ancient serpentinites therefore provide the potential to trace the composition of early surface environments. Antigorite-serpentinites locally carbonated to talc-magnesite schist outcropping in a low strain zone within the Eoarchean Isua supracrustal belt (Greenland) are investigated here, to test the retention of paleo-atmospheric noble gases and Eoarchean seawater halogens, and to further determine the genetic setting and metamorphic history of some of Earth's oldest serpentinites. Based on field relationships, whole rock major and trace element geochemistry, and mineral chemistry, the investigated serpentinites are shown to represent hydrated and variously carbonated magmatic olivine $\pm$ orthopyroxene + Cr-spinel cumulates emplaced at the base of a lava flow of boninitic affinity pillowed in its upper portion. In addition, rare zircons extracted from one of the serpentinitised cumulates have distinct magmatic trace element signatures and a U-Pb age of 3721 ± 27 Ma indicating the pillowed lava flow erupted on the Eoarchean seafloor. The serpentinites have high concentrations of noble gases, but the presence of parentless radiogenic 'excess' ^{40}Ar , introduced by crustal-derived metamorphic fluids, obscures the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of Eoarchean seawater. Local carbonation of the serpentinites also caused halogen loss and fractionation. However, the least carbonated antigorite serpentinites preserve Br/Cl and I/Cl ratios within the range of modern seafloor serpentinites, which is interpreted as indicating Archaean serpentinising fluids were similar in composition to modern seawater-derived fluids. Importantly, the lowest measured I/Cl ratio of $29 (\pm 2) \times 10^{-6}$, taken as a maximum value for the Eoarchean ocean, is an order of magnitude lower than estimates for the primitive mantle I/Cl value. Iodine has a low concentration relative to Cl in modern seawater because it is sequestered by organic matter. If the inferred low I/Cl of Eoarchean seawater is correct, then similar I-sequestration was likely occurring in the Eoarchean, a process requiring the presence of significant biomass in Earth's early oceans. Further constraining the Precambrian evolution of seawater I/Cl via serpentinites or other proxies may provide a novel method to explore the emergence and evolution of terrestrial biomass.

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Halogens in serpentinites from the Isua supracrustal belt, Greenland: an Eoarchean seawater signature and biomass proxy?

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Serpentine in modern seafloor and ophiolitic environments incorporates and often retains high concentrations of atmospheric noble gases and seawater-derived halogens. Ancient serpentinites therefore provide the potential to trace the composition of early surface environments. Antigorite-serpentinites locally carbonated to talc-magnesite schist outcropping in a low strain zone within the Eoarchean Isua supracrustal belt (Greenland) are investigated here, to test the retention of paleo-atmospheric noble gases and Eoarchean seawater halogens, and to further determine the genetic setting and metamorphic history of some of Earth's oldest serpentinites.

Based on field relationships, whole rock major and trace element geochemistry, and mineral chemistry, the investigated serpentinites are shown to represent hydrated and variously carbonated magmatic olivine $\pm$ orthopyroxene + Cr-spinel cumulates emplaced at the base of a lava flow of boninitic affinity pillowed in its upper portion. In addition, rare zircons extracted from one of the serpentinitised cumulates have distinct magmatic trace element signatures and a U-Pb age of 3721 ± 27 Ma indicating the pillowed lava flow erupted on the Eoarchean seafloor.

The serpentinites have high concentrations of noble gases, but the presence of parentless radiogenic 'excess' ^{40}Ar , introduced by crustal-derived metamorphic fluids, obscures the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of Eoarchean seawater. Local carbonation of the serpentinites also caused halogen loss and fractionation. However, the least carbonated antigorite serpentinites preserve Br/Cl and I/Cl ratios within the range of modern seafloor serpentinites, which is interpreted as indicating Archaean serpentinitising fluids were similar in composition to modern seawater-derived fluids. Importantly, the lowest measured I/Cl ratio of $29 (\pm 2) \times 10^{-6}$, taken as a

maximum value for the Eoarchean ocean, is an order of magnitude lower than the primitive mantle I/Cl value. Iodine has a low concentration relative to Cl in modern seawater because it is sequestered by organic matter. If the inferred low I/Cl of Eoarchean seawater is correct, then similar I-sequestration was likely occurring in the Eoarchean, a process requiring the presence of significant biomass in Earth's early oceans. Further constraining the Precambrian evolution of seawater I/Cl via serpentinites or other proxies may provide a novel method to explore the emergence and evolution of terrestrial biomass.

Keywords: Early earth, halogens, serpentinites, early life, Isua supracrustal belt (ISB)

1 Introduction

The evolution of Earth's early atmosphere and oceans was critical to the development of life on our planet. The composition of the Archaean atmosphere and ocean is poorly preserved in the geologic record, with much of our current knowledge about the physical and chemical character of the early surface reservoirs coming from studies of: i) marine sediments (e.g., Hren et al., 2009; Nutman et al., 2017); ii) fluid inclusions preserved in ancient alteration minerals (e.g., Channer et al., 1997; Touret, 2003; Foriel et al., 2004; Pujol et al., 2013; Farber et al., 2015; Marty et al., 2018); and, iii) the composition of ancient hydrous minerals (e.g., Hanes et al., 1985; Pope et al., 2012; Ishida et al., 2018).

Fluid inclusions trapping evolved seawater have been reported from a number of Archaean localities including the ~2.7 Ga Abitibi greenstone belt in Canada, the 3.2-3.4 Ga Barberton greenstone belt in South Africa, the ~3.5 Ga Pilbara craton, Western Australia and the 3.7-3.8 Ga Isua supracrustal belt (ISB) in southwestern Greenland (Channer et al., 1997; De Ronde et al., 1997; Appel et al., 2001; Touret, 2003; Foriel et al., 2004; Weiershäuser and Spooner, 2005; de Vries and Touret, 2007; Pujol et al., 2011; Pujole et al., 2013; Farber et al., 2015; Avicé et al., 2017; Avicé et al., 2018; Marty et al., 2018). However, attribution of fluid inclusions to a primary Archean origin is often controversial (e.g., Lowe and Byerly, 2003; Heijlen et al., 2006) and with

the interpretation of the fluid inclusion record further complicated by the trapped fluids having variable salinity and compositions that show they represent mixtures of several hydrothermal components. Alternatively, fluid signatures preserved in ancient apatite formed within diverse genetic settings, i.e., sedimentary, magmatic and/or metasomatic (e.g., Ishida et al., 2018, Wudarska et al., 2018; Birski et al., 2019) as well as ancient metasomatic minerals including hornblende (Hanes et al., 1985) and serpentine (Pope et al., 2012) can provide a window into earth's early surface environment.

The Eoarchean ISB has been affected by higher degrees of deformation than the other younger Archean localities cited above, with metamorphic conditions ranging from uppermost greenschist to amphibolite facies (e.g., Rollinson, 2003; Arai et al., 2015). However, the presence of low strain domains with primary volcanic, sedimentary and possibly biological structures (Nutman et al., 1984; Appel et al., 1998; Fedo et al., 2001; Nutman et al., 2012; Nutman et al., 2016) means the Isua area still provides some of the earliest records of the terrestrial surface environment.

Serpentine is an especially important alteration mineral because it incorporates up to 13 wt. % water and has high concentrations of many fluid mobile elements including S, C, B, Sb and As (e.g., Alt et al., 2013; Deschamps and Hattori, 2013). Recent studies have shown serpentine can also trap high concentrations of noble gases and all halogens (John et al., 2011; Kendrick et al., 2011; Kendrick et al., 2013). Furthermore, the high temperature polymorph of serpentine, antigorite, can preserve some of the geochemical characteristics of serpentinising fluids over geological timescales and up to eclogite facies metamorphic conditions (Wenner and Taylor, 1973; Scambelluri et al., 1997; Scambelluri et al., 2004; Kendrick et al., 2011). A study of 114 mineral separates from samples collected from metamorphosed basalt, gabbros and ultramafic bodies occurring throughout the ISB reported variable hydrogen and oxygen isotope signatures in metasomatic minerals. However, antigorite-serpentinites from one low strain zone outcrop retained hydrogen and oxygen isotope signatures interpreted as preserving the characteristics of Eoarchean seawater (Pope et al., 2012). We re-sampled the serpentinites from the same locality and as closely as possible the same sites as studied by Pope et al. (2012), plus we collected additional material from an adjacent outcrop, to test if these rocks also preserve argon and halogen signatures representative of the Eoarchean surface reservoirs.

The measurements of $^{40}\text{Ar}/^{36}\text{Ar}$ and Cl, Br, and I elemental abundances were obtained using ^{40}Ar - ^{39}Ar methodology, which enable full quantification of the atmospheric, *in situ* and crustally-derived ‘excess’ or ‘parentless’ ^{40}Ar components. In addition, a detailed petrological and geochemical study of the serpentinites was undertaken to further constrain the context and origin of the halogen signatures. The goal of this study is to reconstruct early seawater compositions potentially placing significant new controls on hydrosphere and atmosphere evolution and discuss the implications for biomass development.

2 Geological setting

2.1 The Isua supracrustal belt

The amphibolite facies ISB, located in the Nuuk region, southern West Greenland, is an arcuate belt of about 30 km in length and up to 4 km wide exposed at the margin of the Inland Ice (e.g., Allaart, 1976; Nutman et al., 1984; Komiya et al., 1999; Nutman and Friend, 2009). The belt contains the world’s best preserved Eoarchean sedimentary and volcanic rocks and is dominated by amphibolites derived from basaltic, picritic and boninitic mafic protoliths, with lesser amounts of felsic volcanic and volcano sedimentary rocks, as well as dolostones, cherts and banded iron formations (Nutman et al., 1984; Appel et al., 1998; Fedo et al., 2001; Myers, 2001; Friend et al., 2008; Nutman and Friend, 2009; Nutman et al., 2010; Nutman et al., 2017). The ISB is surrounded and locally intruded by Eoarchean quartzo-felspathic orthogneisses derived from tonalites, granodiorites and granites (Moorbath et al., 1972; Pankhurst et al., 1973; Allaart, 1976; Nutman et al., 1984; Nutman et al., 1996).

Extensive U-Pb geochronology (e.g., Compston et al., 1986; Baadsgaard et al., 1986; Nutman et al., 1997; Nutman et al., 2002; Crowley, 2003; Kamber et al., 2005; Nutman et al., 2009) as well as detailed mapping of the area (Nutman and Friend, 2009) enabled two tectonic domains to be recognized, an older ~3800 Ma one in the south and a ~3700 Ma one in the north, that were juxtaposed in the Eoarchean (Nutman et al., 1997; Nutman et al., 2002; Nutman and Friend, 2009). Even though the geotectonic setting of the ISB remains controversial, an accretionary arc environment has been postulated (Komiya et al., 1999; Polat et al., 2002; Komiya et al., 2004; Jenner et al., 2009; Nutman and Friend, 2009; Hoffmann et al., 2010; Arai et al., 2015).

Strong geochemical evidence for this includes the close resemblance of the mafic volcanic rocks in both terranes with Phanerozoic island arc tholeiites, picrites and boninites generated at convergent plate boundaries (Polat et al., 2002; Polat and Hofmann, 2003; Jenner et al., 2009).

The ISB's ~3700 Ma northern domain is overall less deformed than the ~3800 Ma southern domain and therefore the preferred location to study the volcano-sedimentary rock record (Nutman et al., 2017 and references therein). The northern domain comprises tectonically intercalated rocks of different origins juxtaposed in the Eoarchean (e.g., Nutman et al., 2009). Detailed mapping complemented by U-Pb geochronology indicates that tectonic intercalations in the northern terrane started at ~3710 and were followed by collision with the southern ~3800 Ma portion of the belt between 3690 and 3660 Ma (Nutman et al., 2007 and references therein). All lithologies were therefore affected by several distinct deformation events at metamorphic conditions reaching up to amphibolite facies conditions prior to the emplacement of the Ameralik dyke swarm at ~3500 Ma (Nutman et al., 2004). The pre-3500 Ma deformation and metamorphism obliterated the primary structures, textures and mineralogy of most lithologies. Deformation throughout the belt is however heterogeneous, and rare areas with little pre-3500 Ma deformation preserve primary volcanic and sedimentary features such as pillows, hyaloclastites, sheet flow in lavas, ocelli, as well as graded sedimentary layering (Nutman et al., 1984; Appel et al., 1998; Fedo et al., 2001; Friend et al., 2008; Appel et al., 2009; Nutman et al., 2017). These low strain zones, including the serpentinite lens studied here (Pope et al., 2012), are a prime target to explore early terrestrial environments.

2.2 Isua ultramafic rocks

ISB ultramafic rocks occur as elongate lenses dispersed throughout the supracrustal units (Allaart, 1976; Nutman et al., 1984; Dymek et al., 1988; Nutman and Friend, 2009). Ultramafic units are often intercalated with pillow lavas but despite their close association, the original stratigraphic relations are often obscured by later deformation (Dymek et al., 1988; Furnes et al., 2007). The absence of clear field relationships combined with strong alteration (e.g., Allaart, 1976; Nutman et al., 1984; Dymek et al., 1988; Rose et al., 1996) often impedes identification of the ultramafic protoliths, which include: picritic sills, Eoarchean mantle slices,

layered intrusion cumulates and cumulate portions of basaltic to picritic lava flows (Dymek et al., 1988; Myers, 2001; Frei and Jensen, 2003; Friend and Nutman, 2011; Szilas et al., 2015). Depending on the degree of hydration and/or carbonation, olivine $\pm$ pyroxene lithologies are variously altered to chlorite schist, talc-magnesite schist and massive serpentinites dominated by antigorite (e.g., Dymek et al., 1988; Szilas et al., 2015). Dymek et al. (1988) attested that most ultramafic units represent strongly metasomatised cumulates within either extrusive lava flows or intrusive sills. A more recent study targeting the western arm of the Isua supracrustal belt confirmed that some ultramafic lenses are formed mainly by crystal fractionation of olivine + spinel ($\pm$ orthopyroxene) (Szilas et al., 2015). In contrast, a few meta-dunitic lenses in the north-eastern part of the belt (lens A and B in Fig. 1) have been identified as remnants of Eoarchean sub-arc mantle (Friend and Nutman, 2011).

