

Petrogenesis and Geochemistry of Archean Komatiites

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ABSTRACT

Komatiites are products of decompression melting of mantle so hot that they are almost exclusively restricted to the Archean. The high degree of partial melting (F) and pressure (P) required for their generation facilitates comparison between the magma composition and its mantle source. To investigate compositional variations in Archean komatiites, a global selection of 38 Archean komatiites spanning five cratons (Kaapvaal, Zimbabwe, Yilgarn, Pilbara, Superior) were analysed for their major and trace element contents. Included are the Aluminium-Depleted (ADK, Barberton-Type) and Aluminium-Undepleted (AUK, Munro-Type) petrogenetic types that have been equated with high P /moderate F and moderate P /high F , respectively, on the basis of their Al/Ti and Gd/Yb ratios. Following calculation of the primary magma composition of each suite, we show that the absolute Al content at a specified MgO proves a more sensitive indicator of P than either of the above two ratios and hence we introduce a new classification using Al. The Mg# is a reliable proxy for F , independent of the two endmember melting styles, fractional and batch. We demonstrate that most komatiites form by batch melting, ceding to fractional melting with decreasing pressure as the density contrast between the liquid and solid grows. The Munro AUKs are the only suite to show evidence of fractional melting, with melt extraction occurring at the lowest F and P , $\approx 25\%$ melting at 5 GPa (mantle potential temperature, $T_P = 1750^\circ\text{C}$) whereas the ADKs of Barberton segregated at the highest F and P ($\approx 40\%$, 9 GPa, $T_P = 1950^\circ\text{C}$). The petrogenetic type is a combination of P and F , where, at a given pressure, higher F will produce AUKs over ADKs as majorite is consumed in the source. Through numerical simulations, it is shown that both types can occur within the same mantle plume, with ADKs forming in its cooler, distal fringes whereas AUKs occur along its axis. Furthermore, and contrary to previous views, there is no temporal distinction between the two komatiite types, with both AUKs and ADKs occurring throughout the Archean. By contrast, younger, 2–7 Ga komatiites tend to have sources that are more depleted than those of older, 3–5 Ga komatiites. Komatiites are invaluable records of the mantle's chemical and physical evolution during the Archean.

Key words: komatiite; partial melting; geochemistry; thermodynamics; temperature; mantle plume

INTRODUCTION

Since the recognition of komatiites in the Komati formation of the Barberton Greenstone Belt (Kaapvaal Craton, South Africa) as a distinct type of highly magnesian magma (Viljoen & Viljoen, 1969a), they have caused considerable interest in the geochemical community. The scarcity of komatiites in post-Archean terranes, coupled with their high MgO contents and H₂O-poor nature (Shimizu *et al.*, 2001; Berry *et al.*, 2008) require their derivation from mantle hotter than the contemporary mantle (Jarvis & Campbell, 1983; Arndt, 2003). The high eruption temperatures of komatiites, ~1450–1600°C, dictate that high degrees of melting are needed for their formation (Herzberg, 1992; Herzberg & O'Hara, 2002; Arndt *et al.*, 2008). As a consequence, in the absence of crustal contamination, they should faithfully reflect the incompatible trace element composition of their mantle source.

Compositional differences of komatiites have led to their classification as either Aluminium-Depleted Komatiites (ADKs) or Aluminum-Undepleted Komatiites (AUKs) (Nesbitt & Sun, 1979). The terms Barberton- and Munro-type, respectively, have been suggested for these two groups (Arndt *et al.*, 1977). However, because both types occur in the Barberton Greenstone Belt (Parman *et al.*, 2004), we will refer to the distinct petrogenetic types as AUK and ADK. A third, less common type, Aluminium-Enriched Komatiites (AEK), has also been defined (Jahn *et al.*, 1982), but no samples of this type are included in this study owing to their paucity in Archean terrains. ADKs are typified by subchondritic Al/Ti ratios (≈ 10) and superchondritic Gd/Yb_N ratios (≈ 1.3 – 1.6) and are interpreted to reflect partial melting in the presence of residual (majoritic) garnet (Nesbitt & Sun, 1979; Nesbitt *et al.*, 1982), which sequesters the Al and heavy rare earth elements (HREE) with respect to Ti and the middle REE (MREE). As pressure increases, garnet becomes increasingly stable in peridotitic compositions (Ringwood & Major, 1971; Zhang & Herzberg, 1994), and, accordingly, ADKs are considered to have been sourced from high pressures (between 8 and 13 GPa; Herzberg, 1995; Walter, 1998; Robin-Popieul *et al.*, 2012) at moderate degrees of partial melting ($\approx 30\%$) so as not to exhaust garnet. Conversely, AUKs have chondritic Al/Ti ratios (≈ 20) and unfractionated Gd/Yb_N ratios, and are therefore thought to have formed by larger degrees of partial melting ($\approx 50\%$) at lower, garnet-absent pressures (Arndt, 2003).

The komatiite samples analysed in this study span an age range from ≈ 2.7 to ≈ 3.5 Ga, and originate from five cratons (Kaapvaal, Zimbabwe, Yilgarn, Pilbara, Superior) and 12 separate stratigraphic units, offering a diverse range in space and time that allows for a detailed study of their geochemistry and the genesis of komatiites as a magmatic class. Although it is tempting to draw connections between the compositions of komatiites and their mantle sources, in practice, this link is often obscured by a combination of alteration, metamorphism and crustal contamination (Beswick, 1982;

Rollinson & Roberts, 1986; Hill *et al.*, 1988; Lahaye & Arndt, 1996; Barnes & Leshner, 2008). In this contribution, these effects are quantitatively investigated and the chemistry of the primary magma is computed such that comparison between komatiite magmas and their mantle sources is made possible.

To better constrain the chemical evolution of the Archean mantle we use high-precision trace element data to show that the sources of komatiites range from primitive mantle-like in older komatiites from the Kaapvaal (Barberton) and Pilbara cratons, extending towards more depleted compositions in komatiites from younger, Neoproterozoic cratons. These systematics are mirrored in their initial Nd isotope compositions, based on data compiled from the literature, revealing a dichotomy between the older, more fertile suites and the younger komatiites with radiogenic Nd isotope compositions with respect to an initially chondritic mantle. This co-dependence between different komatiite suites suggests an ancient depletion event in the sources of 2.7 Ga komatiites (Blichert-Toft & Puchtel, 2010) and that batch melting was the dominant form of melt extraction. On the other hand, radiogenic isotopes are uncorrelated with komatiite type (ADK or AUK), which is instead controlled by the presence or absence of garnet.

As komatiites represent the hottest magmas erupted on Earth, they present a unique window into the dynamics of the Archean mantle. The petrogenesis of komatiite magmas has hitherto focused on the distinction between AUKs and ADKs, and their pressure of melting in a simplified model in which ADKs are lower degree melts at higher pressures and AUKs represent higher degree melts at comparatively lower pressures (Herzberg, 1992; Walter, 1998; Arndt, 2003). Here, we quantitatively demonstrate that komatiite type is a function of both P and F , and therefore introduce a new classification scheme, underpinned by experimental data based on the Al content of the parental komatiite magmas, to better constrain average melting pressures of between 5 and 9 GPa. Estimates for the degrees of partial melting are calculated using the well-calibrated $K_D^{\text{Fe-Mg}}$ exchange between olivine and melt, which yields values between 25 and 40% batch melting.

Reconciling the petrogenetic conditions of komatiite formation to those found in mantle plumes has proved challenging for lack of petrological information and the complexity of modelling melting processes in the mantle (e.g. Leitch & Davies, 2001; Farnetani & Hofmann, 2010). In an attempt to remedy this, an equation relating degree of melting to pressure and temperature is formulated and applied in a computer simulation of mantle plume ascent to track the distribution of melts in a plume tail. Aluminium-Depleted Komatiites are the first to be generated, under high pressures and/or low melt fractions, and these, upon continued decompression melting, become increasingly AUK-like. However, AUKs may be derived from higher pressures than ADKs if the mantle potential temperature is high enough to

consume garnet. The chemistry and physical properties of komatiite liquids are consistent with batch melting. Because most komatiites are produced by close to 30% melting, their escape is probably controlled by the critical threshold melt fraction of 0.3, at which the system has the properties of a suspension. Small melt fractions and density contrasts at higher pressures ensure contact between melt and solid in the transition zone. Komatiite ascent is rapid through the lithosphere and the magma retains the chemical signature of its deep-seated source.

SAMPLE DESCRIPTIONS AND GENERAL GEOLOGY

In attempting to reduce the effects of olivine addition or removal on komatiite composition, care was taken to select samples that approximate a liquid composition. With this in mind, most samples in this study are spinifex-textured komatiites, which formed near the upper margins of flow units (Pyke *et al.*, 1973), where the melt experienced quenching; these are characterised either by fine-grained, random spinifex textures, or by an absence of crystalline phases, both of which are indicative of rapid cooling and growth (Nesbitt, 1971; Donaldson, 1976, 1982). Spinifex textures coarsen downwards from the top of the flow, where the olivine defines a preferential alignment, reflecting crystal growth under a thermal gradient at a moderate cooling rates (5°C h^{-1} ; Faure *et al.*, 2006). The komatiites are grouped into spinifex-textured (STK), in which olivine is oriented either randomly (-r) or parallel (-p), and olivine cumulates (OC) that result from crystal settling beneath the carapace.

Barberton Greenstone Belt, Kaapvaal Craton, South Africa

All five samples from the Barberton Greenstone Belt are fine- to coarse-grained (1 mm to 5 cm) spinifex-textured komatiites collected from the A1 and A2 zones of flows in the Spinifex Stream type section of the 3.48 Ga Komati Formation (Viljoen & Viljoen, 1969a, 1969b; Smith *et al.*, 1980; Viljoen *et al.*, 1983). Although textural preservation is very good, with partial recrystallisation, all samples with the exception of 49J are completely altered, with olivine having been replaced by serpentine, chlorite and magnetite in a tremolite groundmass. Sample 49J, an AUK notable for its use in the pioneering experiments of Green (1975) and Green *et al.* (1975), contains some relic olivine and is comparatively fresh (Fig. 1a). Samples 331/81, 331/777a (Fig. 1b) and 331/783 have been previously analysed for their major and trace element compositions (Nesbitt & Sun, 1979) with inductively coupled plasma mass spectrometry (ICP-MS) trace element data also reported by Campbell (2003). For the latter two samples, new powders of existing hand-samples were analysed in this study, totalling seven separate rocks.

Belingwe Greenstone Belt, Zimbabwe Craton, Zimbabwe

Seven komatiites from the 2.7–2.9 Ga Belingwe Greenstone Belt, Zimbabwe Craton, were analysed, with samples coming from two sources. Samples 331/434, 331/487 and 331/488 were first analysed by Bickle *et al.* (1975) and Nisbet *et al.* (1977), and represent their samples NG7628, NG157 and NG208, respectively. Sampled from stream exposures in the Reliance Formation, these samples are completely altered to serpentine (after olivine) and tremolite (after clinopyroxene). The latter two samples come from the centre of flows, whereas NG7628 is an ultramafic pillow. Komatiite samples B-R1, B-R2, B-B5 and B-H2 were originally collected for the study of Bolhar *et al.* (2003) from the Reliance (2.7 Ga), Bend and Hokonui formations (2.9 Ga, Wilson *et al.*, 1995). In samples from the Bend and Hokonui formations, the olivine is typically replaced by serpentine–chlorite aggregates. However, B-R1 and B-R2 are remarkably fresh samples from the SASKMAR drill-core (Nisbet *et al.*, 1987) and have excellent mineralogical and textural preservation of abundant hopper olivine in an interstitial groundmass containing spinifex olivine, Cr-spinel and plumose and chain-structured augite. Major element analyses are from Bolhar *et al.* (2003), but trace elements were re-analysed by us on the same powders as used by those researchers.