2.3 The Pope locality

A serpentinised ultramafic lens outcrops at 65°07'53.6" N, 50°10'01.8" W (WGS 84 datum), within the western arm of the ~3700 Ma northern portion of the Isua supracrustal belt (see Fig. 1 and map of Nutman and Friend, 2009). This is Location A in Pope et al. (2012) and is referred to here as the Pope locality. Antigorite ($\pm$ lizardite) separated from serpentinites at this locality are reported to have δD values ranging from -56 to -53 ‰, $\delta^{18}O$ values ranging from +4.1 to +4.9 ‰, suggesting Eoarchean seawater as the source of the serpentinising fluid (Pope et al., 2012).

Four samples were collected from the Pope locality (Fig. 1, samples G12/36, G12/37, G12/38, and G12/39). Care was taken to collect samples closely matching those analysed by Pope et al. (2012), with sampling guided by outcrop photographs in their publications and the identification of hammer scars on the rock from the previous collection. The Pope locality is however highly heterogeneous on the outcrop scale. The hand specimens collected range from massive rocks with a characteristic blue to dark grey colour on fresh surfaces that preserve circular aggregates of up to a few mm across (G12/36) to schistose rock with a much lighter grey colour (G12/39). In addition to the four samples from the Pope locality, a fifth serpentinised sample (G12/66) was collected from a second outcrop situated ca. hundred meters along strike and south of the Pope locality

(Fig. 1, WGS'84 datum, 65°07'50.1" N, 50°10'3.9" W). This second outcrop lies in the same low strain zone as the original Pope locality (Fig. 1) and preserves relic pillow structures demonstrating a subaqueous volcanic protolith (Fig. 2). Importantly, the serpentinised samples from the Pope locality directly stratigraphically underlie the relic mafic pillows from the southern outcrop.

In addition to the serpentinised samples, this study provides data from two samples of amphibolite facies meta-doleritic dykes (G11/27 and G11/28) of the Paleoarchean Amealik dyke swarms (McGregor 1973; Nutman et al., 2004). The Amealik dykes were sampled in the 3720-3690 Ma orthogneisses exposed on the northern side of the ISB (see full map in Nutman and Friend, 2009; WGS'84 datum, 65°09'48" N, 50°03'23" W) and were metasomatised in a Neoarchean event (section 5.2.4). The two partially (G11/27) to strongly amphibolitised (G11/28) samples were selected to evaluate the efficacy of different alteration mineral for the preservation of noble gas signatures and potentially evaluate differences between early and late Archean fluids. A previous study demonstrated amphibole has the potential to preserve paleo-atmospheric Ar isotopic signatures from the Archean (Hanes et al., 1985). In contrast with serpentine, however, amphibole fractionates halogens, the larger Br and I being largely excluded from the amphibole structure (e.g., Kendrick et al., 2011; Kendrick et al., 2015; Chavrit et al., 2016). In this study, amphibole was therefore selected as the best candidate for preservation of Archean Ar isotopic signatures while serpentine was investigated for the preservation of both noble gas and halogen signatures.

3 Methods

3.1 Petrography

The serpentinites and the Amealik dyke samples were prepared as thin sections and investigated by optical microscopy and SEM imaging coupled with qualitative EDS analyses using the JEOL JSM-6610A at the Research School of Earth Science (RSES), at the Australian National University (ANU) (operating conditions of 15kV and working distance of 10 mm). In addition, representative ca. 2 g aliquots of each investigated sample were powdered in an agate mill and the mineral phases were identified by X-Ray diffraction on the Siemens D5005 Diffractometer (Bragg-Brentano geometry) at the RSES using CoK α radiation and run at 40

kV and 40 mA. The prepared powders were loaded in side-packed sample holders and scanned between 4° and $84^\circ 2\theta$, at a step width of 0.02° and scan speed of 1° per minute. Data reduction as well as phase identification was performed using the Siemens software package Diffracplus Eva 12. In addition, the identification of the serpentine polymorph was confirmed by *in situ* Raman spectroscopy on a Horiba Jobin Yvon T64000 micro-Raman system. Spectra were acquired on thin sections with a 532 nm green laser excitation and an acquisition time of 10 sec. Peak shapes and positions at high spectral range ($3550\text{--}3850\text{ cm}^{-1}$) associated to OH stretching vibrations were compared to serpentine spectra from the literature after baseline subtraction (e.g., Petriglieri et al., 2015; Fig. A1, electronic supplement).

3.2 Major and trace element geochemistry

Each sample was chipped using a hand press with care taken to avoid surficial alteration and veins. Representative aliquots were then powdered in an alumina mill. Sample powder aliquots of 1.5 g were dried and precisely weighed for Loss on Ignition (LOI) determinations, with the ignited powders subsequently fused with pure metaborate flux. Major elements analysis on the fused pellets were conducted on a SPECTRO XEPOS energy dispersive polarization X-ray fluorescence spectrometer (XRF) at the University of Wollongong, Australia.

Trace elements including REE, HFSE, LILE and transition metals were determined by solution aspiration ICP-MS at RSES, ANU, following the analytical procedures previously described by Norman et al. (1998). Weighed ca. 50 mg splits of the sample powders were dissolved in concentrated HF and HNO₃ ultra-pure (Teflon distilled) acids in screw-top Savillex® vials at low temperature ($<140^\circ\text{C}$) on a hotplate in a laminar flow hood in the SPIDE²R lab, ANU. In order to check for incomplete sample dissolution, the four serpentinite samples were also digested at high pressure in Parr® bombs with concentrated HF and HNO₃ and at temperatures of 200°C . Following dissolution, the samples were repeatedly taken to dryness and fluxed with HNO₃ until clear solutions were attained. The solution was brought to a final volume of 50 ml in 2% HNO₃ to reach a dilution factor of 1000 and spiked with 5 $\mu\text{g/g}$ Be, 0.5 $\mu\text{g/g}$ In, 0.5 $\mu\text{g/g}$ Re and 0.5 $\mu\text{g/g}$ Bi as internal standards.

Solution ICP-MS analyses were conducted on a Varian 820 quadrupole ICP-MS at RSES. Each analysis represents an average of 5 replicates over the mass range using a dwell time of 20 ms per mass. BCR-2 was set as the internal calibration standard for element sensitivities, except for Rb, Sr, Y, Zr, Mo, Ba, La and Ce for which BIR-1 was chosen as internal calibration due to over-saturation of these elements in the BCR-2 standard solution. Correction for instrumental drift was performed by interpolating between the internal standard masses assuming linear drift along the mass range, except for Li (normalized to Be) and Th and U which were normalized to Bi. Total procedural blanks for both dissolution methods were subtracted from the drift-corrected data. Tafahi-4 as well as BIR-1 were analysed as unknowns to monitor accuracy (Table A2, electronic supplement).

3.3 Electron microprobe

In situ major and minor element abundances of spinel and antigorite (with additional analyses on chlorite, magnesite and talc) were determined by wavelength dispersive spectrometry (WDS) using a Cameca SX100 electron microprobe at RSES and the JEOL 8530 plus electron microprobe at the Centre of Advanced Microscopy at the ANU. Measurements were performed using an accelerating voltage of 15 kV and a beam current of 20 nA, reduced to 10 nA for analyses performed on serpentine. Raw data were corrected using a ZAF routine and standardized against well-characterized natural and synthetic oxides and silicates. Limits of detection were typically between 200-400 µg/g with counting times ranging from 15 to a maximum of 30 sec. on Cl.

3.4 *In situ* SHRIMP U-Pb zircon geochronology and trace element composition

A zircon fragment was first detected on a test mount of sample G12/39, the most carbonated of the investigated serpentinite samples, suggesting a possible metasomatic origin. Additional zircon fragments were hand-picked from a heavy mineral separate of sample G12/39 prepared using methylene iodide and magnetic separation was first avoided to prevent the loss of rare zircons fragments. The suspected zircons extracted from the <150 µm fraction of the heavy mineral separate were mounted in a 2.5 cm diameter epoxy resin disc together with two zircon reference materials, Temora-2 (416.8 ± 1.3 Ma; Black et al., 2004) and OG-1 ($^{207}\text{Pb}/^{206}\text{Pb}$ age of

3465.4 $\pm$ 0.6 Ma; Stern et al., 2009). Further processing of the <150 μ m fraction of the heavy mineral separate was performed using a Frantz magnetic separator operated at a 15° tilt and currents ranging from 0.5 to 1.5 A. Suspected zircons in the magnetic separate were mounted in a second epoxy disc with the same reference materials. The two mounts were polished at a 1 μ m finish to expose the crystal interiors and were photographed in transmitted and reflected light. Secondary electron (SE) and cathodoluminescence (CL) imaging of the grains internal texture were undertaken on the JEOL JSM-6610A SEM at RSES and confirming the presence of three zircon fragments on the first epoxy disc and one additional fragment in the second disc. The main mount was then coated with a 40 nm thick high purity Au coating and used for *in situ* U-Pb and trace element measurements by SHRIMP.

U-Pb-Th isotopic ratios and concentrations were obtained from the SHRIMP II ion microprobe at RSES, following the procedure described by Williams (1998). Each analysis consisted of 6 scans through the 196-254 mass range, with Temora-2 and OG-1 zircon reference materials intercalated between the G12/39 zircon analyses. The U-Pb-Th isotopic ratios were calibrated with reference to Temora 2 ($^{206}\text{Pb}/^{238}\text{U} = 0.0668$) while Th and U abundances were calibrated from the reference material SL13 (U = 238 μ g/g) placed in a set-up mount. The common Pb correction was performed using the measured ^{204}Pb and the Stacey and Kramers (1975) lead composition for the age of the grains when the latter was above the limit of detection. When the ^{204}Pb was below detection, age calculation was based on the uncorrected $^{207}\text{Pb}/^{206}\text{Pb}$. Data reduction and plotting was performed using the Excel macro SQUID and the ISOPLOT program of Ludwig (2001).

In situ zircon trace element analyses were conducted on the SHRIMP-RG instrument, after lightly re-polishing, cleaning and re-coating of the mount. The higher mass resolution permitted by the reverse geometry allows molecular interferences affecting the REE to be better resolved. In addition, energy filtering was applied to lower molecular interferences (transmitting ca. 20 % of the total beam), the efficacy of which was confirmed by measuring two isotopes for each trace element whenever possible. The average raw count rates of three measurement cycles for each isotope (^{49}Ti , ^{91}Zr , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{146}Nd , ^{147}Sm , ^{149}Sm , ^{151}Eu , ^{153}Eu , ^{155}Gd , ^{157}Gd , ^{159}Tb , ^{161}Dy , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{167}Er , ^{169}Tm , ^{171}Yb , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{180}Hf) were normalized to the Zr count rates and a stoichiometric Zr abundance in zircon and are reported as elemental

abundances. The reference material NIST 611 was used to derive specific calibration factors for each elements and the two reference zircons Temora-2 (Black et al., 2004) and OG-1 (Stern et al., 2009) were used as quality controls.

3.5 Noble gases and halogens geochemistry

Halogens and noble gases were measured in irradiated mineral separates (ca. 60 mg) by the extended ^{40}Ar - ^{39}Ar method (Kendrick, 2012), which enables precise measurement of Cl, Br, I, K and Ca via the irradiation-produced proxy isotopes $^{38}\text{Ar}_{\text{Cl}}$, $^{80}\text{Kr}_{\text{Br}}$, $^{128}\text{Xe}_{\text{I}}$, $^{39}\text{Ar}_{\text{K}}$, $^{37}\text{Ar}_{\text{Ca}}$ together with the naturally occurring isotopes of Ar, Kr and Xe.

The sub-mm sized mineral separates were prepared under a binocular microscope. Care was taken to avoid vein material, however the purity of the serpentine separates strongly depended on the sample grain sizes. High purity antigorite separates were obtained from the best preserved and relatively coarse antigorite serpentinites (G12/36, G12/38). In contrast, antigorite separates obtained for sample G12/37 contained some impurities and we could only obtain whole rock chips free of vein material for the finest grained antigorite bearing samples (G12/39, G12/66). For the two Ameralik dyke samples, we obtained an amphibole separate (with minor chlorite) from G11/28 and a mixed pyroxene/amphibole separate from the less altered sample G11/27.

The selected grains were cleaned in an ultrasonic bath with distilled water and acetone and then packed in Al-foil and placed into a silica glass canister together with the ^{40}Ar - ^{39}Ar flux monitor Hb3Gr (Roddick, 1983), Ca and K-salts and aliquots of three scapolite gems used as halogen standards (Kendrick, 2012; Kendrick et al., 2013). Samples were irradiated in two separate irradiations in the central position of the McClellan Nuclear Radiation Centre at the University of California, Davis, United States (RS#2 irradiated for 50 hours in March 2014 and RS#4 for 47 hours in February 2017). The samples received total neutron fluences of $3.4\text{--}3.5 \times 10^{18}$ neutrons cm^{-2} with a fast to thermal neutrons ratios of close to 1 in both irradiations (irradiation details in electronic supplement; Table A5, A6).

Following irradiation, samples were returned to the noble gas laboratory, repacked in Sn foil and loaded into the Ultra High Vacuum tantalum resistance furnace sample holder attached to the MAP-215-50 noble gas mass spectrometer at RSES, ANU. The furnace was outgassed at 1600°C and the line was baked at ca. 150°C for at least 24 hour prior to analysis. In a first set of experiments, samples from RS#2 were analysed by stepped heating (e.g. 300°C, 600°C, 800°C, 1000°C and 1400°C) to maximize the number of heating steps from which paleo-atmospheric Ar with a low $^{40}\text{Ar}/^{36}\text{Ar}$ ratio might be resolved. In a second set of experiments, samples from irradiation RS#4 were re-measured in two steps (300°C and 1500°C) with the aim of maximizing the signal for halogen proxy isotopes and thereby improving the precision of halogen measurements. The only exception was the gas-rich amphibole bearing Ameralik dyke samples (G11/27 and G11/28) which required further gas splitting. The sample gas was exposed to a Ti foil getter pump operated at 650°C throughout the 20 minute heating steps and the extracted gases were further purified in the ultra-high vacuum extraction line using a series of four SAES getters over periods ranging from 30 min to ca. 3 hours depending on the samples and the heating temperature. Further details are available in Tables A5 and A6 of the electronic supplement.