Norseman–Wiluna Greenstone Belt, Yilgarn Craton, Western Australia

Eight komatiitic rocks from four localities within the extensive 2.7 Ga Norseman–Wiluna Belt in the Yilgarn Craton (Australia) have been analysed in this study. From north to south, these are the Yakabindie (331/347), Marshall Pool (331/531, 331/948), Scotia (SD4/193, SD5/354.5, SD6/290, SD6/400) and Mt. Burges (331/144/42) samples, which were chosen as a representative cross-section of the 500 km long strike section of the belt (Barnes & Fiorentini, 2012). All except sample SD6/290 (an olivine orthocumulate) are fine- to coarse-grained (<1 mm to 8 cm) spinifex-textured komatiites from the A1 and A2 zones of flows. They exhibit well-preserved spinifex textures, even though the olivines are mostly altered to serpentine–magnetite in a tremolite–chlorite matrix. Samples from Scotia and Mt. Burges retain sparse fresh olivine. Nesbitt & Sun (1976) reported major element data for samples 331/347, SD4/193 and 331/144/42 and an analysis of 331/531 was given by Nesbitt & Sun (1979). Trace element data for these samples were presented by Campbell (2003). Data for 331/948 are from a new powder of an existing hand sample, whereas the remaining Scotia komatiite samples were sourced from drillcore (Stolz & Nesbitt, 1981; Stolz, 1981).

Regal–Ruth Well komatiites, West Pilbara Superterrane, Pilbara Craton, Western Australia

Komatiites from the West Pilbara Superterrane of the Pilbara Craton (Van Kranendonk *et al.*, 2007) are derived

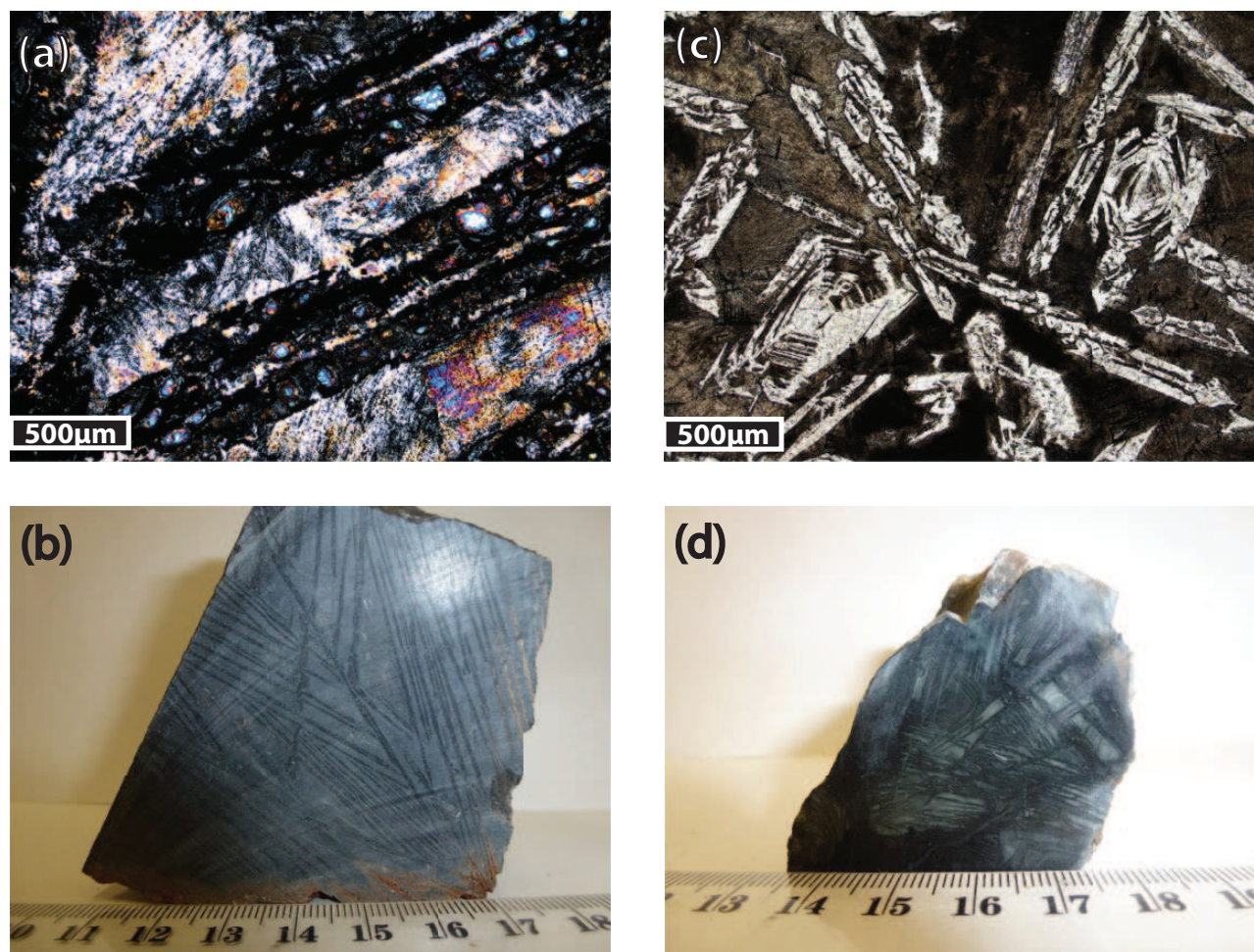


Fig. 1. Photomicrographs and hand samples of natural komatiites used in this study. (a) Sample 49J, cross-polarised light. Acicular olivines with relic fresh kernels in a talc-tremolite groundmass. (b) Sample 331/777a. Elongate blades of olivine, completely altered to serpentine, in a chlorite-rich matrix. (c) Sample 422/95, plane-polarised light. Randomly oriented skeletal and hopper olivines in a chlorite-tremolite matrix. (d) Sample 422/94. Random arrangement of centimetre-sized acicular, wholly serpentinised olivine needles.

from two locations: sample 331/497 (Nesbitt & Sun, 1979) is from the Ruth Well site (3.28 Ga Roebourne Group; Hickman, 2004); samples 176/723, 176/724 and 176/725 are from the Dampier Railway section of the c. 3.2 Ga Regal Formation (Kiyokawa *et al.*, 2002; Smithies *et al.*, 2005, 2007). The Ruth Well sample is a fine-grained spinifex-textured komatiite, whereas samples from the Regal Formation are olivine orthocumulates. Texturally, these samples are characterised by glomeroporphyritic clumps of olivine in what is interpreted to have been a clinopyroxene-glass matrix in the low-MgO samples, and by coarse-grained olivine adcumulates in the high-MgO samples. The Regal samples are completely altered to serpentine (formerly olivine) with tremolite and rare chlorite now constituting the intercumulus matrix, although sample 331/497 retains some relic olivine.

Coonterunah Subgroup, East Pilbara Terrane, Pilbara Craton, Western Australia

The 3.515 Ga rocks of the Coonterunah Subgroup of the Warrawoona Group (Green *et al.*, 2000; Arndt *et al.*,

2001; Smithies *et al.*, 2007; Van Kranendonk *et al.*, 2007) are the oldest komatiite suite sampled for this study. A total of four rocks, comprising two spinifex textured komatiites (179/755 and 179/751) and two olivine-clinopyroxene orthocumulates (179/756 and 179/757) were sampled from the Table Top Formation of the Coonterunah Subgroup (Smithies *et al.*, 2005, 2007). As with their West Pilbara counterparts, the Coonterunah komatiites have been subjected to extensive greenschist-facies metamorphism, with hydration resulting in the conversion of primary olivine and clinopyroxene to serpentine and tremolite-actinolite, respectively. The abundant groundmass is largely composed of chlorite, although relic Cr-spinels are also present, along with secondary magnetite and ilmenite.

Munro Township, Abitibi Belt, Superior Craton, Canada

Pyke Hill in Munro Township (Pyke *et al.*, 1973; Arndt *et al.*, 1977) preserves a well-exposed sequence of komatiite flows from which the six lavas analysed in this

study were sampled. The suite includes three spinifex-textured komatiites, 422/91, 422/94 (Fig. 1d) and 422/95 (Fig. 1c), which have random, fine-grained spinifex textures typical of the A1 zone. These samples are wholly altered to a tremolite–chlorite matrix with serpentinised olivine. However, sample 422/95 (Nesbitt & Sun, 1976; Campbell, 2003) contains fresh hopper and spinifex-textured olivine. This sample has been analysed twice for this study, the second time using a new powder of the existing hand sample. Three olivine orthocumulates from the A3 and B1 zones of the flow (samples 422/84, 422/86 and 422/96) were newly analysed as a part of the study.

ANALYTICAL TECHNIQUES

X-ray fluorescence (XRF)

For major element analyses, 1 g of sample powder was weighed and mixed with 4 g of lithium borate flux (comprising 35.3% tetraborate and 64.7% metaborate). The mixture was melted in a Pt–Au crucible at 1150°C for ≈8 min before being poured into a circular Pt mould and quenched in air to produce a flat disc. For trace element determinations, 10 g of sample powder was pressed into a pellet using an ethanol–PVA binding agent. Analyses on both the fused discs and pressed pellets were performed at the University of Adelaide using a Philips PW 1480 spectrometer running a dual Sc–Mo anode X-ray tube operating at 40 kV and 75 mA. The analytical procedure has been described by Norrish & Hutton (1969).

Fe is total iron, expressed as Fe_2O_3 , following Nesbitt & Sun (1976), with no assumptions or corrections made for $\text{Fe}^{3+}/\Sigma\text{Fe}$. The major elements were re-normalised to the XRF total, rather than to 100%, after performing a loss-on-ignition (LOI) heating procedure, which entailed heating the powder for 8 h at 1000°C.

Solution ICP-MS

The analyses were performed using two methods. Samples marked ‘Eggins’ in Table 1 were analysed using the protocol described by Eggins *et al.* (1997) in which enriched isotope spikes of elements bracketing the entire mass range were used to correct for mass bias effects. Because of improvements in ICP-MS technology, and the difficulties of re-calibrating enriched isotope spikes, another method, in which Re and Rh corrected for mass bias, was used for samples listed under ‘Sossi’. Briefly, 100 mg of powder was dissolved in a concentrated HCl–HF– HNO_3 (1:0.5:0.2) mixture at 140°C on a hot plate. As the solution was dried down, 15.7 M HNO_3 was added periodically to convert the residue to nitrates, which were re-dissolved in 2 ml of 15.7 M HNO_3 containing a few drops of concentrated HF. These solutions were then placed in PTFE Teflon-lined high-pressure bomb vessels and heated to 200–210°C to ensure dissolution of chemically stable phases, particularly chromite. After drying down, the samples

were re-dissolved in 2 ml of 15.7 M HNO_3 . Typically, 50 μl of this solution was diluted 100 $\times$, to 5 ml, with 2% (0.317 M) HNO_3 spiked with 10 ppb of Rh and Re, resulting in a total dilution factor of $\approx 1000 \times$ (Eggins *et al.*, 1997). At these concentrations, detection limits were of the order of 0.1 ppt (0.1 ppb in the original powder). Calibration was performed by standardisation against synthetic solutions diluted to the 500, 100, 10, 1, and 0.1 ppb levels. These solutions were used in conjunction with BHVO-2 to correct for differences in the matrix between samples and the synthetic calibrators, and for oxide interferences, particularly on the REE. Additionally, the Rh and Re internal standards were corrected for mass bias effects, where masses <138 were corrected to Rh and masses ≥ 138 to Re. Samples were introduced by a glass nebuliser to a Peltier-cooled glass spray chamber coupled to an Agilent 7700 quadrupole ICP-MS system at the Australian National University. Collision–reaction cell gases were not used in this study.

We present analyses for six standard reference materials, BHVO-2, PCC-1, Allende, W2, DNC and BIR, using both the Sossi and Eggins analytical schemes. It was found that the relative standard deviation (RSD) is normally between 0.1 and 2%, and rarely exceeded 5%. The constancy of invariant trace element ratios, such as Zr/Hf, Y/Ho and Nb/Ta, whose pairs span a large mass range, illustrates the robustness of both procedures (Supplementary Data Appendix A; supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>).