Data reduction was performed following the procedure of Kendrick (2012). Halogen abundances and noble gas isotopic ratios were calculated after correcting the data for instrumental blank (typically <1%; Tables A5 and A6, electronic supplement), for standard ^{40}Ar - ^{39}Ar interference reactions, Cl-derived ^{36}Ar and U-derived ^{84}Kr . Analytical precision for the elemental halogen ratios are typically ranging from 3% to 5% at the 2σ level with the exception of halogen poor samples in which uncertainties are higher. The long term repeatability of this technique has been demonstrated as 5% for Cl and Br and 10% for I by the analysis of scapolite reference material in multiple irradiations (Kendrick et al., 2013) and the accuracy has been verified by analysis of eight international rock reference materials (Kendrick et al., 2018a).

4 Results

4.1 Petrography

The four serpentine bearing samples from the Pope locality have been fully hydrated and/or carbonated. Relict anhydrous silicate phases of igneous and/or mantle origin such as olivine and pyroxene are not preserved,

however, the Pope locality samples have highly variable textures and alteration mineralogy. The samples range from massive antigorite-serpentinites with globular textures (G12/36, G12/38) to highly carbonated magnesite-talc schist with minor serpentine (G12/39) (Fig. 3 and Table A1; electronic supplement). Antigorite was the only serpentine polymorph identified based on Raman spectroscopy (Fig. A1; electronic supplement), with spectra characterized by a doublet with the main peaks occurring at 3665 and 3695 cm^{-1} (e.g., Petriglieri et al., 2015).

In the antigorite serpentinites preserving the globular texture (G12/36, G12/38), pale green antigorite occurs as fine-grained crystals in the matrix and as radiating to aligned blades in the globules, which are interpreted as pseudomorphs after olivine and/or orthopyroxene (Fig. 3a-b-c-d). Chlorite occurs locally as larger crystals but is pervasive as fine-grained aggregates intermixed with antigorite in the matrix surrounding the antigorite globules (Fig. 3b). The antigorite in the pseudomorph globules is largely devoid of oxides but abundant magnetite occurs as coarse aggregates in the matrix and thereby defines the globule boundaries (Fig. 3a). Antigorite blades are locally altered to talc and smaller oxides are also found along cracks and veins associated with talc and magnesite in zones of preferential fluid pathways (e.g. in the interstitial space between globules). Accessories include needles of colourless to green amphibole (tremolite-actinolite) in sample G12/37 and rare occurrences of dolomite.

In contrast to the antigorite serpentinites with pseudomorphic cumulate textures, the magnesite-talc schist G12/39 from the Pope locality contains only minor antigorite and chlorite. In this schistose sample, grains are typically $<100\ \mu\text{m}$ across with magnesite forming granular aggregates inter-layered with talc-dominated zones. Talc is very fine-grained and fibrous and small ($\sim 50\ \mu\text{m}$) irregular oxides are pervasive throughout the sample. Antigorite and chlorite blades are mainly found intermixed with talc and magnesite along the boundary of talc-magnesite globules interpreted as replacing antigorite (Fig. 3f-g-h).

Sample G12/37 is heterogeneous on the thin section scale with domains that preserve antigorite globules interpreted as pseudomorphic cumulate textures and domains of stronger talc and magnesite overprint. The antigorite globules are smaller than in sample G12/36 and small oxides ($<100\ \mu\text{m}$) are ubiquitous. In addition,

minor green amphibole (tremolite-actinolite) up to a few hundreds of micrometres across are present in the talc and magnesite matrix. Sample G12/66 from the southern outcrop that preserves pillow lavas (Fig. 2) is an amphibole-bearing chlorite-serpentinite with similar mineralogy.

The two Ameralik dyke samples are partially (G11/27) to fully amphibolitised micro-gabbros (G11/28) both preserving igneous textures. Sample G11/27 has a sub-ophotitic texture and contains abundant plagioclase present as small laths of a few mm in size or as megacryst as well as remnants of pyroxenes. In contrast, sample G11/28 has an ophitic texture, with a higher proportion of mafic igneous minerals completely replaced by brown to green amphiboles rimmed with minor chlorite. The mineralogy of the investigated samples and their GPS coordinates are given in the electronic supplement (Table A1).

4.2 Major and trace element geochemistry

The whole rock major and trace element composition of the antigorite serpentinites and talc schist of the Pope locality (including the southern outcrop) and the amphibole-bearing Ameralik dyke samples are reported in Table 1. Totals of the major element analyses by XRF and Loss on Ignition (LOI) are 99.9 ± 0.6 wt. %. The antigorite serpentinites and talc schist have elevated LOI values ranging from 10.7 to 19.8 wt. %. The LOI increases above the expected ~13 wt. % for pure serpentine as a function of MgO reflecting the proportion of magnesite in the carbonated samples. The results in Table 1, which include LOI in the totals, have been recalculated on a volatile free basis for comparison with literature data in our figures.

The antigorite serpentinites and talc schist from the Pope locality and southern outcrop are rich in MgO with concentrations ranging from 35.5 - 41.5 wt. % on a volatile free basis. They have variable Fe_2O_3 ranging from 10.3 - 17.5 wt. %, 4.3 - 6.8 wt. % Al_2O_3 and 38.4 - 45.0 wt. % SiO_2 . CaO concentrations are low and range from 0.01-1.8 wt. % and TiO_2 concentrations are < 0.2 wt. %. The minor oxides Na_2O , K_2O and P_2O_5 are close to or below detection limits. MgO increases and Fe_2O_3 decreases as a function of the LOI and increasing talc-magnesite alteration. The other major elements do not show systematic behaviours as a function of the degree of alteration/carbonation.

Trace element concentrations obtained from the two digestion methods are similar, with the exception of Zr and Hf. Higher Zr and Hf concentrations in the solution prepared at high pressure probably reflect the presence of micro-zircons which were not completely dissolved by the low pressure hot plate digestion procedure. Hence, the reported Zr and Hf concentrations in the samples G12/36, G12/37, G12/38 and 12/39 are from the solutions prepared following the high pressure digestion method while all other values were obtained from the low pressure digestion solutions. In addition, although both methods always give similar relative abundances of HREE, the absolute concentrations of HREE in sample G12/39 are up to 65% higher in the solution prepared at high pressure. This discrepancy probably indicates variable dissolution of a dominant HREE bearing accessory phase in this sample. The complete data set including total procedural blanks and quality controls is available in the electronic supplement (Table A2).

The antigorite serpentinites and talc schist from the Pope locality have 53 to 268 $\mu\text{g/g}$ Ni and ~ 3700 to more than 15,000 $\mu\text{g/g}$ Cr (Table 1). These samples also have fractionated chondrite normalized rare earth element (REE) patterns and sub-chondritic REE concentrations with the exception of the heaviest REE (Fig. 4b). The samples have distinctive positive relative enrichment of the normalised HREE ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 0.1\text{-}0.3$, except sample G12/37) and significant negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.12\text{-}0.65$) (Fig. 4b). The talc schist G12/39 has a much larger Eu anomaly than the antigorite serpentinites (G12/36, G12/38) and a negative Ce anomaly is only present in sample G12/36 ($\text{Ce}/\text{Ce}^* = 0.35$) (Table 1). The light rare earth (LREE) patterns are varied, with both positive and negative slopes ($\text{La}_\text{N}/\text{Sm}_\text{N} = 0.6\text{-}1.7$). Sample G12/37 which contains amphibole and has a unique texture comprising fine grained antigorite pseudomorphs and carbonated zones, differs to all the other serpentine bearing samples in that it lacks a significant Eu anomaly, it has a concave upward REE pattern with flat HREE ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 0.9$) and near chondritic REE concentrations (Fig. 4b). The two Ameralik dyke samples (G11/27 and G11/28) have similar patterns, with flat slopes ($\text{La}_\text{N}/\text{Yb}_\text{N} = 0.8$), negligible negative Eu anomalies, but they have much higher REE concentrations of up to ca. 10 times chondritic values (Fig. 4b).

The Pope locality samples have primitive mantle normalized trace element patterns significantly depleted in Sr, Ba and Eu and enriched in Cs and Ti compared with other elements (Fig. 4a). In addition, most samples have significant U and minor Y positive anomalies. Decoupling of Nb and Ta results in sub-chondritic Nb/Ta

with the lowest ratios reported for the talc schist samples G12/39 (Nb/Ta of 2.6). Finally, a negative Zr anomaly is only present in the antigorite-serpentinite G12/36 and the serpentinite sample G12/66 from the relict pillow outcrop (Fig. 4a). Most trace elements in the Pope locality samples have concentrations indicating depletion by a factor of 10 compared to primitive mantle values. However, sample G12/37 is distinguished by higher trace element concentrations, subdued negative Eu anomaly and a small negative anomaly in Y (Fig. 4a).

The two Ameralik dykes samples have higher trace element concentrations reaching up to ca. 10 times primitive mantle values and overall flatter trace element patterns. On the relatively unfractionated trace element pattern the dykes have positive Pb and minor negative Sr, Zr, and Y anomalies (Fig. 4a).

4.3 Mineral Chemistry

4.3.1 Spinels

Oxide grains are common in all the antigorite serpentinites and talc schists from the Pope locality. They vary from large sub-mm idiomorphic grains in the interstitial space between antigorite globules in the antigorite-serpentinites (G12/36 and G12/38), to irregular small ($\sim 50\text{-}100\ \mu\text{m}$) grains in the talc schist G12/39 and the talc-rich zones of sample G12/37. The smaller oxides in these samples (G12/39 and G12/37) contain both talc and/or magnesite inclusions and they occur either in the talc-dominated matrix or as inclusions in larger magnesite grains. The compositional range of oxides are summarized in Table 2. Each analysis is plotted on the spinel chemical classification diagram after normalization to 3 cations per formula unit (p.f.u.) and recalculation of the Fe^{3+} based on stoichiometry and charge balance (Fig. 5c).

The vast majority of the oxides analysed have compositions falling between the magnetite and Cr-magnetite end-members in the ternary spinel classification diagram (Fig. 5c) and in addition to spinel, minor ilmenite was observed (Table A3; electronic supplement). Most spinel have $\text{Cr\#}$ ($=\text{Cr}/(\text{Cr}+\text{Al})$) close to 1, very low $\text{Mg\#}$ ($=\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) \leq 0.01$) and variable $\text{Fe\#}$ ($=\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Al}+\text{Cr})$) ranging from ca. 0.5 to 0.95. However, the core of a single spinel in sample G12/39 preserves an Al-rich composition surrounded by a Cr-magnetite

rim (Fig. 5b-c). The spinels define a trend from almost pure Fe-magnetite in the antigorite serpentinites (G12/36, G12/38) to more Cr-rich compositions in the talc and magnesite rich samples G12/39 and G12/37. Therefore we recognize three generations of spinel; a primary Al-bearing igneous spinel is preserved as a single core in sample G12/39; Fe-rich magnetite dominates in the antigorite serpentinites and Cr-rich magnetite formed during carbonate alteration dominates in the talc-magnesite domains.

4.3.2 Antigorite chemistry

The average chemical composition of the Pope locality antigorite are reported in Table 3 together with antigorite from the high pressure Cerro del Almirez massif and the Val Malenco ophiolite (Padrón-Navarta et al., 2008 and reference therein). Analyses performed on the fine grained matrix that may be intermixed with chlorite are distinguished in Table 3 and on figure 6. Representative analyses on coarse-grained crystals indicate the Pope locality antigorite have elevated Al_2O_3 ranging from 1.25 to 4.6 wt. % with an average of 3.4 wt. % and FeO ranging from 6.2-9.5 wt. % (Table 3).

The compositional range of the antigorite normalised to 116 oxygen per formula unit (Mellini et al., 1987) is shown in figure 6 together with the ideal antigorite end-members formed by Tschermak's substitution (Padrón-Navarta et al., 2013). Trivalent cations such as Al and possibly Fe^{3+} and Cr^{3+} are incorporated into antigorite by a coupled substitution of two trivalent cations (Al) for an Mg and a Si cation (i.e., Tschermak's exchange; Padrón-Navarta et al., 2013). The ISB antigorites in this study, however, have a compositional range deviating from the ideal Tschermak's exchange (Fig. 6) with a small excess of Al at any given Si content and a clear deficiency in divalent cations occupying the octahedral site. These features could be explained by stabilization of some Al (and possibly Fe^{3+} and/or Cr^{3+}) in the octahedral site (e.g., Padrón-Navarta et al., 2008).

4.4 *In situ* SHRIMP U-Pb zircon geochronology and trace element composition

4.4.1 U-Pb geochronology

Sample G12/39 yielded four small idiomorphic fragments of translucent to pale grey zircon (< 100 μm in size) characterized by weak oscillatory and sector zoning in CL images. Two fragments (zr-3, zr-4) have

distinctive homogeneous dark rims in CL images as well as magnesite along micron-scale cracks (Fig. 7).

Four SHRIMP U-Pb analyses including two on the largest fragment (Zr-2) reveal the zircons are U-poor (3-11 $\mu\text{g/g}$) and have unusually high Th/U ratios ranging between 14 and 22 (Table 4). Common lead was below the detection limit in spots Zr-2-1 and Zr-3-1 and has a very low abundance in spots Zr-2-2 and Zr-4-1 (Table 4 and Fig. 7), meaning that the common Pb correction has a negligible effect on the calculated ages. The four analyses show significant scatter in weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages ($\text{MSWD} > 1$) that is attributed to ancient Pb loss rather than to a heterogeneous zircon population. By progressively excluding the youngest ages attributed to Pb loss, a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3721 ± 27 Ma (95% confidence, $\text{MSWD} = 0.06$) is obtained for the repeat analyses of the largest zircon fragment Zr-2. This fragment lacks inclusions, cracks and the dark rim in CL images that probably represents a metamorphic overgrowth or recrystallization (Fig. 7). In addition, Zr-2 has the lowest concentrations of 3-6 $\mu\text{g/g}$ U and 35-138 $\mu\text{g/g}$ Th (Table 4), which supports a less disturbed Pb isotopic composition. Nonetheless, all analyses were concordant at the 2σ level and a Concordia age including the four analyses is within error of the preferred weighted mean average age of 3721 ± 27 Ma interpreted as the zircon crystallization age (Fig. 8).

Trace element concentrations including REE, Ti and Hf were obtained from six ca. 20 μm SHRIMP-RG spots on the three zircon fragments (Zr-2, Zr-3, Zr-4), including three analyses of the largest zircon (Zr-2) from core to rim (Fig 9; Table A4). The chondrite normalised REE patterns in the G12/39 zircons are strongly fractionated with sub-chondritic LREE to more than a 1000-fold enrichment for most of the HREE (Fig. 9). Ce positive and Eu negative anomalies are present in all analyses. There are however some variations between grains. The U-poor grain (Zr-2) has the lowest REE abundances, with decreasing concentrations from core to rim, and the strongest Ce positive anomalies ($\text{Ce}/\text{Ce}^* = 32\text{-}37$) associated with sub-chondritic La ($\text{La}_N < 0.01$). The remaining analyses have slightly higher La abundance ($\text{La}_N > 0.1$) with subdued Ce positive anomalies ($\text{Ce}/\text{Ce}^* = 2.53\text{-}4.02$). All analyses display strong Eu negative anomalies ranging from $\text{Eu}/\text{Eu}^* 0.02$ to 0.05 . Finally, the REE trace element patterns have a characteristic shoulder in the lightest HREE (Gd-Ho) with flattening of the pattern for the heaviest REE (Ho-Lu).

All zircon trace element analyses show high Ti concentrations ranging from ca. 45 to 91 $\mu\text{g/g}$ that suggest high crystallization temperatures. Using the revised Ti in zircon calibration of Ferry and Watson (2007), we obtain a mean apparent crystallization temperature of $960 \pm 68^\circ\text{C}$ (2σ). However, the conditions for using the Ti in zircon thermometer are not satisfied because the zircons are not in equilibrium with quartz and rutile (Watson and Harrison, 2005; section 5.1.3).

4.5 Argon and halogen geochemistry

4.5.1 Argon

The step heating experiments undertaken on separates from the antigorite-serpentinites and talc schist of the Pope locality and the two Ameralik dyke samples included in RS#2 extracted argon with variable isotopic composition at different temperatures (Table A5). The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios range from 460 to $\sim 38,000$ (excluding measurements with 1σ uncertainties exceeding 30 %) with the lowest ratios, which remain higher than the modern atmospheric value of 299, measured in the lowest temperature steps (Table 5 and electronic supplement Table A5). More than 90% of the total ^{40}Ar extracted from the high purity antigorite separates (G12/36 and G12/38) was released between 600 and 800°C (Table A5). In contrast, a larger proportion of the gas was released from the finer grained talc schist (G12/39) in lower temperature steps; and, more than 50 % of the total ^{40}Ar was released from amphibole-bearing samples (G12/37, G11/28, and G11/27) at higher temperatures of $1000\text{--}1400^\circ\text{C}$. Taken together the Pope locality samples have total fusion ^{36}Ar concentrations ranging from $3.4\text{--}4.5 \times 10^{-13} \text{ mol g}^{-1}$ that fall within the lower range of values reported for Phanerozoic antigorite serpentinites previously (Fig. 10b). Amphibole and pyroxene separates of the Ameralik dyke samples have slightly higher total fusion ^{36}Ar concentrations of $7.5\text{--}7.7 \times 10^{-13} \text{ mol g}^{-1}$ (Fig. 10b).

The $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{40}\text{K}/^{36}\text{Ar}$ ratios measured in individual heating steps in antigorite serpentinites with measurable K concentrations (G12/36, G12/37 and G12/38) and in the amphibole fraction of the Ameralik dyke sample G11/28 are plotted on a K-Ar isochron diagram (Fig. 10a). Reference slopes with $^{40}\text{Ar}^*/^{40}\text{K}$ ratios that correspond to the formation age of 3.7 Ga and have intercepts equivalent to the modern atmosphere $^{40}\text{Ar}/^{36}\text{Ar}$ value of 299 (Lee et al., 2006) and a possible Archaean atmosphere $^{40}\text{Ar}/^{36}\text{Ar}$ value of 143 (Pujol et

al., 2013) are included in Fig. 10a. In comparison with the 3.7 Ga reference lines, the K-poor antigorite dominated samples (G12/36 and G12/38) are strongly enriched in excess ^{40}Ar and have unrealistic apparent ages of 8.9 to 9.3 Ga that reflects an initially trapped excess component with $^{40}\text{Ar}/^{36}\text{Ar}$ of ~3,000-20,000 (Fig. 10a). In contrast, analyses of the amphibole bearing serpentinite G12/37 and the amphibole fraction of the Ameralik dyke G11/28 lie much closer to the 3.7 Ga reference slope, however, minimum apparent ages in individual heating steps of ~4000-7000 Ma also reflect the presence of trapped excess ^{40}Ar components with initial $^{40}\text{Ar}/^{36}\text{Ar}$ ranging from ~300 up to ~5000 (Fig. 10a; Tables 5 and A5). Four heating steps of sample G12/37 do lie on a poorly defined regression with an apparent age of 3.8 ± 2.3 Ga and an intercept of 1151 ± 2300 (95% conf., regression calculated with the Isoplot add-in of Ludwig, 2001). However, the ubiquitous presence of excess ^{40}Ar means that none of the samples define meaningful ages (Fig. 10a).

The proportions of atmospheric $^{40}\text{Ar}_\text{A}$ ($^{40}\text{Ar}_\text{A} = 299 \times ^{36}\text{Ar}$), initially trapped excess (parentless) $^{40}\text{Ar}_\text{E}$, *in situ* radiogenic $^{40}\text{Ar}_\text{R}$ (produced from the measured K concentration in 3.7 Ga) and the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of each sample, calculated by subtracting the *in situ* radiogenic $^{40}\text{Ar}_\text{R}$ from the total ^{40}Ar are given in Table 5. Trapped paleo-atmospheric Ar with a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of < 299 was not resolved in any of the samples. The proportions of *in situ* radiogenic $^{40}\text{Ar}_\text{R}$, atmospheric $^{40}\text{Ar}_\text{A}$ and excess $^{40}\text{Ar}_\text{E}$ are highly variable, with the largest proportions of excess ^{40}Ar representing ~90-96% of the total Ar in K-poor antigorite-serpentinites (G12/36 and G12/38) and the talc schist sample (G12/39) (Table 5). In contrast, the amphibole fraction of the Ameralik dike sample G11/28 which has the highest K concentration of 1610 $\mu\text{g/g}$, as well as the K-rich antigorite serpentinite G12/37 with 600 $\mu\text{g/g}$ K have much larger proportions of ~66-67% radiogenic $^{40}\text{Ar}_\text{R}$ (Table 5).

4.5.2 Halogens

The Pope locality serpentinites (G12/36, G12/37 and G12/38) have concentrations ranging from 306 to 380 $\mu\text{g/g}$ Cl; 250 to 340 ng/g Br and 11 to 26 ng/g I (Table 6). The amphibole-bearing serpentinite G12/66 sampled at the relic pillow outcrop (Fig. 2) is slightly enriched in comparison with ca. 616 $\mu\text{g/g}$ Cl, 670 ng/g Br and 15 ng/g I. The range of concentrations is broadly similar to those reported for Phanerozoic antigorite

serpentinites (Fig. 11b-c; John et al., 2011; Kendrick et al., 2011; Kendrick et al., 2013; Kendrick et al., 2018b; Pagé and Hattori, 2017). In contrast, the carbonated antigorite-bearing schist G12/39 contains only 33 ± 9 $\mu\text{g/g}$ Cl, 121 ± 40 ng/g Br and 8.9 ± 7 ng/g I (2σ uncertainties). Assuming similar initial concentrations, these differences suggest that extensive carbonate alteration of the serpentinites led to the loss of roughly 92% of the original Cl, 55% of the original Br and 26% of the original I. The suggested halogen loss during carbonation is consistent with electron microprobe measurements showing 300-400 $\mu\text{g/g}$ Cl in antigorite from the Pope locality samples, but Cl concentrations below the EPMA detection limit of 50-250 $\mu\text{g/g}$ in magnesite and talc in the carbonated talc schist G12/39 (Table A3, electronic supplement).

The extensively carbonated talc-schist G12/39, which has lost halogens, is characterized by Br/Cl of 3.7×10^{-3} and I/Cl of ca. 270×10^{-6} . In comparison, the antigorite bearing serpentinites have tightly clustered Br/Cl ratios ranging from 0.7 to 1.3×10^{-3} and I/Cl from 23.7 to 85.0×10^{-6} (Table 6) that fall within the range of values reported for modern antigorite serpentinites from Cerro del Almiraz (Fig. 11a; Kendrick et al., 2018b).

The two Ameralik dyke samples have halogen concentrations ranging from 1095 $\mu\text{g/g}$ Cl, 3880 ng/g Br and 183 ng/g I in the least altered pyroxene dominated fraction from sample G11/27 to 1354 $\mu\text{g/g}$ Cl, 2176 ng/g Br and ~60 ng/g I in the fully amphibolitised fraction of sample G11/28. The amphibole separate therefore has lower Br/Cl and I/Cl ratios of ~ respectively 1.6×10^{-3} and 44×10^{-6} (Fig. 11a, Table 6) than the mixed pyroxene/amphibole fraction of sample G11/27 (Fig. 11b-c, Table 6), which is consistent with the known preferential incorporation of Cl into amphibole relative to Br and I (e.g., Kendrick et al., 2015).

5 Discussion

The field observations (Fig 2), petrography and geochemical data reported above indicate that the studied ultramafic unit has a complex multi-stage metasomatic history. The following discussion contains four sections. Section 5.1 examines evidence from immobile major and trace elements and preserved zircons to reveal the origin of the ultramafic protolith. Section 5.2 describes the metamorphic and metasomatic history of the samples focussing on the measured Ar isotopic signatures and the chemical composition of serpentine and spinel. Section 5.3 examines the halogen composition of the antigorite serpentinite studied here and

potentially acquired from Eoarchean seawater and section 5.4 discusses the implications of the measured halogen signatures for early terrestrial surface environments.

5.1 Magmatic protolith of the Pope locality serpentinites

5.1.1 Major and trace element geochemistry

Serpentinisation by seawater has been shown to have limited impact on the major element composition of serpentinite protoliths (Deschamps and Hattori, 2013), with most elements redistributed only locally at the outcrop scale, with the exception of CaO systematically depleted by serpentinisation (e.g., Iyer et al., 2008). In contrast, the carbonated talc-schist at Isua has significantly higher Mg and lower Fe concentrations compared to the antigorite serpentinites (Table 1), suggesting mobility of these elements during carbonation. We therefore focus on the major element compositions of the least carbonated antigorite serpentinites (G12/36 and G12/38) as most representative of the protolith's original signature.

An origin from mantle peridotite is not favoured because the antigorite serpentinites (G12/36 and G12/37) have volatile free concentrations of 17.5-18.3 wt. % Fe_2O_3 that are higher than typical mantle peridotites with < 10 wt. % Fe_2O_3 (Bodinier and Godard, 2007). Furthermore, the studied samples also lie outside of the terrestrial mantle array on the MgO/SiO_2 vs. $\text{Al}_2\text{O}_3/\text{SiO}_2$ variation diagram (Fig. 12b), which has previously been used to identify Eoarchean mantle samples (Friend et al., 2002; Rollinson, 2007). An origin from komatiites is not favoured because as showed by Szilas et al. (2015), the ISB flow or sill related ultramafic units have much higher Fe and Al than komatiites. Furthermore, komatiites have not been identified in the ISB (e.g., Polat et al., 2002; Jenner et al., 2009). The serpentinites studied here also have higher concentrations of Cr and higher Cr/Ni ratios of >1 than ISB mafic volcanic rocks (Fig. 12c). The reported Cr concentrations and Cr/Ni ratios are however consistent with accumulation of Cr-spinel and olivine in a magmatic cumulate. A magmatic cumulate origin is also supported by the large idiomorphic oxides and the pseudomorphic cumulate texture preserved in the antigorite samples (Fig. 3a). Additionally, the primary Al-chromite core in sample G12/39 (Fig. 5) has a composition closely related to chromites found in Archaean layered gabbro-peridotites (Fig. 5a; Rollinson, 2007).

Serpentinisation usually has a limited effect on the trace elements considered as fluid immobile including the high field strength elements (HFSE) and the HREE but serpentinites can be strongly enriched in fluid mobile elements such as the LILE (Cs, Rb, K, Ba, Sr), B, Cl, Pb and U (e.g., Deschamps and Hattori, 2013). In addition to the trace elements mobilized during hydration, carbonation exerts a strong influence on Pb and Sr, which are hosted by carbonate phases.

The ISB serpentinites studied here exhibit many of the trace element features of modern abyssal serpentinites including positive U, Pb and Cs anomalies, but they have strong negative Sr and Eu anomalies (Fig. 4a-b). Carbonation of the antigorite serpentinites possibly intensified the Eu negative anomaly (e.g., Allen and Seyfried, 2005), but the Eu and Sr anomalies are present in all the Pope locality samples and given that Sr is enriched by both serpentinisation and carbonation the negative Sr anomalies, which are correlated with negative Eu anomalies, are interpreted as a characteristic of the magmatic protolith rather than an alteration feature. These negative anomalies could be explained by fractional crystallization and removal of plagioclase under reducing conditions, which is consistent with the proposed origin of the protolith as an olivine and spinel rich cumulate. We note however, that it is unclear if plagioclase saturation was reached in the Isua volcanics (Szilas et al., 2015).

An origin from a magmatic cumulate allows the observed factor of ~5 variation in concentrations of fluid immobile trace elements like Zr and Hf to be explained by different relative proportions of cumulus minerals and inter-cumulus residual and/or late percolating melts in each sample. Finally, the decoupling between Nb and Ta (Fig. 4a) in the ISB serpentinites studied here results in sub-chondritic Nb/Ta ratios. Similar signatures were previously reported in abyssal serpentinites (Deschamps and Hattori, 2013); however, sub-chondritic Nb/Ta ratios in the ISB volcanics were previously interpreted as an inherited compositional characteristic of the Eoarchean mantle sources rather than a post-magmatic alteration signature (Polat and Hofmann, 2003).