RESULTS

The major and trace element compositions of all komatiites are presented in Table 1 and their salient characteristics are plotted in Figs 2 and 3.

Major elements

As a consequence of metamorphism and alteration, some of the chemical signatures of the original komatiitic magmas, even those from the SASKMAR drillhole (Nisbet *et al.*, 1987), have been modified. This invariably results in secondary hydration, and so, to restore them to their original composition, all analyses have been normalised to 100 wt % anhydrous. The MgO concentration monitors the degree of olivine fractionation or accumulation, and, for a melt, is a positive function of the temperature of eruption (e.g. Nisbet, 1982). Alumina contents and the Al/Ti ratio are frequently employed as sensors for the pressure of melt extraction (e.g. Arndt, 2003).

The Barberton spinifex-textured sample 49J has an MgO content of 32.16 wt %, markedly higher than the other STKs from the Komati Formation, which tightly cluster about 26 wt % (Table 1; Fig. 2a). Sample 49J has lower Al_2O_3 at 3.66 wt % and 0.2 wt % TiO_2 , giving an Al/Ti of 16.2, placing it near the AUK group. The others fall

Table 1: Major (wt %) and trace element (ppm) compositions of the komatiites from this study

Sample: Texture: Type/location:	Barberton							
	49J STK-r AUK	49J STK-r AUK	331/81 STK-r ADK	331/81 STK-r ADK	331/777a STK-r ADK	331/777a STK-r ADK	331/783 STK-r ADK	331/779 STK-r ADK
SiO ₂	45.23	45.23	47.95	48.41	48.05	46.71	46.80	48.26
TiO ₂	0.2	0.2	0.42	0.41	0.41	0.42	0.42	0.42
Al ₂ O ₃	3.66	3.66	4.64	4.40	4.43	4.45	4.51	4.62
Fe ₂ O ₃	12.2	12.2	12.86	12.02	12.41	13.71	13.27	11.67
MnO	0.22	0.22	0.24	0.19	0.19	0.20	0.21	0.18
MgO	32.16	32.16	25.29	26.26	25.10	26.69	26.27	26.76
CaO	5.28	5.28	7.40	7.32	7.28	7.35	7.20	7.46
Na ₂ O	0.44	0.44	0.84	0.71	0.85	0.28	0.33	0.69
K ₂ O	0.17	0.17	0.09	0.04	0.05	0.01	0.02	0.04
P ₂ O ₅	0.02	0.02	0.04	0.03	0.06	0.04	0.06	0.04
SO ₃					0.01		0.01	0.01
LOI	6.31	6.31	5.10	5.37	4.68	5.54	5.43	5.89
Total	99.58	99.58	99.77	99.79	98.84	99.86	99.11	100.16
Mg#	83.9	83.9	79.6	81.2	80.0	79.4	79.7	82.0
Ca/Al	1.95	1.95	2.15	2.25	2.22	2.23	2.15	2.18
Fe/Mn	50.1	50.1	48.4	57.1	58.7	61.9	57.5	57.3
Al/Ti	16.16	16.16	9.75	9.47	9.50	9.35	9.49	9.65
	Eggins	Sossi	Eggins	Eggins	Sossi	Eggins	Sossi	Sossi
Li	1.70		2.51	1.54		3.66		
Be	0.13		0.19	0.15				
P	87	93	175	131	202	175	192	
K					602		336	
Sc (XRF)	15.0		23.0	25.0	22.0	25.0	22.6	23.0
Sc	13.1	14.2	21.7	20.7	21.6	20.3	21.2	19.1
Ti (XRF)	1200		2520	2460		2520		
Ti		1025			2540		2523	2613
V (XRF)	92.0		129.0	134.0	132.0	137.0	140.0	127.0
V		92.5			127.2		126.2	126.9
Cr (XRF)	3190		2960	2875	2835	2942	2894	2706
Cr		2689			2717		2457	2332
Co (XRF)	108		97		104		101	96
Co	112.1	112.8		93.5	101.8	100.0	95.3	98.4
Ni (XRF)	1931		1380	1233	1351	1229	1286	1231
Ni		1882			1431		1200	1289
Cu	4.5	4.3	5.3	3.7	3.6	56.0	63.6	3.8
Zn	48.8	68.3	83.3	69.5	68.0	56.0	66.0	84.0
Ga	3.62	3.58	5.30	5.39	5.26	5.28	5.29	5.07
Ge					0.69		0.74	
Rb (XRF)	4.0		2.0	1.0		2.0		4.0
Rb		3.5	1.33	0.38	0.40		0.97	0.44
Sr (XRF)	31.0		46.0	36.0	38.3	30.0	29.1	36.0
Sr	3.6	37.8	45.9	35.9	42.1	30.0	31.8	35.3
Y (XRF)	3.0		10.0	9.0	9.7	9.0	8.9	9.0
Y	4.28	4.02	9.08	9.40	9.17	9.69	9.07	8.02
Zr (XRF)	9.6		27.0	25.0	29.4	26.0	28.6	27.0
Zr	9.21	9.39	26.40	24.85	24.90	23.90	22.81	22.15
Nb (XRF)	1.0		3.0	2.0	2.4	2.5	3.3	2.0
Nb	0.58	0.57	2.29	1.74	1.82	1.73	1.75	1.59
Mo		0.12			3.60		0.14	0.39
Cd		0.09			0.09		0.14	0.04
Sn		0.49						0.62
Sb		0.02						
Cs		0.45	0.21	0.21	0.19		0.70	0.23
Ba (XRF)	11		25		16	6	3	4
Ba	9.62	9.45	21.10	12.15	7.96	3.43	3.69	4.11
La	0.649	0.648	1.971	1.850	1.870	1.880	2.100	1.427
Ce	1.621	1.655	5.710	5.245	5.239	5.390	5.875	4.041
Pr	0.258	0.246	0.830	0.810	0.794	0.847	0.917	0.598
Nd	1.226	1.213	4.090	3.910	3.946	4.186	4.583	2.957
Sm	0.402	0.396	1.227	1.177	1.196	1.259	1.386	0.897
Eu	0.147	0.152	0.404	0.386	0.444	0.389	0.449	0.308
Gd	0.541	0.530	1.446	1.463	1.495	1.467	1.703	1.124
Tb	0.102	0.098	0.260	0.261	0.243	0.267	0.279	0.202
Dy	0.649	0.663	1.568	1.576	1.541	1.580	1.749	1.270
Ho	0.145	0.143	0.323	0.333	0.323	0.340	0.368	0.266
Er	0.422	0.431	0.928	0.936	0.917	0.968	1.018	0.776

(continued)

Table 1. Continued

Barberton								
Sample:	49J	49J	331/81	331/81	331/777a	331/777a	331/783	331/779
Texture:	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r
Type/location:	AUK	AUK	ADK	ADK	ADK	ADK	ADK	ADK
Tm		0.062			0.131		0.144	0.116
Yb	0.398	0.439	0.820	0.815	0.843	0.867	0.934	0.751
Lu	0.062	0.065	0.124	0.124	0.126	0.132	0.137	0.112
Hf	0.245	0.245	0.707	0.666	0.713	0.687	0.654	0.567
Ta	0.043	0.034	0.137	0.110		0.116		
W								
Pb	0.480	0.460	0.614	0.730	0.536	0.252	0.694	0.492
Th	0.048	0.048	0.217	0.173	0.164	0.179	0.154	0.210
U	0.015	0.016	0.054	0.038	0.047	0.045	0.045	0.045
n	8	2	1	17	1	10	4	3
Belingwe								
Sample:	331/434	331/487	331/488	B-R1	B-R2	B-B5	B-H2	
Texture:	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	
Type/location:	Reliance	Reliance	Reliance	Reliance	Reliance	Bend	Hokonui	
SiO ₂	45.88	46.61	46.66	46.66	46.64	50.09	53.91	
TiO ₂	0.31	0.29	0.28	0.29	0.3	0.15	0.25	
Al ₂ O ₃	6.01	6.25	6.00	6.21	6.3	3.75	5.5	
Fe ₂ O ₃	11.68	11.94	12.04	11.77	11.81	10.02	10.67	
MnO	0.20	0.23	0.24	0.18	0.18	0.19	0.21	
MgO	29.62	28.06	29.45	27.72	27.54	27.48	23.46	
CaO	5.87	5.79	5.22	6.32	6.33	8.21	5.17	
Na ₂ O	0.29	0.22	0.22	0.75	0.8	0.12	0.7	
K ₂ O	0.17	0.45	0.25	0	0	0	0.1	
P ₂ O ₅	0.03	0.02	0.02	0.01	0.01	0	0.02	
SO ₃								
LOI	7.16	7.28	8.01	2.05	2.44	5.04	4.61	
Total	100.06	99.86	100.38	99.91	99.91	100.01	99.99	
Mg#	83.4	82.3	82.9	82.4	82.2	84.5	81.3	
Ca/Al	1.32	1.25	1.17	1.37	1.36	2.96	1.27	
Fe/Mn	52.7	46.9	45.3	59.1	59.3	47.6	45.9	
Al/Ti	17.12	19.03	18.92	18.90	18.54	22.07	19.42	
	Eggins	Eggins	Eggins	Sossi	Sossi	Sossi	Sossi	
Li	2.87	3.23	3.81					
Be	0.08	0.09	0.07					
P	131	87	87	301	130		174	
K				1237	544		1310	
Sc (XRF)		23.0	21.0					
Sc	21.1	24.2	22.7	25.7	26.2	47.6	29.0	
Ti (XRF)	1860	1740	1680	1732	1782	889	1519	
Ti	1645	1700		1598	1285	2366	1276	
V (XRF)		118.0	107.0	135.2	136.3		114	
V	129.0	131.0		134.6	137.8	228.0	102	
Cr (XRF)		2610	2600	2587	2640	2724	2510	
Cr	4432	2407		2696	2709		2901	
Co (XRF)								
Co	94.75	96.55	102.40	88.22	67.13		55	
Ni (XRF)		1390	1555	1481	1466	1487	645	
Ni		1338		1335	1415		510	
Cu	40.7	36.3	44.5	64.1	44.8		28	
Zn	55.2	51.4	48.7					
Ga	5.07	6.00	5.57	6.24	5.81		6.02	
Ge				0.70	0.52		0.60	
Rb (XRF)		14.0	9.0					
Rb	6.58	13.87		1.15	1.30	2.52	8.39	
Sr (XRF)		23.0	27.0	37.8	39.7	21.7	58.7	
Sr	14.8	21.5	26.0	28.0	35.0	17.1	52.6	
Y (XRF)		6.0	6.0					
Y	6.09	6.73	6.42	6.34	6.54	9.23	6.39	
Zr (XRF)		12.0	11.0	13.4	15.4	10.6	26.4	
Zr	12.28	13.13	12.32	13.84	15.14	20.25	21.74	
Nb (XRF)		1.0	1.0					
Nb	1.39	0.54	0.64	0.43	0.48	0.80	0.69	
Mo	0.53	0.42		3.37	0.34		0.23	
Cd	0.03	0.04						

(continued)