5.1.2 Boninitic-like signature

Previous workers have identified two magmatic trends in the ~3700 Ma portion of the ISB (e.g., Polat et al., 2002; Polat and Hofmann, 2003; Polat et al., 2011; Szilas et al., 2015). The first series has geochemical

features comparable to Phanerozoic boninites such as low TiO_2 , Zr, Nb, high $\text{Al}_2\text{O}_3/\text{TiO}_2$, U-shaped REE patterns, and the second series resembles Phanerozoic island arc basalts and picrites (e.g., Polat et al., 2011). The two magmatic series are well distinguished on the Th/Yb vs. Nb/Yb discrimination diagram of Pearce (2008) (Fig. 12d) and on the basis of their $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (Fig. 12a). Szilas et al. (2015) have shown that the geochemical distinction between the two series is also present in the associated cumulates.

The best preserved antigorite serpentinites from the Pope locality (G12/36 and G12/38) have high $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios (Fig. 12a), low Th/Yb and Nb/Yb ratios (Fig. 12d), relatively low Zr, Nb and Ti content, U-shaped REE pattern with steep HREE slopes (Fig. 4a), that resemble ISB volcanic rocks of boninitic affinity more closely than those of basaltic affinity (Figs. 4a and 12a; Polat et al., 2002; Polat and Hofmann, 2003; Polat et al., 2011; Szilas et al., 2015). Sample G12/37, however, has much higher trace element concentrations (Fig. 4a-b) and geochemical signatures closer to the basalt series (Fig. 12a). The dominance of the boninite signature in the best-preserved serpentinites is in accord with these rocks occurring within a broad unit of amphibolite previously interpreted to have a boninitic affinity (Polat et al., 2002; Polat and Hofmann, 2003).

The whole rock geochemical data presented in this study favour formation of the Pope locality ultramafic protolith by igneous accumulation of mainly olivine and orthopyroxene together with Cr-spinel. This is consistent with the work of Szilas et al., (2015) that demonstrated many ultramafic rocks in the ISB formed by fractional crystallisation of olivine + spinel and suggested interaction between the crystallizing cumulates and more evolved liquids could account for slightly elevated SiO_2 , normative orthopyroxene and fluid immobile trace element concentrations.

5.1.3 Magmatic zircons with 3721 ± 27 Ma crystallization age

The zircons in G12/39 are interpreted as having an igneous origin meaning the U-Pb age of 3721 ± 27 Ma represents the time at which the boninitic lava flow erupted on the Eoarchean seafloor.

An igneous origin is favoured because the oscillatory zoning and internal texture of the analysed zircons are unlike metamorphic zircons formed by crystallization from metamorphic fluids, or by recrystallization of

primary igneous zircons (e.g., Rubatto, 2002; Hoskin and Schaltegger, 2003;). The zircons lack internal morphologies such as inherited cores, low-luminescence centre and convoluted zonings (Hoskin and Ireland, 2000). However, very narrow rims of a few micrometers in thickness have been identified in two zircons fragments (Fig. 7). These rims were too small to fit a 20 μm SHRIMP spot, but probably represent metamorphic/metasomatic overgrowth or recrystallisation.

The studied zircons have elevated Th/U ratios of 14-22 (Table 4) that are much higher than the accepted range for metamorphic zircons with Th/U ratios of <0.1 and in most cases <0.01 (Rubatto, 2002; Hoskin and Schaltegger, 2003). Elevated Th/U ratios are however commonly observed in magmatic zircons extracted from gabbroic rocks, and ISB meta-gabbros yielded zircons with Th/U ratios of up to 2.9 (sample G07/26 in Friend and Nutman, 2010). In addition, the zircons recovered in G12/39 have strong negative Eu anomalies as well as igneous-like REE patterns (Fig. 9), whereas metamorphic zircons commonly have subdued Eu negative anomalies (Rubatto, 2002).

Zircon trace element discrimination diagrams can be used as petrogenetic indicators (e.g., Grimes et al., 2007; Carley et al., 2014; Grimes et al., 2015). In the discrimination diagram employing U (an incompatible fluid mobile element) and Yb (an incompatible fluid immobile element) G12/39 zircons plot on the extreme lower end of the oceanic MORB field indicative of an anhydrous melt source (Fig. 13a-b). The zircons also have elevated Ti concentrations and they plot in the least fractionated end-member on Ti vs. U/Yb and Ti vs. Gd/Yb variation diagrams (Fig. 13d-e), indicating a high temperature magma source that has undergone only limited fractionation. G12/39 zircons have Ti concentrations of 45-91 $\mu\text{g/g}$, largely exceeding the concentrations reported in zircons from intra-continental silica-saturated granitoids, but similar to the Ti concentrations reported in zircons from kimberlites and gabbros (Fu et al., 2008). Ferry and Watson (2007) demonstrate that in rutile- and quartz-free magmatic rocks, low TiO_2 and SiO_2 activities (< 1) have opposite effects on the Ti in zircon thermometer. The degree to which these effects compensate is however difficult to quantify in the case of the G12/39 zircons as the SiO_2 activity of the magma from which the zircons crystallized cannot be constrained. Despite these limitations, the elevated Ti concentrations and the obtained Ti in zircon temperatures of $960 \pm 68^\circ\text{C}$ (2σ) suggest the G12/39 zircons are unlikely to be xenocrystic zircons derived

from Isua felsic rocks, where lower Ti in zircon temperatures of ~ 700 °C (Hiess et al., 2008) and much lower Th/U ratios are recorded. The temperature estimate is less than the expected liquidus of boninitic melts; however zircons might have crystallized from a more evolved late-stage inter-cumulus melt sufficiently enriched in trace elements to achieve Zr saturation.

The 3721 ± 27 Ma date for the magmatic protolith of the Pope locality serpentinites coincides within error with the 3711 ± 11 Ma date reported for the gabbro sample G07/26 outcropping in the same unit (Fig. 1; Friend and Nutman, 2010). In addition, amphibolites preserving relic pillow structures within the same geological unit are crosscut by a tonalite sheet (sample G07/25) dated at 3712 ± 6 Ma (Nutman and Friend, 2009) suggesting a precise lower limit for the mafic lavas of boninitic affinity in the northern portion of the ISB. The 3721 Ma age for G12/39 is the first direct age from an ISB ultramafic lava flow confirming this unit formed simultaneously to the surrounding mafic volcanic rocks of boninitic affinity.

5.2 Metamorphism and metasomatic alteration

The Pope locality samples include antigorite serpentinites with pseudomorphic cumulate textures that are crosscut by magnesite veins and minor talc alteration, and a magnesite-talc schist (G12/39), which preserves some antigorite and faint pseudomorphic globules (Fig. 3f-g-h). The antigorite serpentinites and the talc-schist also have similar concentrations in the least mobile trace elements (e.g., REE, Fig. 4b) providing strong evidence they formed by progressive metasomatism of a common protolith (section 5.1). The ubiquitous presence of excess ^{40}Ar (Fig. 10) indicates that some noble gases were introduced into all of the investigated samples during regional metamorphism. However, several lines of evidence suggest earlier Eoarchean seawater-derived geochemical signatures including O and H isotopes (Pope et al., 2012) and possibly halogens have been preserved in some of the serpentinites. This section evaluates how the Eoarchean signature was introduced and potentially preserved.

5.2.1 Serpentinisation of the cumulate protolith on the seafloor and/or during regional metamorphism

The investigated unit is pillowed in its upper portion (Fig. 2) indicating subaqueous emplacement and suggesting that initial serpentinisation of the olivine rich cumulate is likely to have occurred on the seafloor at ~3720 Ma. Al-bearing antigorite is stable between ~ 350°C and 650°C and over a wide range of pressures extending from the seafloor to eclogite facies conditions (Bromiley and Pawley, 2003; Deschamps and Hattori, 2013 and references therein). The Pope locality antigorites are rich in Al and Fe (Table 3) and antigorite with similar Fe concentrations have been reported in samples recovered from Atlantis Massif drill cores where antigorite precipitated from high temperature fluids by replacement of olivine close to the seafloor (Beard et al., 2009). Alternatively, we cannot preclude that antigorite in the investigated samples replaced low temperature polymorphs of serpentine during regional metamorphism. Peak metamorphic conditions in the western arm of the northern domain of the ISB were estimated at 620°C (Domain IV; Rollinson, 2003) with pressure conditions exceeding 600 MPa, the lower limit to stabilize kyanite in this part of the ISB (Rollinson, 2002). These conditions are within the critical range of antigorite stability and the samples preserve no petrologic indications of antigorite breakdown. If the antigorite formed by replacement of a lower temperature polymorph, the phase transition is likely to have occurred under nearly fluid absent conditions. This is because Fe-rich serpentine has been shown to be unstable in fluid dominated systems and the study of Beard et al. (2009) demonstrates desilication of serpentine in the presence of fluids leads to formation of magnesian serpentine accompanied by magnetite. The lack of oxides within the antigorite globules (Fig. 3) as well as the elevated Fe concentrations of the antigorite at the Pope locality therefore favour a lack of re-equilibration under open system conditions. In addition, most of the spinel grains present in the best-preserved antigorite-serpentinites (G12/36 and G12/38) have extremely low Mg# and high Cr# that are characteristic of metamorphic spinels (e.g. Barnes and Roeder, 2001). The Fe-magnetite in these samples are interpreted as cumulate Cr-spinel that were reset by isomorphic recrystallization during the main stage of antigoritisation. In either scenario, seafloor serpentinisation under hydrothermal conditions or antigoritisation of seafloor serpentinites in a rock dominated system, antigorite could preserve some of the volatiles signatures acquired

from the Eoarchean seawater-derived fluids.

5.2.2 Carbonation and introduction of the excess ^{40}Ar component

In a metasomatic event post-dating antigoritisation, CO_2 bearing fluids locally infiltrated the serpentinites resulting in various degrees of antigorite replacement by talc and magnesite. Alteration of serpentinite by CO_2 -bearing fluids has been investigated both experimentally (e.g., Klein and Garrido, 2011) and in natural samples (e.g., Hansen et al., 2005). The absence of quartz in the Pope locality samples indicates that carbonation of the serpentinitised protolith did not go to completion but culminated in a talc-magnesite assemblage, which might be explained by elevated alteration temperatures ($> 200^\circ\text{C}$) shifting the talc-quartz-magnesite equilibrium to very high $a\text{CO}_{2,\text{aq}}$ during serpentinite carbonation (Klein and Garrido, 2011). The reaction $\text{antigorite} + \text{CO}_2 \rightarrow \text{magnesite} + \text{talc} + \text{H}_2\text{O}$ is observed at the margins of the ultramafic lenses, which have a schistose texture and were most strongly affected by external fluid infiltration and carbonation. In contrast, the central part of the outcrop preserves antigorite serpentinites with pseudomorphic cumulate textures (G12/36 and G12/38) where carbonate and talc is mostly limited to veins and to the inter-cumulus space between antigorite globules (Fig. 3). This demonstrates a much lower degree of fluid infiltration partly explaining how Eoarchean O and H isotope signatures might be preserved (Pope et al., 2012). Furthermore, samples most affected by carbonation contain spinel grains that recrystallized during the carbonation event, in equilibrium with talc and magnesite. The increased Cr content in the magnetite recrystallized during carbonation (Fig 5c) probably reflects local re-equilibration between the different mineral assemblages. Potential Cr sources include destabilization of Cr-rich chlorite and/or of Cr-bearing antigorite (Table A3, electronic supplement). Importantly, the whole rock Cr content is not changed by sample carbonation indicating redistribution of Cr occurred at a localised scale. The variability in grain size and spinel composition between the well-preserved antigorite and the talc-magnesite schist also suggest a much lower degree of fluid infiltration in the central part of the Pope locality outcrop. It is however inescapable that the presence of excess ^{40}Ar in all investigated samples demonstrates infiltration of some metamorphic fluid into the serpentinites following seafloor alteration and this is likely to have occurred during carbonation.

The high $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratios of 1644-8059 (total fusion; Table 5) in the Pope locality serpentinites and talc schist are characteristic of metamorphic fluids that contain crustally-derived excess $^{40}\text{Ar}_\text{E}$ rather than the seawater-derived fluids. In contrast, modern seafloor serpentinites are dominated by atmospheric noble gases with $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ of close to the atmospheric/seawater ratio of 299, or with slightly elevated $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratios of up to ~340, which could indicate the presence of a minor magmatic component in the seafloor alteration system or fluid interaction with K-rich sediments (Kendrick et al., 2013). In contrast, metamorphosed serpentinites in ophiolites can have elevated $^{40}\text{Ar}/^{36}\text{Ar}$ ratios as a result of fluid interaction and chemical exchange between greater varieties of subduction zone lithologies (e.g., Kendrick et al., 2018b). The extreme $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratios of up to ~16,000 in the Pope locality samples and up to ~37,000 in the Ameralik dykes indicate the presence of excess ^{40}Ar , which is consistent with previous $^{40}\text{Ar}/^{39}\text{Ar}$ dating studies at Isua showing many minerals and rocks have been affected by excess ^{40}Ar and/or ^{40}Ar loss (Pankhurst et al., 1973; Roskamp and Schultz, 1985). The $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratios reported for the Isua serpentinites are higher than is typical of most modern lithologies because ^{40}K has a half-life of 1.25 Gyr, meaning that for any given K content, the $^{40}\text{Ar}^*$ production rate was ca. 8 times higher at 3.7 Ga. The high production rate favours rapid accumulation of excess radiogenic $^{40}\text{Ar}^*$ in fluid interacting with K rich lithologies. In addition, the amphibole-bearing serpentinite G12/37 has a lower $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ than other antigorite-serpentinites from the same outcrop (Fig. 10a), potentially indicating some local variation in alteration fluids.