Table 1. Continued

	Belingwe							
Sample:	331/434	331/487	331/488	B-R1	B-R2	B-B5	B-H2	
Texture:	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	STK-r	
Type/location:	Reliance	Reliance	Reliance	Reliance	Reliance	Bend	Hokonui	
Sn	0.30	0.21						
Sb	0.04	0.03						
Cs	1.02	2.02		0.16	0.17	0.78	4.56	
Ba (XRF)		60	40					
Ba	14.81	54.92	34.60	10.39	12.91	6.66	82.90	
La	0.590	0.607	0.599	0.636	0.715	0.960	2.792	
Ce	1.630	1.689	1.582	1.598	1.622	2.420	4.624	
Pr	0.272	0.285	0.269	0.285	0.310	0.450	0.652	
Nd	1.460	1.526	1.446	1.476	1.655	2.470	2.702	
Sm	0.529	0.561	0.533	0.545	0.594	0.900	0.688	
Eu	0.207	0.228	0.212	0.233	0.247	0.330	0.250	
Gd	0.762	0.833	0.783	0.798	0.857	1.210	0.864	
Tb	0.148	0.161	0.153	0.151	0.154		0.142	
Dy	0.922	1.017	0.952	0.953	1.017	1.500	0.905	
Ho	0.210	0.232	0.214	0.219	0.221		0.200	
Er	0.614	0.680	0.628	0.608	0.648	0.990	0.587	
Tm				0.096	0.094		0.089	
Yb	0.583	0.648	0.618	0.606	0.641	1.050	0.614	
Lu	0.091	0.100	0.095	0.097	0.098	0.170	0.094	
Hf	0.355	0.379	0.358	0.420	0.444	0.600	0.607	
Ta	0.051	0.037	0.041	0.025	0.033	0.050	0.047	
W	0.540	0.229						
Pb	0.528	0.492	0.489	1.099	0.657	0.830	1.715	
Th	0.067	0.146	0.060	0.095	0.096	0.100	1.293	
U	0.022	0.024	0.020	0.010	0.012	0.020	0.115	
n	12	2	15	1	2	1	1	
	Yilgarn							
Sample:	331/347	331/144/42	331/531	331/948	SD4/193	SD5/354.5	SD6/290	SD6/400
Texture:	STK-p	STK-r	STK-p	STK-r	STK-p	STK-r	OC	STK-r
Type/location:	Yakabindie	Mt. Burges	Marshall Pool	Marshall Pool	Scotia	Scotia	Scotia	Scotia
SiO ₂	45.42	45.58	48.66	47.86	44.95	46.27	44.06	45.16
TiO ₂	0.27	0.30	0.50	0.44	0.28	0.39	0.22	0.34
Al ₂ O ₃	5.63	6.34	9.21	8.16	5.84	7.42	4.22	6.92
Fe ₂ O ₃	11.07	11.92	12.33	12.02	10.72	12.30	11.46	11.48
MnO	0.20	0.23	0.22	0.24	0.18	0.24	0.18	0.13
MgO	31.46	29.11	18.95	23.54	31.94	25.72	37.79	27.99
CaO	5.65	6.10	8.83	7.63	5.68	7.79	2.77	8.70
Na ₂ O	0.31	0.58	1.24	1.11	0.52	0.79	0.27	0.41
K ₂ O	0.01	0.03	0.04	0.12	0.06	0.03	0.04	0.01
P ₂ O ₅	0.02	0.02	0.04	0.04	0.02	0.04	0.02	0.03
SO ₃				0.00		0.00	0.06	0.04
LOI	6.62	6.27	4.17	5.07	6.26	6.00	8.16	7.97
Total	100.04	100.21	100.02	101.16	100.19	101.00	101.08	101.22
Mg#	84.9	82.9	75.3	79.5	85.5	80.6	86.7	82.8
Ca/Al	1.36	1.30	1.29	1.26	1.31	1.42	0.89	1.70
Fe/Mn	50.0	46.8	50.6	44.8	53.8	45.6	59.0	78.9
Al/Ti	18.41	18.66	16.26	16.55	18.41	16.87	16.61	17.73
	Eggins	Eggins	Eggins	Sossi	Eggins	Sossi	Sossi	Sossi
Li	17.10	7.12	2.98		3.03			
Be	0.07	0.09	0.11		0.10			
P								
K								
Sc (XRF)			35.0	29.0		27.0	18.0	27.0
Sc	21.5	23.6	32.0	28.5	21.6	28.1	15.1	25.2
Ti (XRF)	1620	1800	3000	2610	1680	2912	1682	2584
Ti	1655	1860	2860	3128	1690	2307	1511	1922
V (XRF)	115.0	133.0	195.0	160.0	117.0	150.0	86.0	126.0
V	120.0	128.0	188.0	155.3	115.0	149.7	80.7	125.4
Cr (XRF)	2900	3200	2720	2908	2890	3052	3089	2428
Cr	2406	2490	2050	2915	2230	2444	3007	2316
Co (XRF)	100	98		104	98	98	117	92
Co	100.2	97.5	81.5	100.0	98.2	104.1	128.9	96.8
Ni (XRF)	1524	1322	720	968	1562	1138	1974	1175

(continued)

Table 1. Continued

	Yilgarn							
Sample:	331/347	331/144/42	331/531	331/948	SD4/193	SD5/354.5	SD6/290	SD6/400
Texture:	STK-p	STK-r	STK-p	STK-r	STK-p	STK-r	OC	STK-r
Type/location:	Yakabindie	Mt. Burges	Marshall Pool	Marshall Pool	Scotia	Scotia	Scotia	Scotia
Ni	1160	1312	670	909	1608	1169	1901	1201
Cu	29.5	38.5	9.2	167.5	38.2	27.4	4.2	22.8
Zn	56.1	57.2	69.4	93.5	46.9	80.5	63.3	71.0
Ga	5.03	5.55	8.28	7.06	5.33	6.75	3.65	5.94
Ge								
Rb (XRF)	4.0	4.0	1.0	6.0	1.0	4.0	5.0	4.0
Rb	4.18	3.19	0.42	4.00	1.43	0.38	0.38	0.33
Sr (XRF)	17.0	24.0	24.0	24.0	24.0	22.0	9.0	56.0
Sr	16.4	23.0	22.9	25.0	22.8	23.0	4.4	59.4
Y (XRF)	7.0	6.0	10.0	9.0	7.0	8.0	4.0	7.0
Y	6.81	7.31	10.62	8.43	6.85	7.72	3.60	7.39
Zr (XRF)	14.0	16.3	27.0	21.0	15.5	19.7	7.6	18.4
Zr	15.74	17.63	26.19	20.61	14.78	22.32	8.16	18.82
Nb (XRF)	0.4	0.8	2.0	2.0	0.2	2.0	2.0	2.0
Nb	0.50	0.81	1.03	0.95	0.52	0.88	0.38	0.77
Mo	0.01	0.65	0.22	0.25	0.03	0.49	0.07	0.19
Cd	0.02	0.02	0.01	0.02	0.03	0.02	0.03	0.02
Sn	0.18	0.36	0.34	0.48	0.27			
Sb	0.19	0.15	0.01	0.13	0.01	0.18	0.08	0.10
Cs	17.17	2.17	0.02	0.14	0.43	0.17	0.05	0.21
Ba (XRF)	3	9	10	56	16	6	23	4
Ba	2.20	7.66	5.70	51.52	14.25	1.55	3.50	1.22
La	0.558	0.656	1.078	0.735	0.544	0.610	0.332	0.568
Ce	1.659	1.952	3.292	2.253	1.687	1.989	0.980	1.761
Pr	0.293	0.337	0.577	0.393	0.303	0.351	0.169	0.323
Nd	1.652	1.860	3.092	2.153	1.659	1.961	0.901	1.783
Sm	0.607	0.669	1.075	0.780	0.610	0.703	0.330	0.641
Eu	0.241	0.276	0.393	0.326	0.270	0.352	0.131	0.287
Gd	0.883	0.957	1.456	1.120	0.889	1.035	0.458	0.935
Tb	0.168	0.183	0.276	0.209	0.170	0.188	0.085	0.177
Dy	1.051	1.132	1.709	1.382	1.063	1.220	0.575	1.158
Ho	0.234	0.249	0.377	0.298	0.237	0.274	0.123	0.249
Er	0.689	0.741	1.092	0.873	0.686	0.795	0.368	0.739
Tm				0.136		0.117	0.056	0.113
Yb	0.645	0.695	0.988	0.880	0.632	0.809	0.365	0.706
Lu	0.101	0.108	0.146	0.130	0.098	0.123	0.056	0.111
Hf	0.433	0.500	0.734	0.606	0.418	0.572	0.243	0.501
Ta	0.036	0.059	0.068		0.045			
W	0.060	0.755	0.131		4.510			
Pb	1.567	2.891	0.260	3.014	0.342	0.400	1.312	0.916
Th	0.043	0.055	0.170	0.100	0.051	0.091	0.023	0.074
U	0.013	0.015	0.031	0.025	0.014	0.022	0.011	0.019
n	2	2	16	1	9	2	2	2

into the ADK field, with Al_2O_3 near 4.5 wt % and TiO_2 of 0.42 wt %, constraining Al/Ti to ≈ 9.5 (Fig. 2b). Komatiites from Belingwe range in MgO from 21.79 to 29.45 wt %. The Reliance formation is characterised by Al_2O_3 contents just above 6 wt %, TiO_2 around 0.3 wt %, and a constant Al/Ti of ≈ 18.5 , typical of AUKs. Despite being sourced from an extensive area, the Yilgarn komatiites exhibit remarkably similar compositional characteristics, whose variations lie on olivine control lines. Including the olivine cumulate sample, SD6/290, MgO varies from 37.79 to 18.95 wt % for 331/531, an STK with parallel-oriented olivines (Fig. 2a). These same two samples define the extents in Al_2O_3 and TiO_2 with 4.22 and 0.22 wt % at their lowest and 9.21 and 0.5 wt % at the highest (Fig. 2b). The STK-r 331/497 from West Pilbara Regal–Ruth Well is a typical ADK, with Al/Ti of

9.45 and a low Al_2O_3 content of 3.96 wt % at an MgO content of 27.9 wt %. Extensive serpentinisation of the olivine cumulates, as signalled by their high LOI values ($\geq 10\%$) and spread in MgO vs FeO, makes it difficult to ascertain precise major element concentrations. In the East Pilbara, the four Coonterunah samples span a range of MgO contents from 23.54 to 33.18 wt %, with sample 179/755 appearing to have lost Fe (Fig. 2a), artificially increasing its Mg#. Samples 179/751 and 179/756 fall on an expected olivine accumulation trend. Ratios of Al/Ti close to 20 place them in the AUK range. Of the komatiites studied here, the STKs from Munro have the lowest MgO contents (22–23 wt %), coupled with the highest Al_2O_3 concentrations, nearing 9 wt %. Together with their high Ti contents (≈ 0.4 wt %), these samples are AUKs (Fig. 2b). The samples reach MgO

Table 1: Continued

	Regal–Ruth Well			
Sample:	331/497	176/723	176/724	176/725
Texture:	STK-r	OC	OC	OC
Type/location:	Ruth Well	Dampier Rlwy	Dampier Rlwy	Dampier Rlwy
SiO ₂	47.63	44.35	46.77	44.81
TiO ₂	0.37	0.30	0.29	0.31
Al ₂ O ₃	3.96	2.97	3.35	3.46
Fe ₂ O ₃	12.07	9.34	10.67	12.09
MnO		0.21	0.17	0.16
MgO	27.90	31.13	36.35	35.09
CaO	6.70	11.46	2.21	3.65
Na ₂ O	0.56	0.28	0.29	0.37
K ₂ O	0.12	0.01	0.01	0.01
P ₂ O ₅	0.02	0.03	0.04	0.04
SO ₃				
LOI	6.54	13.46	9.84	10.81
Total	99.33	100.07	100.14	100.00
Mg#	82.1	86.9	87.1	85.2
Ca/Al	2.28	5.22	0.89	1.42
Fe/Mn		40.6	57.9	69.7
Al/Ti	9.45	8.73	10.25	9.74
	Eggins	Sossi	Sossi	Sossi
Li	2.18			
Be	0.11			
P	0	79	143	143
K		209	274	167
Sc (XRF)	22.0	16.0	18.0	18.0
Sc	18.3	12.8	16.3	16.9
Ti (XRF)	2220	1559	1559	1679
Ti	2220	1582	1560	1699
V (XRF)	110.0	99.0	95.0	104.0
V	116.0	79.3	103.2	105.7
Cr (XRF)	2710	2433	2747	2686
Cr	2180	2258	2605	2558
Co (XRF)				
Co	103.5	99.8	100.9	119.5
Ni (XRF)	2025	1489	1626	1774
Ni	1423	1482	2073	1953
Cu	8.1	7.6	5.3	2.4
Zn	64.4	71.3	91.0	54.0
Ga	4.88	4.57	4.55	4.16
Ge		0.46	0.65	0.61
Rb (XRF)	2.0			
Rb	1.19	0.58	0.98	0.57
Sr (XRF)	31.0	57.7	23.1	35.0
Sr	30.0	50.6	13.2	31.3
Y (XRF)	7.0	7.0	4.5	4.8
Y	7.17	6.33	5.14	4.55
Zr (XRF)	21.0	3.0	5.0	6.0
Zr	15.47	15.20	14.05	12.50
Nb (XRF)	1.0	0.3		0.4
Nb	0.60	0.55	0.50	0.42
Mo	0.18	1.12	0.75	0.46
Cd	0.02			
Sn	0.42	0.80		0.90
Sb	1.12			
Cs	0.71	0.70	1.58	0.85
Ba (XRF)	15	25		22
Ba	12.12	1.55	2.34	1.78
La	0.931	0.914	0.770	0.622
Ce	2.523	2.161	1.783	1.605
Pr	0.415	0.330	0.260	0.248
Nd	2.213	1.731	1.342	1.346
Sm	0.847	0.652	0.488	0.502
Eu	0.329	0.186	0.177	0.157
Gd	1.183	0.976	0.691	0.747
Tb	0.218	0.173	0.124	0.132
Dy	1.280	1.133	0.802	0.861
Ho	0.265	0.248	0.171	0.185
Er	0.727	0.693	0.468	0.531