The introduction of excess ^{40}Ar does not however preclude preservation of seawater-derived halogen signatures. Halogens in serpentinites have much higher concentrations (e.g., 10s to 100s of $\mu\text{g/g}$ Cl) and previous studies suggest that I and Br can, like Cl, substitute for the OH group in serpentine (e.g. Kendrick et al., 2013). In contrast, the scarce noble gases (~ pg/g range) are mobilized by diffusion and trapped interstitially or within vacant ring sites in the serpentine lattice (Jackson et al., 2013). If the O and H isotopic signatures in the antigorite from the Pope locality are representative of Eoarchean seawater-derived fluids (Pope et al., 2012), halogens hosted in the same structural site are likely to have also retained the Eoarchean seawater signatures.

5.2.3 Timing of metamorphic/metasomatic events

The absolute timing of serpentinitisation and carbonation at the Pope locality likely spans from initial serpentinitisation on the seafloor at ~3720 Ma (section 5.2.1, Fig. 8) to later carbonation during tectonic intercalation and assembly of the northern terrane of ISB before ca. 3660 Ma, or possibly during one of the tectono-thermal events that took place between ~ 3650 to 3510 Ma but before the emplacement of the Ameralik dykes. The lower age limit must be greater than ~3500 Ma, the age of Ameralik dykes as the dykes are not affected by carbonation (Nutman et al., 1996; Nutman et al., 2002; Crowley et al., 2002).

Large scale infiltration metasomatism is particularly well developed in the oldest southern portion of the ISB (e.g., Rose et al., 1996, Rosing et al., 1996) and probably occurred in the early Eoarchean contemporaneously with regional scale Eoarchean metamorphism and intrusion of tonalities (e.g., Frei et al., 2001). This study shows that the northern portion of the ISB has also been affected by carbonate alteration.

Much of the ISB was influenced by later Archean metamorphic events (2500-2800 Ma) (e.g., Rollinson, 2003), which resulted in local partial resetting of some of the isotope systems including U-Pb, Pb-Pb and K-Ar (e.g., Frei et al., 1999; Frei and Rosing, 2001; Gruau et al., 1996; Nutman and Collerson, 1991; Pankhurst et al., 1973). Amphibolitisation of the Ameralik dykes studied here and sampled within the orthogneisses exposed at the northern border of the ISB is associated with these Neoproterozoic events (e.g., Pankhurst et al., 1973).

5.3 Halogen signatures from the Eoarchean Ocean?

The serpentinite and talc schists from the Pope locality preserve a range of halogen concentrations and Br/Cl and I/Cl ratios. The antigorite separates from samples lacking amphibole and least affected by carbonate alteration (G12/36, G12/38) have the highest concentrations of halogens and preserve the lowest measured Br/Cl and I/Cl ratios (Fig. 11a and Table 6), which are considered representative of the antigorite-serpentinites composition prior to carbonation (section 5.2.1). Previous studies have suggested that serpentine traps halogens (Cl, Br, I) with relative abundance ratios close to the serpentinitising fluid (e.g., Kendrick et al., 2013) implying that the elemental ratios of halogens in the best preserved serpentinites from the Pope locality could be close to the composition of the Eoarchean serpentinitising fluids (Fig. 11a). In this section, the halogen

composition of antigorite serpentinites from Isua is compared to Phanerozoic analogues including seafloor serpentinites dominated by chrysotile and lizardite, and antigorite serpentinites formed by replacement of chrysotile/lizardite.

The Isua antigorite serpentinites have much lower Br/Cl compared to most modern seafloor serpentinites, but have Br/Cl and I/Cl similar to antigorite serpentinites from the Cerro del Almirez massif (Fig. 11a; Kendrick et al., 2018b). Relatively few studies have investigated antigorite-serpentinites together with related seafloor serpentinites (e.g., Pagé and Hattori, 2017; Kendrick et al., 2011; Kendrick et al., 2013). However, modern serpentinites formed on the seafloor tend to have Br/Cl ratios similar to seawater and relatively low I/Cl ratios of about ~10 times seawater (Fig. 11a). In contrast, serpentinites in ophiolites and forearc settings have elevated Br/Cl and I/Cl ratios that overlap sedimentary pore waters reflecting the addition of Br and I from sedimentary sources (Fig. 11a; e.g., Kendrick et al., 2013). Recent work shows that up to ca. 90 wt. % of the Cl present in chrysotile/lizardite can be lost during the antigorite transition if fluids are present (Kodolányi and Pettke, 2011) and studies of Phanerozoic antigorite serpentinites show that loss or gain of others halogens during antigoritisation is possible (Pagé and Hattori, 2017, Pagé et al., 2018; Kendrick et al., 2018b). However, antigorite-serpentinites from the high pressure Erro-Tobbio ultramafic units preserve Br/Cl and I/Cl similar to their lower grade counterparts (John et al., 2011; Kendrick et al., 2011; Kendrick et al., 2013) (Fig. 11a). These examples suggest the presence of external fluid might exert a major control on halogen loss and/or fractionation during antigoritisation. Antigorite from Isua and Cerro del Almirez have similar Br/Cl and I/Cl (Fig. 11a), however the interpretation of these values is different. There are multiple lines of evidence showing the antigorite-serpentinites at Cerro del Almirez exchanged with surrounding lithologies during both antigoritisation and subsequent metamorphism (e.g, Kendrick et al., 2018; Marchesi et al., 2013). In contrast, the Isua antigorite serpentinites are interpreted to have formed either on the seafloor or by replacement of a lower temperature polymorph in a rock dominated system (section 5.2.1), and preserve high concentrations of halogens. The Pope locality antigorite serpentinites are therefore expected to have preserved Br/Cl and I/Cl ratios close to the original seawater-derived serpentinitising fluid. In addition, if the O and H isotopic signatures in the antigorite from the Pope locality are representative of Eoarchean seawater-derived fluids (Pope et al.,

2012), halogens hosted in the same structural site are likely to have also retained the Eoarchean seawater signature. This implies the measured Br/Cl ratio of $0.7\text{--}1.1 \times 10^{-3}$ should be close to the composition of serpentinising fluids derived from Eoarchean seawater and the I/Cl ratio of $28.9\text{--}58.2 \times 10^{-6}$ represents an upper limit for Eoarchean seawater.

5.4 Implications for surface processes on the early Earth

The halogens F, Cl and Br are considered 'conservative' in modern seawater meaning that they have constant concentrations, whereas the concentration of I, which is an essential element for life, typically varies from ~50 to 60 ng/g and is correlated with other seawater nutrients (Elderfield and Truesdale, 1980; Huang et al., 2005). The extent to which seawater concentrations of Cl, Br and I have varied over geological time is unknown. Assuming halogens and water outgassed early in Earth's history (e.g. by catastrophic outgassing e.g., Holland, 1984; Porcelli and Turekian, 2003 and references therein), the salinity of the earliest ocean would have been influenced by the amount of liquid water present in the ocean and the size of the evaporite reservoir. Furthermore, because the halogens (Cl, Br, I) have similar mantle incompatibility (Kendrick et al., 2017), the surface reservoirs on the early Earth would be expected to have Br/Cl and I/Cl similar to the composition estimated for the Primitive mantle. Following the emergence of halogen biogeochemistry, possibly marking the emergence of life (Crockford, 2009), the Br/Cl and I/Cl ratios of the seawater must have been controlled by the amount of Cl stored in evaporites (which preferentially exclude Br and I, Fig. 11a) and the amount of iodine and bromine stored in organic matter (e.g., Muramatsu et al., 2007; Kendrick 2018). The halogen composition of the seawater through time can therefore provide important constraints on the environmental and biological evolution of Earth, by indicating surface conditions favouring formation and preservation of evaporite deposits and by recording the accumulation of biomass in the sedimentary record (e.g., Channer et al., 1997; Foriel et al., 2004).

The Br/Cl ratios of 0.0007–0.0011 implied for the seawater derived serpentinising fluids at the Pope locality are 3–5 times lower than the modern seawater value of 0.0035 (Fig. 11a). Modern seawater has been estimated to contain $37 \pm 5\%$ of surface Cl, with a further $22 \pm 5\%$ of surface Cl present in evaporites (Kendrick et al.,

2017). The total mass of Cl stored in brines and evaporites on Earth is difficult to estimate, however, previous workers have suggested that dissolving the Cl stored within continental settings would make the early Archaean ocean up to 2 times more saline than the modern ocean (Knauth, 2005). These figures mean it is unlikely that the Br/Cl ratios of the Pope locality serpentinites are representative of Eoarchean seawater, as dissolving all the evaporites on Earth would reduce the Br/Cl ratio of modern seawater by a factor of less than ~2. Furthermore a recent study of fluid inclusions suggested that the salinity of the Archaean ocean was similar to the modern ocean (Marty et al., 2018). Therefore, the low Br/Cl ratios of the Isua serpentinites cannot be representative of Eoarchean seawater. Instead, the low Br/Cl ratio of the serpentinites is probably representative of seawater-derived hydrothermal fluids with slightly fractionated Br/Cl, which might result from phase separation or fluid-rock reactions (e.g., Wu et al., 2012).

In contrast to Br/Cl, the I/Cl ratios of the Pope locality serpentinites ($29\text{--}58 \times 10^{-6}$) are however still interpreted as an upper limit for Eoarchean seawater. This is justified because all modern serpentinites have I/Cl higher than seawater (Kendrick et al., 2013). Eoarchean seawater is therefore suggested to have had an I/Cl ratio of less than ($29\text{--}58 \times 10^{-6}$), which is substantially lower than the primitive mantle value of $270 \pm 120 \times 10^{-6}$ (Kendrick et al., 2017). Anoxic Eoarchean seawater would have been dominated by iodide (rather than iodate, which dominate modern seawater) and iodide is excluded from most alteration minerals (Kendrick, 2019). The low I/Cl ratio of Eoarchean seawater is most easily explained if a significant portion of the surface iodine inventory was already incorporated into organic-rich sediments in the Eoarchean. It is impossible to unambiguously quantify the amount of iodine in organic sediments in the Eoarchean from the available data; however, if the salinity of the Eoarchean ocean was similar to the modern ocean, then a maximum seawater I/Cl ratio of $29\text{--}58 \times 10^{-6}$, that is approximately 10-20 times higher than modern seawater, implies 10-20 times less I was stored in organic-rich sediments in the Eoarchean than today. If this was the case, then considering the shorter period of time that had passed for sediment accumulation, there must have been significant biological activity in the Eoarchean oceans and storage of I-rich material in Eoarchean sediments.

The interpretation that abundant Eoarchean life sequestered I into the lithosphere is supported by multiple other types of chemofossil evidence for life identified in the ISB (e.g., Rosing, 1999; Dauphas et al., 2004;

Craddock and Dauphas, 2011; Stüeken, 2016) and including proposed but contested 3.7 Ga stromatolites (Nutman et al., 2016; Allwood et al., 2018; Nutman et al., 2019). Iodine probably played a critical evolutionary role in the development of life on Earth (e.g., Crockford, 2009). Iodine acts as a powerful antioxidant and is crucial to all living organisms including humans (Fuge, 1996; Fuge and Johnson, 2015). Crockford, (2009) suggests that the earliest anaerobic cells could have used iodine in their biochemical pathways and consequently argues that iodine is a potential chemofossil for the emergence and/or evolution of life.

Finally, this study exemplifies the promising potential of halogen elemental abundances to investigate Eoarchean seawater composition in metasomatic minerals. Precise measurements of Cl, Br and I in rocks and fluid inclusion samples are scarce in the geological record and the evolution of the halogen signature of the ocean through time is not well-constrained. This approach can be extended to other Archaean lithologies as well as other Archaean terranes to evaluate the global and local factors influencing the halogen ratios. A better understanding of the modern processes controlling halogen mobility and experimental constraints on halogen partitioning between fluids and different minerals will also improve our interpretation of the Archaean surface environment.

6 Conclusions

A detailed petrological and geochemical study of well-preserved antigorite serpentinites from the ISB, indicates that the protolith of the ultramafic rocks is a cumulate (olivine + Cr-spinel $\pm$ orthopyroxene) extracted from a mafic flow pillowed in its upper portions. *In situ* U-Pb dating and trace element measurements of rare zircons extracted from the ultramafic rocks demonstrate an Eoarchean age of 3721 ± 27 Ma.

Comparison of halogens and noble gases in antigorite, carbonated schists and amphibolitised dykes confirm that metasomatic minerals have the potential to complement the fluid inclusion record of Archean surface volatiles. Serpentine appears to be particularly well-suited as a paleo-environmental proxy for halogens (this study) and stable isotopes (Pope et al., 2012). The Eoarchean antigorite serpentinites yielded halogen signatures strikingly similar to modern analogues, which provides new constraints on the composition of seawater-derived hydrothermal fluids. Importantly, the lowest measured I/Cl ratio of $29 (\pm 2) \times 10^{-6}$, interpreted

as a maximum value for the Archaean ocean is an order of magnitude lower than primitive mantle estimates, indicating the need for I fractionation from Cl in the Archaean ocean. As the concentration of iodine (relative to Cl) in modern seawater is dominantly controlled by organic matter, the I/Cl ratios in the best preserved serpentinites are interpreted as indicating a significant biomass was already present by 3700 Ma and in accord with other lines of evidence for early life recorded in the ISB rocks.

In contrast with halogens, the noble gases have been strongly overprinted by later metamorphic fluids, which also perturbed the halogen signatures of talc-carbonate schists. The variation in halogen and noble gas signatures of antigorite-serpentinites and talc-carbonate schists from Isua is explained by variably overprinting an original hydrous signature preserved in antigorite by later ^{40}Ar -rich and CO_2 bearing metamorphic fluids.

This study also highlights the need of expanding both experimental and natural data on halogen partitioning during geological processes. This is particularly true for iodine, the least abundant of the halogens, which shows potential as a novel biomarker for tracing the emergence and evolution of the biomass through Earth history.

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Figure 1: Geological map and sample location.

Geological map showing the field relations between the Pope locality and the southern outcrop in the western arm of the Isua supracrustal belt (modified from Nutman and Friend, 2009). The two Ameralik dyke samples included in this study are from the orthogneiss outcropping at the northern border of the Isua supracrustal belt which consists mainly of 3720-3690 Ma tonalites (outside of the map area, see full map in Nutman and Friend, 2009). Note that the coordinates do not coincide with the WGS84 datum used in GPS sample positions from 1997 onward but are from Nutman (1986) 1:40,000 scale map.