(continued)

Table 1. Continued

Sample: Texture: Type/location:	Regal–Ruth Well			
	331/497 STK-r Ruth Well	176/723 OC Dampier Rlwy	176/724 OC Dampier Rlwy	176/725 OC Dampier Rlwy
Tm		0.097	0.067	0.073
Yb	0.643	0.623	0.436	0.476
Lu	0.095	0.084	0.061	0.069
Hf	0.454	0.379	0.371	0.393
Ta	0.045	0.043	0.049	0.049
W	0.549			
Pb	0.896	1.262	0.826	1.084
Th	0.159	0.141	0.129	0.128
U	0.046	0.034	0.043	0.032
n	1	1	1	1
Coonterunah				
Sample: Texture: Type/location:	179/755 STK-r K1	179/751 STK-r K1	179/756 OC K1	179/757 OC K1
SiO ₂	49.49	48.89	47.29	45.97
TiO ₂	0.29	0.42	0.27	0.25
Al ₂ O ₃	6.87	8.19	6.22	5.57
Fe ₂ O ₃	10.36	11.88	10.86	11.28
MnO	0.18	0.18	0.15	0.17
MgO	24.29	23.54	29.15	33.18
CaO	8.30	7.29	5.68	3.27
Na ₂ O	0.18	0.29	0.08	0.03
K ₂ O	0.02	0.02	0.01	0.01
P ₂ O ₅	0.02	0.04	0.02	0.02
SO ₃		0.01		
LOI	5.89	5.79	7.64	9.71
Total	100.00	100.74	99.74	99.74
Mg#	82.3	79.7	84.2	85.4
Ca/Al	1.63	1.20	1.23	0.79
Fe/Mn	53.1	60.9	64.2	60.5
Al/Ti	21.02	17.24	20.20	19.81
Sossi				
Li				
Be				
P	110		120	101
K	204		165	149
Sc (XRF)	27.0	29.0	25.0	23.0
Sc	25.2	28.9	23.6	22.7
Ti (XRF)	1631	2511	1505	1343
Ti	1588	2854	1675	1245
V (XRF)	112.0	163.0	99.0	100.0
V	115.6	155.7	114.2	100.9
Cr (XRF)	3636	3709	4699	5034
Cr	3242	3808	4664	4558
Co (XRF)		87		
Co	73.8	97.1	99.8	93.4
Ni (XRF)	1005	817	1286	1589
Ni	949	774	1280	1503
Cu	49.7	163.4	12.5	15.8
Zn	58.0	139.0	96.9	101.4
Ga	6.15	7.19	5.36	4.24
Ge	0.54		0.65	0.61
Rb (XRF)		4.0		
Rb	0.52	0.38	0.23	0.24
Sr (XRF)	32.8	35.0	52.7	22.6
Sr	24.4	35.1	54.8	13.8
Y (XRF)	5.6	9.0	4.8	3.7
Y	6.01	7.31	5.76	3.99
Zr (XRF)	16.0	25.0	14.0	11.0
Zr	15.43	23.14	15.12	10.56
Nb (XRF)	0.7	3.0	0.6	0.4
Nb	0.73	1.38	0.67	0.47
Mo	0.09	0.11	0.10	0.17
Cd				

(continued)

Table 1. Continued

Sample: Texture: Type/location:	Coonterunah			
	179/755 STK-r K1	179/751 STK-r K1	179/756 OC K1	179/757 OC K1
Sn				
Sb				
Cs	0.12	0.19	0.09	0.05
Ba (XRF)		18		
Ba	6.80	17.31	6.58	3.59
La	1.139	1.159	0.816	0.622
Ce	2.615	2.925	2.215	1.502
Pr	0.407	0.455	0.333	0.242
Nd	2.051	2.206	1.718	1.294
Sm	0.666	0.734	0.573	0.418
Eu	0.260	0.218	0.134	0.099
Gd	0.891	1.001	0.768	0.590
Tb	0.155	0.178	0.136	0.104
Dy	1.054	1.239	0.901	0.700
Ho	0.236	0.276	0.205	0.155
Er	0.698	0.823	0.610	0.471
Tm	0.105	0.130	0.091	0.069
Yb	0.732	0.845	0.630	0.486
Lu	0.113	0.128	0.095	0.073
Hf	0.451	0.600	0.395	0.318
Ta	0.050		0.036	0.029
W				
Pb	0.701	1.922	0.907	11.201
Th	0.111	0.141	0.092	0.034
U	0.020	0.036	0.020	0.014
n	1	2	1	1

Sample: Texture: Type/location:	Munro						
	422/95 STK-r Pyke Hill	422/95 STK-r Pyke Hill	422/91 STK-r Pyke Hill	422/94 STK-r Pyke Hill	422/96 STK-p Pyke Hill	422/84 OC Pyke Hill	422/86 OC Pyke Hill
SiO ₂	45.85	45.84	45.11	45.07	47.99	45.35	46.08
TiO ₂	0.35	0.41	0.44	0.45	0.29	0.30	0.27
Al ₂ O ₃	8.35	8.46	8.96	8.98	5.96	6.18	5.12
Fe ₂ O ₃	12.17	12.27	12.91	11.97	8.69	10.24	9.56
MnO	0.22	0.19	0.22	0.22	0.13	0.18	0.18
MgO	23.45	22.47	21.90	22.41	28.71	30.32	32.45
CaO	8.74	8.58	8.87	9.19	6.55	5.83	4.74
Na ₂ O	0.83	0.92	0.64	0.40	0.25	0.19	0.16
K ₂ O	0.15	0.16	0.06	0.03	0.01	0.01	0.01
P ₂ O ₅	0.02	0.06	0.06	0.06	0.05	0.04	0.03
SO ₃		0.05	0.04	0.03	0.15	0.06	0.08
LOI	3.63	3.41	4.87	5.07	6.847	7.415	8.072
Total	100.13	99.43	99.22	98.80	98.78	98.71	98.67
Mg#	79.2	78.4	77.1	78.8	86.7	85.4	87.0
Ca/Al	1.41	1.37	1.34	1.38	1.10	0.94	0.92
Fe/Mn	49.96	56.94	52.31	50.01	59.87	51.22	47.77
Al/Ti	21.1	18.08	18.17	17.74	20.40	20.43	19.13
	Eggins	Sossi	Sossi	Sossi	Sossi	Sossi	Sossi
Li	8.69						
Be	0.0675						
P	87	189	178.17	169	140		
K		1661	717	410	321		
Sc (XRF)		26.3	29.8	31.0	21.0	21.6	17.9
Sc	28.5	30.7	27.5	32.7	20.5	18.0	10.1
Ti (XRF)	2100	2477	2610	2679	1752	1815	1606
Ti	2345	2559	2739	2639	1864	1987	1826
V (XRF)	159.0	161.0	188.0	195.0	127.0	125.0	68.0
V	179.0	177.6	191.8	185.5	123.9	112.5	56.3
Cr (XRF)	3250	3271	3460	3464	3060	2902	2900
Cr	2605	3094	3333	3181	3372	2499	2468
Co (XRF)	93	99	95	91	91.00	92.0	80.0
Co	89.1	94.3	97.3	87.7	89.3	99.5	91.2
Ni (XRF)	1049	1129	907	857	1368	1413	1462
Ni	919	1043	950	855	1396	1435	1609

(continued)

Table 1. Continued

	Munro						
Sample:	422/95	422/95	422/91	422/94	422/96	422/84	422/86
Texture:	STK-r	STK-r	STK-r	STK-r	STK-p	OC	OC
Type/location:	Pyke Hill	Pyke Hill	Pyke Hill	Pyke Hill	Pyke Hill	Pyke Hill	Pyke Hill
Cu	55.4	64.5	63.8	51.2	1035.8	7.1	5.6
Zn	61.7	71.0	74.0	104.0	70.2	57.4	66.9
Ga	8.38	9.07	9.06	8.58	7.34	5.77	4.99
Ge		0.65	0.61	0.58	0.93		
Rb (XRF)	3.0	3.6	3.0	2.1	1.4	1.1	0.9
Rb	2.81	2.87	1.93	1.30	0.32	0.09	0.08
Sr (XRF)	38.0	39.6	10.8	7.5	6.4	25.0	25.6
Sr	37.9	44.9	11.1	8.3	6.2	25.6	26.2
Y (XRF)	10.0	10.3	10.6	11.2	6.4	6.0	6.0
Y	10.07	9.83	10.20	10.44	5.10	2.07	1.77
Zr (XRF)	18.4	19.8	22.8	21.7	14.5	9.0	14.8
Zr	17.62	17.76	19.62	17.87	10.45	3.13	2.54
Nb (XRF)	1.2	1.5	1.9	2.1	1.7	1.3	0.9
Nb	0.68	0.47	0.43	0.47	0.39	0.31	0.33
Mo	0.19	0.48	0.44	0.34	0.07	0.10	0.08
Cd	0.03						
Sn	0.21						
Sb	0.01						
Cs	0.33	0.29	0.37	0.31	0.19	0.18	0.22
Ba (XRF)	13	19	9	7	25	1	3
Ba	17.77	14.15	3.95	3.07	4.39	0.15	0.95
La	0.405	0.408	0.370	0.472	0.150	0.084	0.074
Ce	1.291	1.291	1.213	1.529	0.533	0.239	0.234
Pr	0.243	0.239	0.225	0.265	0.093	0.042	0.044
Nd	1.487	1.481	1.434	1.590	0.603	0.243	0.259
Sm	0.679	0.707	0.726	0.730	0.312	0.123	0.114
Eu	0.295	0.312	0.297	0.394	0.116	0.050	0.067
Gd	1.174	1.195	1.211	1.234	0.533	0.220	0.203
Tb	0.237	0.226	0.233	0.237	0.106	0.044	0.040
Dy	1.553	1.569	1.605	1.640	0.735	0.309	0.270
Ho	0.353	0.354	0.362	0.369	0.162	0.069	0.060
Er	1.043	1.033	1.063	1.084	0.473	0.199	0.175
Tm		0.152	0.156	0.162	0.070	0.031	0.028
Yb	0.977	1.009	1.042	1.087	0.445	0.197	0.171
Lu	0.150	0.152	0.152	0.163	0.066	0.030	0.025
Hf	0.536	0.573	0.628	0.587	0.279	0.104	0.090
Ta	0.033						
W	0.176						
Pb	0.133	0.478	0.310	0.289	1.450	1.652	8.063
Th	0.026	0.032	0.025	0.036	0.028	0.012	0.017
U	0.011	0.010	0.010	0.011	0.009	0.006	0.008
n	11	3	3	3	3	2	2

Analyses for each sample were performed using either the 'Sossi' or 'Eggins' method, and are labelled accordingly. Both techniques are described in the 'Solution ICP-MS' section under 'Analytical techniques'.

values of 32.45 wt %, defining an olivine accumulation trend that results in lower FeO (down to 8.69 wt %) and Mg# values up to 87.