Figure 2: Relic pillow from the southern outcrop.

Photograph of a relic pillow (P) from the southern outcrop that indicates a submarine volcanic origin (pen in lower left for scale).

Figure 3: Transmitted light and BSE images of Pope locality samples.

a) Sample G12/36 has a globular texture with magnetite grains (Cr-Mgt) surrounding antigorite globules pseudomorphed after olivine and/or orthopyroxene. **b)** Backscattered electron image (BSE) of sample G12/36 showing antigorite (Atg) globules surrounded by a fine grained chlorite (Chl) and antigorite matrix and locally by magnesite (Mgs) with minor dolomite. **c)** Cross polarized image (XPL) of an antigorite globule pseudomorphed after olivine/pyroxene and composed of radiating blades of antigorite (G12/36). The pseudomorphitic antigorite globule is locally rimmed by minor talc. Chlorite (Chl) and minor talc (Tlc) on the left and magnesite (Mgs) on the right bottom corner, sporadic throughout the sample. **d)** Plane polarized (PPL) image of G12/38 with smaller antigorite globules (heterogeneous grainsize distribution in the protolith). Magnesite veins (Mgs-vein) crosscut the Atg-globules and fine grained alteration minerals commonly surrounds them. **e)** XPL image, same as d). **f)** BSE image of G12/39 dominated by fine grained talc (Tlc) and magnesite (Mgs) replacing antigorite globules and by recrystallized oxides (Cr-Mgt). **g)** PPL image of G12/39 with faint globules composed of talc (Tlc) and magnesite (Mgs). **h)** XPL image of G12/39. Faint globules (composed of Tlc + Mgs) are surrounded by a dark rim along which Atg and Chl blades are often preserved together with fine grained oxides.

Figure 4: Whole rock REE and selected trace elements of the Isua samples and magmatic trends at Isua.

a) Selected trace elements in the Isua samples from the Pope locality and Ameralik dykes have been normalized to the primitive mantle (PM) values of Palme and O'Neill (2003). **b)** Rare earth element patterns for the Isua samples, normalized to CI chondrite values of Palme and O'Neill (2003). **c)** The Isua trace element patterns are compared to literature data for the basaltic and boninitic magmatic trends at Isua. The basaltic and boninitic magmatic trends at Isua have been compiled from data in Polat et al., (2002), Polat and Hoffman (2003), Szilas et al., (2015) and Nutman et al., (2015). The median value is represented as a bold line and the shaded area corresponds to the interquartile range (IQR). n = number of analyses included in the median calculation. **d)** REE patterns of the boninitic and basaltic magmatic trends at Isua. See c) for references. The Isua samples of the Pope locality have lower trace element concentrations compared to the magmatic volcanic rocks at Isua, but they share many anomalies and similarities with the amphibolites of boninitic affinity.

Figure 5: Spinel chemistry.

a) $\text{Cr}\#$ vs. $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ variation plot of the Isua spinel as a petrogenetic indicator of the source rock. Fields for boninite, and arc picrites are from Rollinson (2005) and the harzburgite (Harz.), chromitite (Chtt), lherzolite (Lherz.) and chromite composition occurring in early Archaean layered gabbro-peridotite are from Rollinson (2007) and references therein. Most analyses are plotting at high $\text{Cr}\#$ and $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ indicating resetting during alteration. The preserved core in G12/39 is incompatible with a mantle origin. **b)** BSE image of the preserved Al-chromite core in sample G12/39, the only Al bearing oxide grains observed in the available thin sections. It is surrounded by a Cr-magnetite rim containing talc and magnesite micro-inclusions. **c)** Chemical classification diagram for the spinel group minerals in the four ultramafic samples analyzed in this study showing progressive Cr increases in the smallest recrystallized oxides in highly carbonated samples.

Figure 6: Antigorite chemistry.

Antigorite composition in the Isua serpentinite, atom per formula unit normalized to 116 oxygens, corresponding to the ideal antigorite polysome ($m=17$) (Mellini et al., 1987). The antigorite endmembers in the MSH (atg^*) and MASH ($atgts^*$) systems have been calculated by (Padrón-Navarta et al., 2013). The Isua antigorite have Al content clustering around the maximum Al stability (4 Al apfu, corresponding to 4.5 wt. % Al_2O_3) calculated in antigorite for a pressure range of 0.3-2 Gpa (Padrón-Navarta et al., 2013). The composition of most analyses cannot be explained by Tschermak's substitution. Isua antigorite have an excess in Al at any given Si content (a) and a deficiency in divalent cations occupying the octahedral site (b).

Figure 7: G12/39 zircons morphology and internal textures.

Cathodoluminescence (CL) and secondary electron (SEI) images of the zircons extracted from G12/39 with location of the shrimp U-Pb dating spots. Reported dates are $^{207}\text{Pb}/^{206}\text{Pb}$ dates preferred for Archaean zircons with 1σ analytical errors. Note the presence of cracks and inclusions of magnesite in Zr-3 and Zr-4 that coincides with slightly younger ages.

Figure 8: Terra-Wasserburg $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{238}\text{U}/^{206}\text{Pb}$ for the Isua zircons in G12/39.

Analytical uncertainties of single analyses are portrayed at the 1σ level. The Concordia age was calculated with the Isoplot Excel add-in of Ludwig (2001) and errors are given at the 95% confidence level. The Concordia age includes all data points and the preferred weighted mean average age was calculated based on the older dates recorded in the two analyses on Zr-2.

Figure 9: Rare earth element patterns of the G12/39 zircons.

REE composition of zircons analyzed by SHRIMP RG and normalized to CI values from Palme and O'Neill (2003). The Temora-2 igneous zircon (Black et al., 2004) analyzed during the same Shrimp session are plotted as a reference. Analyses on fragment Zr-2 were taken from core (Zr2-1) to rim (Zr2-3) and show a progressive decrease in REE concentrations from the center to the rim. The G12/39 zircons have fractionated REE patterns with significant Eu negative anomalies closely matching igneous zircons trace element patterns.

Figure 10: Ar isotopic signatures and concentrations.

a) $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{40}\text{K}/^{36}\text{Ar}$ (K-Ar isochron diagram) for the Isua serpentinites and Ameralik dyke separates (errors are portrayed at the 1σ level). The step heating data of the antigorite serpentinites lie on trend indicating K-Ar maximum ages of 8.9-9.3 Ga. In contrast G12/37 and the amphibole fraction G11/28 are lying on parallel trends indicating maximum ages of ~ 3.8 Ga. The choice of the $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratio, either modern atmospheric (299) or estimated Archaean (~ 143) (Pujol et al., 2013) for the 3.7 Ga reference isochron has no implications for the interpretation of the results. Age information and determination of the $^{40}\text{Ar}/^{36}\text{Ar}_{\text{initial}}$ ratio are hindered by the ^{40}Ar excess component in all samples, however amphibole bearing samples are less perturbed than serpentinites (see main text). **b)** ^{36}Ar concentrations in the Isua serpentinites compared to available literature data for sea-floor, fore-arc and ophiolitic serpentinites (Kendrick et al., 2013), for antigorite bearing serpentinites and chlorite harzburgite (Kendrick et al., 2011, Kendrick et al., 2018b), as well as mantle wedge peridotites (Sumino et al., 2010; Kobayashi et al., 2017). The Isua serpentinites plot at the lower end of the ^{36}Ar concentration range (errors are portrayed at the 1σ level).

Figure 12: Major and trace element variations of the Pope locality serpentinites and talc-schist.

Isua magmatic trends for mafic and ultramafic rocks of boninitic and tholeiitic chemical affinity are compared to the Isua serpentinites of this study. Data for volcanic rocks are from Polat et al., (2002), Polat and Hofmann (2003) and Szilas et al., (2015) whereas data for cumulate rocks are exclusively from Szilas et al., (2015). **a)** $\text{Al}_2\text{O}_3/\text{TiO}_2$ vs. MgO variation diagram based on anhydrous major elements showing high MgO compositions indicative of a cumulate origin and elevated $\text{Al}_2\text{O}_3/\text{TiO}_2$ with most samples having an affinity for the magmatic rocks of boninitic chemical affinity. **b)** MgO/SiO_2 vs. $\text{Al}_2\text{O}_3/\text{SiO}_2$ including the terrestrial array ranging from depleted mantle (DM) to high Mg and low Al mantle residue. The terrestrial array and serpentinite database are from Deschamps and Hattori (2013) and references therein. The Pope locality samples are clearly deviating from the mantle array. **c)** Cr vs. Ni for Isua samples compared to the Isua magmatic trends with clear accumulation of Cr and close resemblance with the Isua cumulate of boninitic chemical affinity. **d)** Th/Yb vs. Nb/Yb variation diagram of Pearce (2008) showing affinity of the serpentinites in this study with mafic volcanics of boninitic character. Arrows represent a subduction component (s), crustal contamination (c) and within plate fractionation (w).

Figure 13. Trace elements in zircon as petrogenetic indicators.

Petrogenetic interpretation diagrams for zircons are based on trace element content and ratios. The zircon database used in the variation diagrams is taken from (Carley et al., 2014) and references therein. The fields defined in a) and b) are from (Carley et al., 2014) and the fractionation arrows in c)-d) and e) are from (Grimes et al., 2015). The zircons from sample G12/39 have U, Yb and U/Yb signatures that are typical of zircons crystallizing in oceanic environments from anhydrous melts (a-b). G12/39 zircons have elevated Ti content as well as U/Yb and Gd/Yb ratios that indicate a high temperature unfractionated melt source (c-d-e).

Table 1. Major and trace element data of the Pope locality samples and the Isua Ameralik dykes.

	Pope Locality samples and southern outcrop					Ameralik dykes	
	G12/36	G12/38	G12/37	G12/39	G12/66	G11-27	G11-28
Major element (wt. %), XRF							
SiO ₂	35.4	33.1	36.2	34.6	40.6	48.9	49.5
TiO ₂	0.09	0.09	0.11	0.05	0.09	0.89	0.87
Al ₂ O ₃	5.1	4.3	3.6	3.8	6.1	14.5	15.0
Fe ₂ O ₃	15.5	15.8	10.8	8.3	10.4	13.1	13.0
MnO	0.10	0.13	0.13	0.11	0.10	0.20	0.20
MgO	31.4	32.5	32.5	33.3	32.5	7.6	7.7
CaO	0.8	0.01	1.3	0.1	0.2	11.2	11.1
Na ₂ O	0.07	0.11	0.15	0.08	0.11	1.82	1.53
K ₂ O	0.003	0.004	0.011	0.002	0.008	0.143	0.179
P ₂ O ₅	bdl	bdl	0.003	bdl	bdl	0.061	0.059
LOI	11.6	13.3	14.2	19.8	10.7	0.6	1.0
Total	100.0	99.4	99.0	100.0	100.9	99.2	100.2
Mg #	80.0	80.3	85.7	88.9	86.1	53.6	54.0
Trace element (µg/g), solution ICP-MS							
Li	0.05	0.1	4.3	0.1	0.1	4.1	16.8
Sc	16.1	11.5	12.4	21.0	22.9	43.6	43.7
Ti	472	502	692	286	470	5368	5126
V	93	129	80	69	72	277	269
Cr	5275	16535	11295	7764	3735	277	278
Co	144	146	124	99	109	51	51
Ni	268	462	496	531	336	45	45
Cu	0.9	2.8	3.3	7.6	0.9	48.5	47.7
Zn	63.2	110.3	103.4	61.0	56.0	81.9	83.0
Ga	3.95	4.52	4.14	3.17	4.14	16.30	15.90
Rb	0.151	0.106	0.341	0.062	0.191	3.106	2.897
Sr	0.9	0.1	1.2	0.1	0.2	58.1	55.9
Y	1.24	0.92	2.06	1.11	1.43	16.48	15.94
Zr	0.86	1.27	5.72	2.41	0.48	40.14	36.02
Nb	0.06	0.06	0.23	0.03	0.15	2.09	1.96
Cd	0.01	0.00	0.02	0.00	0.01	0.15	0.14
Sn	0.11	0.13	0.19	0.09	0.10	0.57	0.57
Sb	0.18	0.17	0.12	0.08	0.11	0.02	0.08
Cs	0.07	0.05	0.06	0.02	0.14	0.12	0.03
Ba	0.62	0.37	0.52	0.37	0.26	20.90	19.86
La	0.15	0.04	0.16	0.06	0.03	2.43	2.33
Ce	0.18	0.10	0.49	0.15	0.08	6.36	6.18
Pr	0.04	0.02	0.09	0.03	0.01	1.20	1.17
Nd	0.19	0.09	0.51	0.12	0.07	6.05	5.86
Sm	0.06	0.03	0.21	0.04	0.03	2.03	1.96
Eu	0.01	0.00	0.06	0.00	0.01	0.69	0.66
Gd	0.09	0.05	0.28	0.07	0.06	2.56	2.46
Tb	0.02	0.01	0.06	0.02	0.02	0.49	0.47
Dy	0.18	0.12	0.39	0.16	0.18	3.32	3.19
Ho	0.05	0.03	0.09	0.04	0.05	0.73	0.70
Er	0.16	0.13	0.25	0.15	0.21	2.10	2.01
Tm	0.03	0.02	0.04	0.03	0.04	0.32	0.31
Yb	0.21	0.18	0.26	0.21	0.36	2.06	1.97
Lu	0.04	0.03	0.04	0.04	0.06	0.31	0.30
Hf	0.04	0.06	0.19	0.09	0.03	1.39	1.27
Ta	0.01	0.01	0.02	0.01	0.01	0.13	0.13
Pb	0.06	0.11	0.77	0.03	0.08	1.68	3.22
Th	0.01	0.01	0.05	0.01	0.02	0.26	0.26
U	0.01	0.04	0.01	0.03	0.01	0.09	0.07
La _N /Yb _N	0.49	0.14	0.42	0.21	0.06	0.82	0.83

La _N /Sm _N	1.71	0.77	0.47	0.90	0.59	0.76	0.76
Gd _N /Yb _N	0.33	0.22	0.89	0.29	0.14	1.01	1.02
Eu/Eu*	0.51	0.36	0.73	0.12	0.65	0.91	0.91
Ce/Ce*	0.55	0.91	0.96	0.95	0.91	0.90	0.90

Trace elements reported were obtained by the low temperature hot-plate digestion procedure excepted for Zr and Hf in samples G12/36, G12/37, G12/38 and G12/39 (for these samples, concentrations are from the solution prepared by pressurized digestion in Parr® bombs). CI values for normalisation of the REE ratios from (Palme and O'Neill, 2003). N = chondrite normalised trace element concentrations, bdl = below detection limit, AN = anhydrous.

Table 2. Average composition of the spinel in the Isua serpentinites from the Pope locality.

	G12/36		G12/37		G12/38		G12/39		G12/39	
	<i>N</i> =18		<i>N</i> =20		<i>N</i> =14		<i>N</i> =12		<i>Preserved Al-spinel</i>	
Major (wt. %)	Avg.	STDV	Avg.	STDV	Avg.	STDV	Avg.	STDV	<i>Core</i>	<i>Rim</i>
SiO ₂	bdl	-	bdl	-	0.12 ^{<i>N</i>=2}	0.03	bdl	-	0.11	0.05
MgO	0.13 ^{<i>N</i>=9}	0.04	0.16	0.05	0.13 ^{<i>N</i>=12}	0.03	0.13	0.07	2.59	0.14
Al ₂ O ₃	0.11 ^{<i>N</i>=4}	0.04	0.14	0.03	0.11 ^{<i>N</i>=11}	0.03	0.20	0.06	15.57	0.17
MnO	0.11 ^{<i>N</i>=13}	0.10	0.42	0.05	0.04	0.01	0.17	0.03	0.36	0.25
FeO ^T	85.90	3.45	68.95	2.22	75.81	3.01	69.58	3.07	31.83	68.93
Cr ₂ O ₃	5.79	3.61	23.09	2.50	15.81	3.34	22.12	3.19	46.75	24.40
TiO ₂	0.33	0.40	0.47	0.09	0.46	0.20	0.70	0.46	0.16	0.38
CaO	bdl	-	bdl	-	bdl	-	bdl	-	bdl	bdl
NiO	0.19	0.02	0.35	0.03	0.30	0.02	0.17	0.02	bdl	0.17
Total	98.72	0.68	98.07	0.40	97.23	0.74	97.38	0.41	98.73	97.63
Cr #	0.99	0.03	0.99	0.001	0.99	0.004	0.99	0.002	0.67	0.99
Mg #	0.004	0.004	0.01	0.003	0.01	0.003	0.01	0.004	0.14	0.01
Fe ³ /(Cr+Al+Fe ³)	0.91	0.06	0.64	0.04	0.75	0.05	0.65	0.05	0.03	0.62

Spinel compositions were normalised to three cations per formula unit. N = number of chemical analyses per samples. See electronic supplements Table A3 for analyses of minor ilmenite. bdl = below detection limit.

Table 3. Average antigorite composition in the serpentinites and talc schist from the Pope locality

Isua, Pope Locality											Cerro del Almirez ¹		Malenco ¹
Sample ID	G12/36		G12/38		G12/37		G12/39		A195-20	A106-43	Mg159		
Source rock	Atg.-serp		Atg.-serp		Atg.-serp-tlc-am.		Mgs-tlc s.		Atg.-serp	Chl.-serp.	Atg.-serp		
	globules N=22		matrix N=7		N=16		N=6		N=5				
Major (wt. %)	Avg.	STDV	Avg.	STDV	Avg.	STDV	Avg.	STDV	Avg.	STDV			
SiO ₂	41.91	0.86	41.08	1.24	40.74	0.52	42.38	1.56	40.13	0.32	41.16	42.54	42.75
MgO	34.10	0.51	33.01	0.49	33.88	0.25	35.81	1.66	32.06	0.16	37.60	37.22	38.40
Al ₂ O ₃	2.76	0.93	4.72	1.13	3.76	0.47	2.85	0.53	4.15	0.37	3.58	2.73	1.39
MnO	0.10	0.07	0.06	0.02	0.06	0.02	0.05	0.01	0.04	0.01	0.06	0.04	0.05
FeO	8.29	0.30	8.03	0.77	7.37	0.17	6.74	0.33	9.22	0.17	3.27	3.98	2.65
Cr ₂ O ₃	0.20	0.17	0.46	0.07	0.96	0.38	0.84	0.53	1.38	0.17	0.43	0.14	0.38
TiO ₂	bdl	-	bdl	-	bdl	-	bdl	-	0.03 ^{N=1}		0.02	0.01	0.01
NiO	0.13	0.03	0.15	0.02	0.22	0.03	0.29	0.02	0.19	0.02	0.09	0.11	0.09
Cl (ppm)	368	68	292	28	300	49	NA	NA	348	59	NA	NA	NA
Total	87.55	0.26	87.57	0.70	87.04	0.22	89.01	2.51	87.21	0.26	87.04	0.22	87.21

Antigorite composition in the Isua serpentinites analysed in this study compared to high pressure antigorite in the Cerro del Almiraz and Val Malenco massifs (Padrón-Navarta et al., 2008)¹. N= number of spots analysed, NA= not analysed, bdl = below detection limit. Analyses in sample G12/36 include well crystallized blades of pseudomorphic antigorite globules (N=22) as well as fine-grained antigorite in the background/matrix (N=7). The matrix also contains fine grained chlorite (see electronic supplements Table A3 for chlorite, magnesite and talc compositions).

Table 4. Summary of zircons SHRIMP U-Pb isotopic results

Sample	U	Th	Th/U	²⁰⁴ Pb/ ²⁰⁶ Pb meas.	²⁰⁶ Pb _c	²³⁸ U/ ²⁰⁶ Pb	err	²⁰⁷ Pb / ²⁰⁶ Pb	err	²⁰⁷ Pb/ ²⁰⁶ Pb	err	disc
G12/39	(ppm)	(ppm)			%	ratio	%	ratio	%	age (Ma)	(Ma)	%
Zr-2-1	3	35	14	bdl	bdl	1.418	9.3	0.3518	1.9	3715	29	+10
Zr-2-2	6	138	22	2.52E-04	0.281	1.315	6.0	0.3537	1.1	3723	16	+3
Zr-3-1	11	224	21	bdl	bdl	1.406	4.6	0.3464	0.8	3691	12	+8
Zr-4-1	9	194	22	1.70E-04	0.190	1.273	5.0	0.3441	1.0	3681	15	-2

Errors are given at the 1 σ level. bdl = below detection limits. The ^{204}Pb measurements on the spots Zr2-1 and Zr3-1 were below detection limits. For these analyses, no common lead correction was applied and the $^{207}\text{Pb}/^{206}\text{Pb}$ ages are calculated from the raw isotopic ratio. $^{204}\text{Pb}/^{206}\text{Pb}$ meas. = measured $^{204}\text{Pb}/^{206}\text{Pb}$, no correction; $^{206}\text{Pb}_c$ = common ^{206}Pb .

Table 5. Summary of K-Ar concentrations, and isotopic ratios for the Isua samples in irradiation RS#2.

	$^{40}\text{Ar}^{\text{tot}}$	%err	^{36}Ar	%err	K	%err	$^{40}\text{Ar}_R$	%err	$^{40}\text{Ar}^*$	%err	$^{40}\text{Ar}_A$	$^{40}\text{Ar}_R$	$^{40}\text{Ar}_E$	Age	error	$^{40}\text{Ar}/^{36}\text{Ar}$	err
	mols		mols		mols		mols		mols		% tot ^{40}Ar			Ma	Ma	initial	%
Antigorite serpentinites																	
G12/36 300°C	1.2E-12	0.1	1.4E-15	7.0					7.4E-13	3.9	36		64			829	7.0
G12/36 600°C	1.8E-11	0.1	2.6E-15	5.3	5.2E-09	25.8	4.5E-13	25.8	1.7E-11	0.2	4	3	93	10017	7596	6669	5.3
G12/36 800°C	3.4E-11	0.1	2.8E-15	8.3	1.6E-08	27.9	1.4E-12	27.9	3.3E-11	0.2	2	4	94	9181	6909	11838	8.4
G12/36 1000°C	2.8E-12	0.1	2.9E-15	3.0					1.9E-12	1.3	31		69			965	3.0
G12/36 1400°C	1.4E-12	0.1	1.8E-15	6.9	3.0E-09	37.3	2.5E-13	37.3	8.7E-13	4.3	38	18	44	5756	4110	636	10.7
G12/36 total fusion	5.7E-11	0.1	1.1E-14	2.8	2.5E-08	20.0	2.1E-12	20.0	5.4E-11	0.2	6	4	90	9313	6447	4834	2.9
G12/38 total fusion	6.9E-11	0.2	1.2E-14	2.4	4.3E-08	12.4	3.7E-12	12.4	6.6E-11	0.2	5	5	89	8655	4987	5295	2.5
Talc-schist																	

G12/39 total fusion	5.2E-11	0.1	6.5E-15	5.2	5.1E-110.2						496					8059	5.2
Amph-Atg serpentinite																	
G12/37 200°C	1.6E-13	1.4	3.4E-16	46.7	5.6E-1484.5						64	36				459	46.8
G12/37 500°C	3.1E-12	0.1	3.3E-15	5.1	1.2E-08	9.0	9.9E-13	9.0	2.1E-12	2.3	31	32	37	4949	1540	642	6.6
G12/37 800°C	4.8E-11	0.2	1.2E-14	1.7	2.7E-07	1.2	2.3E-11	1.2	4.4E-11	0.3	7	48	45	4769	268	2125	2.1
G12/37 1000°C	4.1E-11	0.3	6.8E-15	4.4	3.7E-07	1.4	3.2E-11	1.4	3.9E-11	0.4	5	79	16	4003	205	1281	6.9
G12/37 1400°C	2.8E-11	0.1	2.3E-15	10.7	2.8E-07	1.2	2.4E-11	1.2	2.8E-11	0.3	2	85	13	3924	165	1886	12.6
G12/37 total fusion	1.2E-10	0.1	2.4E-14	2.0	9.4E-07	0.8	8.0E-11	0.8	1.1E-10	0.2	6	67	27	4253	131	1644	2.5
Ameralik dykes																	
G11/28 600°C	4.1E-12	0.1	1.8E-15	6.6	3.5E-121.0						13	87				2299	6.6
G11/28 800°C	3.8E-12	0.1	1.2E-15	7.1	3.7E-09	29.8	3.2E-13	29.8	3.5E-12	0.7	9	8	82	7779	5654	2919	7.6
G11/28 1000°C	2.9E-11	0.1	2.1E-15	19.6	3.0E-07	0.9	2.6E-11	0.9	2.9E-11	0.5	2	88	10	3875	135	1687	20.6
G11/28 1075°C	6.6E-12	0.1	2.4E-15	4.2	6.2E-08	1.8	5.3E-12	1.8	5.9E-12	0.5	11	81	8	3856	232	523	8.5
G11/28 1200°C	1.8E-11	0.1	1.1E-15	21.7	1.3E-07	1.9	1.1E-11	1.9	1.8E-11	0.4	2	61	37	4477	345	6343	21.9
G11/28 1400°C	3.1E-12	0.0	6.7E-16	13.3	3.4E-09	23.7	2.9E-13	23.7	2.9E-12	0.9	6	9	84	7617	5101	4222	13.5
G11/28 total fusion	6.5E-11	0.1	9.3E-15	5.6	5.0E-07	0.8	4.2E-11	0.8	6.2E-11	0.3	4	66	30	4308	147	2394	5.8
G11/27 total fusion	3.4E-10	0.0	8.3E-15	8.9	3.8E-07	3.0	3.2E-11	3.0	2.6E-10	0.1	1	12	87	7220	1741	36571	8.9

Heating steps results are reported for the antigorite-serpentinite G12/36, for the amphibole bearing serpentinite G12/37 and for the amphibole fraction extracted from the Ameralik dyke sample G11/28. For the other samples we report total fusion results. Errors are given at the 1 σ level. $^{40}\text{Ar}_\text{A}$ = atmospheric ^{40}Ar , $^{40}\text{Ar}_\text{R}$ = radiogenic ^{40}Ar and $^{40}\text{Ar}_\text{E}$ = Excess ^{40}Ar . Sample weights, irradiation parameters, representative blanks and the full dataset including heating steps of all samples are available in the electronic supplement Table A5.

Table 6. Total fusion K and halogen concentrations in the Pope locality samples and Ameralik dykes.

	K ($\mu\text{g/g}$)	$\pm$	Cl ($\mu\text{g/g}$)	$\pm$	Br (ng/g)	$\pm$	I (ng/g)	$\pm$	Br/Cl wt. $\times 10^{-3}$	$\pm$	I/Cl wt. $\times 10^{-6}$	$\pm$
Atg-serpentinite												
G12/36	19.77	7.0	379.45	6.6	249.8	6.7	11.0	0.3	0.7	0.02	28.93	1.1
G12/38	21.69	5.0	305.66	3.3	340.5	8.2	17.8	0.8	1.1	0.03	58.23	2.9
G12/37	12.88	5.87	310.09	6.5	416.9	5.3	26.4	0.3	1.3	0.04	85.05	2.3
Mgs-talc schist												
G12/39	40.30	6.2	33.09	4.6	120.9	20.2	8.9	3.6	3.7	0.79	269.60	116.3
Amph-serpentinite												
G12/66	33.03	7.8	616.35	5.7	670.7	19.8	14.6	2.7	1.1	0.03	23.73	4.3
Ameralik dykes												
G11/28 (amph)	961.67	5.5	1353.64	8.8	2176.2	13.1	59.8	1.2	1.6	0.01	44.21	1.0
G11/27 (amph +px)	950.84	63.4	1095.08	11.9	3877.0	26.7	183.1	3.6	3.5	0.05	167.17	4.1

Cl, Br, I and K concentrations and elemental ratios in the Isua serpentinites and associated samples as measured by the noble gas method in sample included in irradiation RS#4. Absolute errors are reported at the 1σ level and the elemental ratios are wt. ratios. Sample weights, individual heating steps, irradiation parameters, representative blanks and noble gas concentrations are reported in the electronic supplement Table A6.

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