Trace elements

The trace element compositions of each of the komatiite suites are plotted on primitive mantle-normalised diagrams in Fig. 3. To emphasise the small differences in their trace element signatures, and given that they span a limited range of concentrations, a linear scale has been used. Elements that are especially prone to disturbance (e.g. Eu, Rb, Sr, Cs, Pb, Ba) have been omitted from the plots, the rationale for which will be discussed in the section below on 'Chemical effects of alteration and metamorphism'. The trace element

abundances have not been corrected for olivine subtraction or addition, processes that displace the curves up and down, respectively. During mantle melting, $D_{La} < D_{Sm}$, but, as $D_{La,Sm} \ll 1$, and the degree of melting is high, $La/Sm_{Melt} \approx La/Sm_{Source}$, and should thus reflect the fertility of the source. As garnet becomes more stable in peridotite as a function of increasing pressure (e.g. Klemme & O'Neill, 2000), HREE, such as Yb, are retained in the source, resulting in higher Gd/Yb ratios in the complementary melts (Nesbitt *et al.*, 1979).

Coupled enrichments in U and Th relative to Nb are observed for the Regal–Ruth Well komatiites (Fig. 3d), whereas the 2.7 Ga Yilgarn and Munro komatiites (Fig. 3c and f) have conspicuous positive Nb and Ta

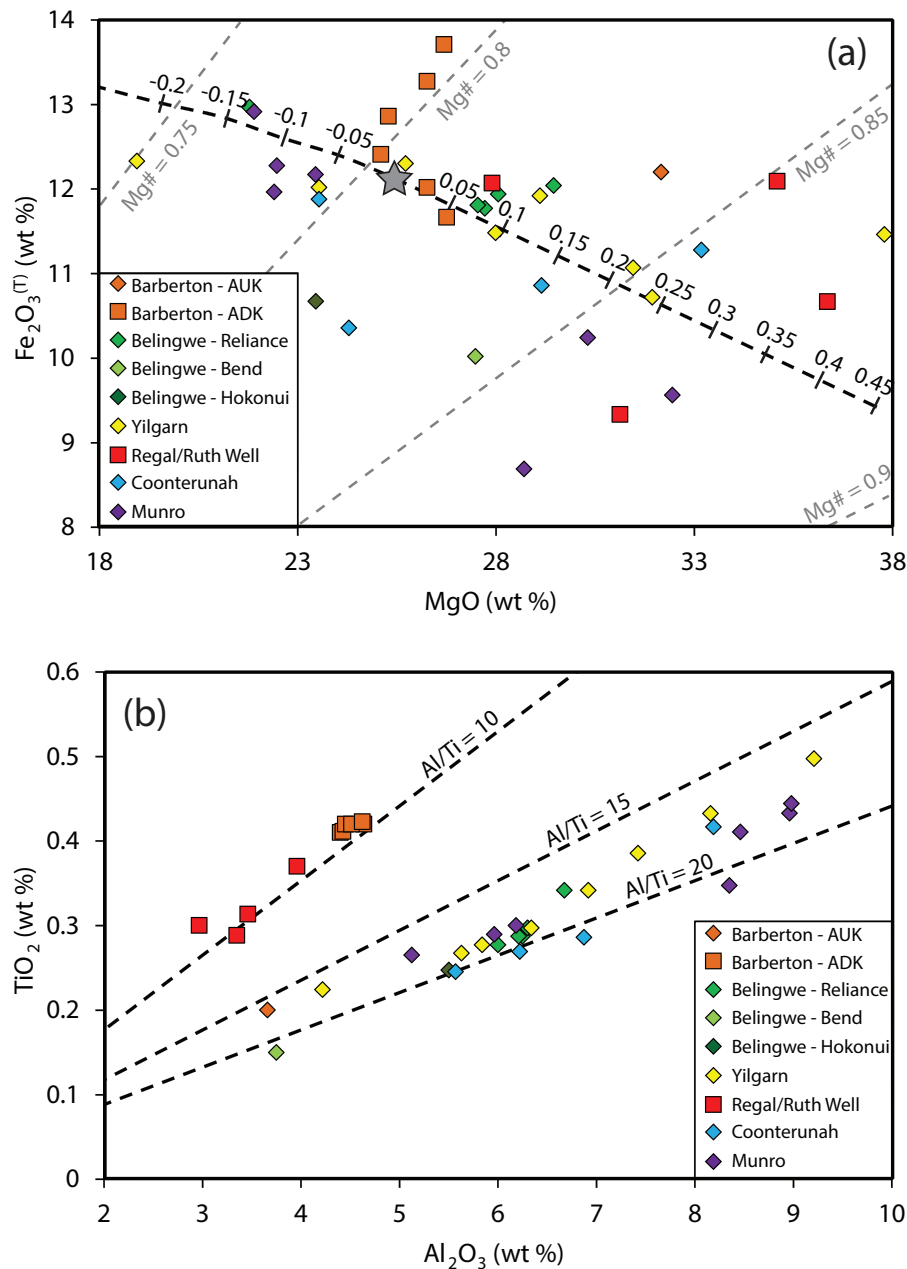


Fig. 2. Binary diagrams. (a) MgO vs $\text{Fe}_2\text{O}_3^{(\text{T})}$. The grey star represents a model primary komatiite melt with 26% MgO and 12% $\text{Fe}_2\text{O}_3^{(\text{T})}$, to which olivine is added or subtracted. Contours of constant Mg# are shown in grey. (b) Al_2O_3 vs TiO_2 . Komatiites form two arrays, following Al/Ti contours of 10 (Aluminium-Depleted) or near 20 (Aluminium-Undepleted).

anomalies. Further, they show low $\text{La}/\text{Sm}_\text{N}$; ≈ 0.6 and ≈ 0.4 , respectively, and $\text{Gd}/\text{Yb}_\text{N} \approx 1$, features shared with komatiites from Belingwe, where a similarly subchondritic La/Sm (≈ 0.75) is coupled with flat HREE patterns (Fig. 3b). The Hokonui sample has a similar pattern on the right-hand side of the plot, but possesses elevated large ion lithophile element (LILE) and light REE (LREE) values. High concentrations of LREE are also typical of the Barberton ADKs [$3 \times$ primitive mantle (PM); Fig. 3a], distinct from the 2.7 Ga komatiite suites. They are typified by negatively sloping HREE abundances, resulting in a Gd/

$\text{Yb}_\text{N} \approx 1.4$. Such a fingerprint is also detected in komatiites from Regal–Ruth Well, which have $\text{Gd}/\text{Yb}_\text{N}$ between 1.3 and 1.5. Interestingly, both ADK suites show negative Zr and Hf anomalies. Such anomalies are absent in Munro and Belingwe, the former possessing the highest abundances of HREE ($2\text{--}2.5 \times \text{PM}$). The Coonterunah komatiites show flat patterns throughout (Fig. 3e), a spectrum mirrored by the Barberton AUK, 49J, with the former extending up to almost $2 \times \text{PM}$, whereas 49J is almost coincident with PM. There is no co-dependence of $\text{La}/\text{Sm}_\text{N}$ and $\text{Gd}/\text{Yb}_\text{N}$. Furthermore, both ADKs and AUKs occur at

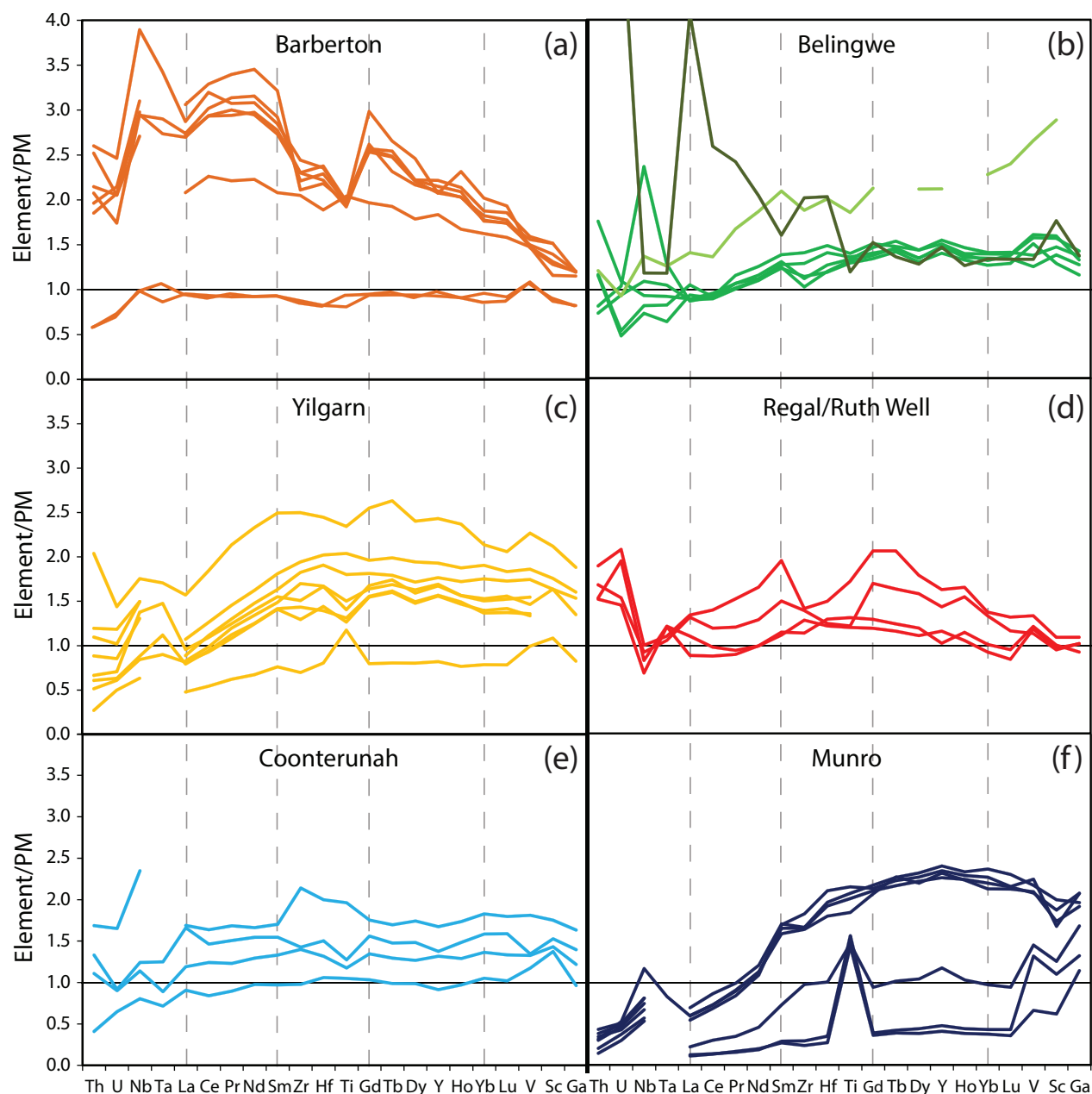


Fig. 3. Primitive mantle (PM)-normalised (Palme & O'Neill, 2014) trace element plots for each sample, grouped by komatiite suite. The linear ordinate should be noted. The horizontal line indicates primitive mantle.

3.5 Ga, and, in the case of Barberton, in the same formation.

DISCUSSION

Determination of primary magma composition

Before the identity and character of the mantle source regions of komatiites can be evaluated, it is necessary to determine the composition of the primary magma. Komatiitic magmas differentiate by olivine crystallisation, the primary phase field of which expands at lower pressures, making it the sole crystallising phase to

200°C below the liquidus at 1 atm (Arndt, 1976; Green, 1981; Kinzler & Grove, 1985; Faure *et al.*, 2006). The olivine stoichiometry places constraints on the chemical evolution path followed by the residual liquid and facilitates correction back to a parental melt composition. This composition for each flow may be found using various techniques, as follows.

1. The simplest method is to analyse the chilled margins of the flow that have had insufficient time to fractionate or accumulate olivine. However, this approach may be compromised by the ingress of fluids along joints and fractures that form upon cooling

- and densification of the flow top, combined with a small quantity of phenocrysts already present in the magma upon emplacement.
2. The well-parameterised $K_D^{\text{Fe-Mg}}$ exchange between olivine and liquid (Roeder & Emslie, 1970; Toplis, 2005) may be used to calculate the Fe/Mg ratio of the parental liquid, which is assumed to be in equilibrium with the most magnesian olivine. However, this requires that fresh olivine be preserved in the flow, that these olivines are consanguineous, and in equilibrium with the melt, which is not always possible to determine. Additional uncertainty arises owing to the undefined $\text{Fe}^{2+}/\text{Fe}^{3+}$ of the komatiitic liquid.
 3. If no fresh olivine is preserved, MgO_{OI} can be estimated by projecting plots of whole-rock MgO versus an element that is perfectly incompatible in olivine to the point at which it is equal to zero.

The major element composition determined for the parental magma also permits correction of the trace element abundances for a given suite. The moderately incompatible and compatible elements (all first-row transition metals, including Ge) were normalised by solving for the magma's parental MgO content. If no correlation was apparent ($r^2 < 0.5$), the average of the data points was taken. Elements above atomic number 32 (Ge) do not partition appreciably into olivine and were corrected through progressive addition or subtraction of olivine (e.g. Robin-Popieul *et al.*, 2012):

$$C_N = C_M \left(\frac{\text{MgO}_{\text{OI}} - \text{MgO}_N}{\text{MgO}_{\text{OI}} - \text{MgO}_M} \right) \quad (1)$$

where the subscript N denotes the normalised concentration, M the measured concentration, and OI the olivine assumed to be in equilibrium with the parental magma composition on the basis of Fe–Mg exchange. Strictly, this adjustment is not correct for re-addition of fractionated olivine because it assumes C_M is a linear function of a single olivine and melt composition, but it is a good approximation, considering that most non-melt compositions are cumulates and not evolved liquids. The preferred major and trace element composition of the parental liquid for each of the seven suites is listed in Table 2.

Comparison with previous work

Barberton

Perhaps the most widely studied of all Archean komatiites are those of the type locality in the Komati River, Barberton Greenstone Belt (Viljoen & Viljoen, 1969a; Nesbitt & Sun, 1979; Smith *et al.*, 1980; Smith & Erlank, 1982; Viljoen *et al.*, 1983; Parman *et al.*, 2004; Robin-Popieul *et al.*, 2012; Puchtel *et al.*, 2013). In their landmark study Viljoen & Viljoen (1969b) presented an analysis of a 'pillowed peridotite from top of flow', sample AU5, which contained 29 wt % MgO on an anhydrous basis, as a preliminary estimate for the composition of the Barberton liquid. Nesbitt *et al.* (1979)

analysed five spinifex-textured komatiites, which had MgO contents ranging from 24.8 to 27.4 wt %, averaging 26.1 wt %. Smith *et al.* (1980) proposed a starting composition of 27.9 wt % MgO, later revised to 29% by averaging 13 aphyric komatiites (Smith & Erlank, 1982). Robin-Popieul *et al.* (2012) used olivine–liquid equilibria to argue that the parental MgO content was likely to have been 27 ± 3 wt %. Indeed, the six spinifex-textured komatiites from the study of Puchtel *et al.* (2013) have MgO contents between 24.3 and 29.4 wt %, with an average of 26.6 wt %. In our study we derive an average of 26.1 ± 0.7 wt % MgO for six samples, falling within the range of previous investigations.

Sample 49J is an AUK from the lower horizon of the Komati formation (Smith & Erlank, 1982; Parman *et al.*, 2004), consisting of randomly oriented acicular olivine blades up to 1 cm in length, set in an originally glassy matrix that has now been converted to tremolite with relic clinopyroxene. The sample shows no textural evidence for olivine accumulation and appears to be very close to a liquid composition (Fig. 2a). Nisbet *et al.* (1993) suggested, on the basis of a lack of equilibrium between the Fo content of the olivine in the sample ($\text{Fo}_{93.6}$, Green *et al.*, 1975) and its Mg/Fe^{2+} ratio that the composition of the parental liquid was slightly less magnesian, near 27.5–29.5% MgO. Other examples of such rare Barberton AUK komatiites have been reported sporadically in the literature [e.g. group I komatiites of Smith & Erlank (1982); sample B89 of Williams & Furnell (1979)]. However, the study of Parman *et al.* (2004) described a comprehensive suite of these rocks (their horizon 1), the average MgO (wt %) of which is 30.5 ± 1.4 ($n=8$). From the trend of whole-rock analyses Robin-Popieul *et al.* (2012), deduced that the initial liquid was in equilibrium with Fo_{94} olivine, yielding a primary melt composition of 30% MgO and 12% $\text{FeO}^{(\text{T})}$. The scatter in the trend contributes to an error of $\pm 2\%$ MgO. We concur with their estimates, which are intermediate between those of Nesbitt & Sun (1976) and Nisbet *et al.* (1993), but encompass both within error, owing to the uncertainties in using spinifex olivine to assess mineral–liquid equilibria.

Munro

The Munro komatiites of the Abitibi belt in Canada, like those from Barberton, have been the subject of intense scrutiny. The pioneering study of Pyke *et al.* (1973) reported a composition containing 23.3 wt % MgO from the A_2 spinifex zone (SA1160). In the more comprehensive study of Arndt *et al.* (1977), a spinifex-textured komatiite from the fractured flow top (A_1 zone) has an anhydrous MgO content of 23.4 wt % (P9-120), whereas other compositions, which were believed to closely resemble liquids, contain between 21.8 and 28.6 wt % MgO. Nesbitt & Sun (1976) analysed three spinifex-textured rocks, which contain between 20.7 and 23.5 wt % MgO. Here we take an average of three Munro spinifex-textured komatiites, 422/95, 422/91 and 422/94, to

Table 2: Major and trace element compositions of komatiite primary liquids for each suite

Group:	Barberton		Barberton		Belingwe		Yilgarn		Regal–Ruth Well		Coonterunah		Munro	
Method:	sp, ol		sp		sp, ol		sp, ol		sp, ol		sp, ol		sp	
Type/location:	AUK	ADK	± (%)	Reliance	± (%)	AUK	± (%)	ADK	± (%)	AUK	± (%)	Pyke Hill	± (%)	
SiO ₂	45.87	47.70	1.6	47.12	0.5	46.16	1.3	46.77	4.2	49.03	1.3	45.47	1.0	
TiO ₂	0.22	0.42	1.3	0.32	1.7	0.36	7.1	0.38	12.5	0.36	14.6	0.41	10.5	
Al ₂ O ₃	4.07	4.51	2.3	6.76	1.7	7.07	2.4	4.16	18.4	8.00	7.6	8.69	3.8	
Fe ₂ O ₃	12.89	12.66	6.1	12.42	2.9	11.75	4.3	13.15	8.3	12.16	11.7	12.33	3.3	
MnO	0.24	0.20	10.1	0.23	18.7	0.22	24.8	0.17	67.1	0.20	18.2	0.21	6.0	
MgO	30.11	26.06	2.7	25.97	n.a.	27.00	n.a.	29.00	n.a.	22.93	n.a.	22.56	2.9	
CaO	5.87	7.33	1.2	6.45	5.6	6.94	16.1	5.90	41.6	7.09	21.4	8.85	2.9	
Na ₂ O	0.49	0.62	40.6	0.54	62.6	0.66	33.7	0.44	23.2	0.16	69.6	0.70	33.4	
K ₂ O	0.19	0.04	67.9	0.19	122.9	0.05	75.0	0.04	126.0	0.02	42.5	0.10	67.4	
P ₂ O ₅	0.04	0.04	26.4	0.02	41.1	0.03	14.7	0.05	46.5	0.03	19.8	0.05	40.6	
SO ₃		0.01	22.1											
LOI	6.31	5.33	7.7	5.48	65.9	7.41	47.6	12.52	33.4	9.18	46.0	4.25	19.9	
Total	100.00	99.59	0.5	100.02	0.3	100.79	0.8	100.05	0.5	99.99	0.5	99.39	0.6	
Mg#	82.23	80.31		80.56		81.99		81.38		78.89		78.38		
Ca/Al	1.44	1.63		0.95		0.98		1.42		0.89		1.02		
Fe/Mn	47.56	56.53		49.27		47.48		69.44		53.76		52.18		
Al/Ti	16.12	9.54		18.85		17.21		9.60		19.40		18.64		
Li	1.96	2.57										8.69		
Be	0.15	0.17										0.07		
P	100	175										149		
K		469										929		
Sc (XRF)	17.1	23.4	5	22.0	6	27.0	4	18.5	14	28.5	3	29.0	8	
Sc	15.8	20.8	5	28.2	2	25.6	3	16.1	15	27.5	6	29.8	8	
Ti (XRF)	1380	2500	1	1842	1	2352	14	2092	12	2146	19	2467	10	
Ti		2559	2	1601	11	2237	13		12	2352	25	2570	7	
V (XRF)	107.9	133.2	4	157.2	4	142.7	4	106.4	5	140.3	18	175.8	10	
V	108.2	126.8	0	142.2	8	140.0	4	101.1	15	139.9	13	183.5	4	
Cr (XRF)	3091	2869	3	2609	1	2898	8	2644	5	3576	5	3361	3	
Cr	2689	2502	8	2607	7	2482	13	2238	2	3513	13	3053	10	
Co (XRF)	108.0	99.6	4			101.0	8					94.5	4	
Co	112.5	97.8	3	88.6	17	98.4	8	105.9	9	91.0	13	92.1	5	
Ni (XRF)	1689	1285	5	1361	2	1209	4	1729	13	839	8	986	13	
Ni	1647	1307	9			1159	12	1436	8	802	9	942	8	
Cu	4.4	22.7	127	47.4	25	26.5	41	5.8	34	60.4	96	58.7	11	
Zn	64.4	71.1	15	50.1	4	74.3	20	70.2	22	98.8	34	77.7	24	
Ga	3.96	5.26	2	6.82	4	6.27	3	4.54	5	6.94	6	8.77	4	
Ge	0.0	0.72	5	0.61				0.38	3	0.60	9	0.61	6	
Rb (XRF)	4.6	2.3	56											
Rb	4.0	0.70	61	3.31	175	2.12	90	0.99	36	0.40	27	2.22	34	
Sr (XRF)	35.7	35.9	17	27.8	61	27.9	50	46.8	36	42.9	37	24.0	72	
Sr	23.8	36.8	17	30.0	15	28.0	55	36.4	44	38.0	58	25.6	73	
Y (XRF)	3.5	9.3	5	6.7	4	7.7	9	6.9	8	6.7	25	10.5	5	
Y	4.77	9.07	6	7.05	4	7.89	5	6.86	8	6.80	10	10.13	3	
Zr (XRF)	11.0	27.2	6	14.1	12	18.7	6	9.7	75	19.2	22	20.7	9	
Zr	10.70	24.17	6	14.69	5	19.36	5	17.20	14	18.79	19	18.22	5	
Nb (XRF)	1.15	2.5	21	1.1	4	1.3	57	0.6	52	1.3	91	1.7	24	
Nb	0.66	1.75	14	0.53	6	0.81	13	0.62	12	0.94	34	0.46	5	
Mo	0.13	1.38	140	1.48	125	0.26	96	0.78	62	0.15	49	0.36	36	
Cd	0.10	0.09	51			0.02	33	0.02						
Sn	0.57	0.62				0.32	26	0.83	49			0.21		
Sb	0.03					0.11	72	1.07						
Cs	0.521	0.31	71	0.54	170	3.46	222	1.22	61	0.13	37	0.33	9	
Ba (XRF)	12.650	11	88			14	115	18	77			12	44	
Ba	10.962	8.74	79	22.62	101	11.59	138	4.77	96	9.66	56	9.74	75	
La	0.746	1.850	12	0.701	5	0.672	12	0.963	13	1.091	10	0.414	10	
Ce	1.884	5.250	12	1.792	4	2.063	11	2.387	7	2.711	10	1.331	10	
Pr	0.289	0.799	13	0.312	3	0.365	10	0.368	7	0.421	9	0.243	7	
Nd	1.402	3.945	14	1.672	3	2.008	9	1.947	6	2.142	5	1.498	4	
Sm	0.459	1.190	14	0.622	4	0.723	7	0.729	8	0.704	6	0.711	3	
Eu	0.171	0.397	13	0.253	3	0.307	6	0.247	20	0.204	26	0.324	15	
Gd	0.616	1.450	13	0.910	4	1.038	6	1.054	6	0.959	5	1.203	2	
Tb	0.115	0.252	11	0.169	4	0.196	7	0.189	7	0.169	6	0.233	2	
Dy	0.754	1.547	10	1.107	5	1.244	4	1.199	3	1.147	7	1.592	2	
Ho	0.166	0.325	10	0.242	4	0.274	5	0.256	4	0.257	7	0.360	2	
Er	0.490	0.924	9	0.721	6	0.802	5	0.713	5	0.767	7	1.056	2	
Tm	0.072	0.130	11	0.101	1	0.116	4	0.101	5	0.116	10	0.157	3	

(continued)

Table 2. Continued

Group:	Barberton			Belingwe		Yilgarn		Regal–Ruth Well		Coonterunah		Munro	
Method:	sp, ol	sp		sp, ol		sp, ol		sp, ol		sp, ol		sp	
Type/location:	AUK	ADK	± (%)	Reliance	± (%)	AUK	± (%)	ADK	± (%)	AUK	± (%)	Pyke Hill	± (%)
Yb	0.481	0.838	7	0.705	5	0.765	2	0.644	5	0.794	6	1.029	5
Lu	0.073	0.126	7	0.110	5	0.117	3	0.091	2	0.120	6	0.154	4
Hf	0.282	0.666	8	0.433	6	0.535	3	0.480	13	0.519	12	0.581	7
Ta	0.044	0.121	12	0.037	20	0.054	16	0.057	25	0.047	10	0.033	
W	0.000					0.332	800	0.524					
Pb	0.541	0.553	31	0.906	40	1.380	86	1.227	22	5.275	152	0.303	47
Th	0.056	0.183	14	0.079	24	0.079	32	0.167	10	0.107	36	0.030	17
U	0.018	0.046	11	0.013	27	0.021	16	0.047	23	0.026	28	0.011	6

n.a., not analysed.

The method for calculation of the parental magma is by an average of spinifex rocks (sp) or olivine composition (ol). Numbers in bold denote the preferred values where both XRF and ICP-MS data are available.

derive an average near 23 wt % MgO, in line with estimates from Arndt and colleagues, who suggested ~25 wt %.

Belingwe

The komatiites from Belingwe are notable for their excellent mineralogical preservation, the best of the Archean occurrences, garnering considerable attention as a result. Nisbet *et al.* (1977) estimated the MgO content of the parent magma at 32 wt % based on sample NG152 from a pillow lava with quenched crystals. However, this sample is extensively altered, thereby calling its chemical fidelity into question. Subsequently, komatiitic rocks from the Reliance formation, retrieved from the SASKMAR drill-hole, revealed fresh chilled samples with 25.8–25.9 wt % MgO (Nisbet *et al.*, 1987, 1993). In substantiation of this evidence, Renner *et al.* (1994) re-constructed the bulk flow composition and calculated a magma composition of 25.6 wt % MgO. We adopt their value and normalise the Belingwe samples to 26 wt % MgO.

Yilgarn

Komatiites occur extensively within the Norseman–Wiluna Greenstone Belt of the eastern Yilgarn Craton and, owing to their associated Ni deposits, are also well studied (Hill *et al.*, 1988; Leshner & Arndt, 1995; Hill, 2001; Barnes *et al.*, 2004; Barnes & Fiorentini, 2012; Thébaud *et al.*, 2012). Although crustal contamination has affected some sequences, notably at Kambalda and Forrestania (Leshner & Arndt, 1995; Perring *et al.*, 1996), care was taken to avoid such compromised samples. Common to most komatiitic sequences in the Yilgarn is a maximum olivine Fo content of ~94, as evidenced by intercepts on MgO–FeO plots and by compositions of olivines from dunite cumulates (Barnes & Fiorentini, 2012). Because the Yilgarn komatiites have around 11 wt % FeO^(T) (Table 1; Barnes & Fiorentini, 2012), and assuming 10% of this was originally Fe³⁺, then applying a K_D^{Fe-Mg} of 0.3 yields a parental MgO content of 27 wt %. Estimates for the parental magma typically range between 25 and 30 wt %, depending on the location. At Mt. Clifford–Marshall Pool, the chilled margins have ~27 wt % MgO (Barnes *et al.*, 1973) and although the

most magnesian olivine is Fo_{94.9}, the vast majority are Fo₉₄ in the dunites (Donaldson *et al.*, 1986; Hill *et al.*, 1988), again suggesting close to 27 wt % MgO in the liquid. Naldrett & Turner (1977) observed spinifex-textured komatiites from Yakabindie to fall into two groups: those containing around 32 wt % MgO, and those with between 25.7 and 29.4 wt %. Using their estimate for the average Fo content of olivine, which again is 94, a melt MgO content of 27 wt % is more reasonable. In our study, sample 331/947 from Yakabindie is an STK with parallel-oriented olivines, a product of crystallization in the A3 zone and not representative of the parental liquid. Spinifex-textured komatiites from Scotia, which occur much further south, preserve a range of MgO contents (26.18–33.09 wt %) with an average of 29.4 wt % and 11.77 wt % Fe₂O₃^(T) ($n = 32$) (Stolz, 1981). True chilled komatiites from Scotia contain 27.77 wt % MgO ($n = 4$). Therefore, despite the spatial extent of these lavas, it can be argued that the parental magma had 27–28 wt % MgO for the majority of flows in the Yilgarn Craton (S. J. Barnes, personal communication, 2013), except for the Perseverance suite, which is closer to 30 wt % (Barnes *et al.*, 1988, 1995; Nisbet *et al.*, 1993) and the Murphy Well komatiites, which extend to 34 wt % (Siegel *et al.*, 2014).

Regal–Ruth Well

Unfortunately, the extensive metamorphism experienced by the Regal Formation renders reconstruction of the primary magma difficult, as there is no fresh olivine preserved. Furthermore, as FeO is disturbed (176/723, 176/725), the olivine control line is blurred. However, where Y and the REE abundances project to zero, the MgO content is ~52–53 wt %. Such an olivine would be in equilibrium with a melt containing ~29 wt % MgO and ~11.6 wt % FeO, in agreement with Nisbet & Chinner (1981) and Arndt *et al.* (2001).

Chemical effects of alteration and metamorphism

During metamorphism and alteration of Archean komatiites, ingress and subsequent loss of fluids has transported labile elements into and out of the rock.

Therefore, central to the assessment of the chemical characteristics of komatiites is the identification of elements that are susceptible to mobility. Here, only post-crystallisation modification of the chemistry of a komatiite suite is considered; this is expected to be more pronounced in rocks with higher olivine contents and hence lower trace element budgets (Barnes *et al.*, 2004). To assess the extent of disturbance, each komatiite is corrected along olivine control lines to the parental magma composition for a given suite. The standard deviation of an element in the parent magma is then calculated.

In Table 2, the standard deviation associated with the mean value for the magma of a suite is given for each element. This is an expression of the spread of values for each corrected whole-rock composition, which is summarised in Fig. 4, where the elements are arranged by concentration (Fig. 4a) and atomic number (Fig. 4b). An average standard deviation across all suites is calculated along with its uncertainty.

Major elements (analysed by XRF) define a log-linear trend with RSD proportional to their concentration (Fig. 4a). Thus, lower uncertainties are expected for elements such as Si (2%) and Mg (3%), but also for the high field strength elements (HFSE), such as Ti (8%) and Al (6%), which plot at relatively low RSD for a given concentration, indicating that they are less prone to disturbance. By contrast, the alkalis, K (84%) and Na (44%), and Ca (15%) to some degree, have comparatively higher RSDs for their abundance, reinforcing that they are susceptible to post-igneous alteration by metamorphism and associated fluid mobility. The alkalis are mobile even in the well-preserved Reliance Formation, although Ca behaves more conservatively there and in other, less altered suites (Barberton and Munro). Therefore, we consider that K, Na, $P \pm Ca$ and Mn do not preserve their original magmatic compositions and they are therefore not included in the petrological appraisal.

From Sc to Ni, the RSD on the corrected value varies between about 5 and 10%, where the variability on the XRF-determined values is comparable with (Sc, Ti and V) or better than (Co, Cr, Ni) those determined by ICP-MS (Fig. 4b). A departure from this behaviour is observed for Cu, and to a lesser extent Zn, which display an order of magnitude greater variability than other first-row elements, even in the Reliance Formation (Table 2). This would suggest post-magmatic mobilization of Cu by metamorphism, a process that can also affect Zn, though only in the more altered suites (Coonterunah, Regal–Ruth Well). Gallium and Ge show a much lower uncertainty, similar to other first-row transition metals at around 5% relative.

As expected, the LILE, Rb and Sr show considerable scatter, even for the Reliance Formation, suggesting that the variability is post-magmatic. Importantly, there is no difference between the data obtained by XRF and ICP-MS methods, ruling out analytical bias. For Y, Zr and Nb, ICP-MS data have improved precision

compared with XRF data, owing to their low concentrations (≤ 25 ppm). Although Y has a very low standard deviation (6%), Zr and Nb are slightly elevated at around 10–15%, perhaps a product of the difficulty of retaining such HFSE in solution. Heightened uncertainties on Hf and Ta (8 and 16%) also support this conclusion. The poor precision on values for Mo, Cd, Sn and Sb means that these elements are of little petrogenetic value. Caesium and barium, as LILE, are also sufficiently disturbed to render them unhelpful. A dramatic change in behaviour occurs for the REE spectrum. The REE exhibit a gradual decrease in uncertainty from La, with a standard deviation of 11%, to Lu, 5%, with only the conspicuous peak of Eu (14%) tainting the trend. The mobility of Eu^{2+} is well documented, whereas the tendency for other REE to remain in the trivalent state ensures their reliability. In detail, Eu behaves coherently in the less-altered suites (Belingwe, Barberton, Yilgarn, Munro), whereas the uncertainty increases to 26% for the Coonterunah suite (Table 2). Thorium and U have rather large uncertainties of about 20%, although this is probably a function of their very low abundances, particularly for U, rather than post-emplacement disturbance. However, Th is present at similar concentrations to Lu but shows greater scatter, implying some degree of mobility. We suggest that Rb, Sr, Mo, Cd, Sn, Sb, Cs, Ba, Pb ($\pm$ Cu, Eu) do not preserve their initial magmatic concentrations in Archean komatiites and these elements are not considered further.

Trace element geochemistry

Unlike major elements, trace elements play no role in dictating phase equilibria. However, they can be used to constrain the conditions of melt generation and characteristics of the mantle source. Considering that komatiites are the products of large degrees of partial melting, and that most trace elements are highly incompatible in olivine and orthopyroxene, they are likely to faithfully reflect the trace element characteristics of their sources, provided they are not affected by subsequent alteration and metamorphism, the presence of residual garnet or crustal contamination. Komatiitic magmas exhibit a spectrum of incompatible trace element patterns relative to the primitive mantle (Fig. 5). The REE can simplify interpretations of the predominant petrogenetic processes; the LREE are sensitive to prior source depletion, whereas HREE abundances are controlled by the degree of partial melting, where their slope is indicative of the presence or absence of residual (majoritic) garnet. As the bulk partition coefficient nears unity, as is the case for the HREE, the style of melting (fractional or batch) becomes unimportant.

The Munro komatiites have elevated HREE ($\sim 2 \times PM$) suggesting low degrees of partial melting relative to other komatiites, especially given the depleted nature of the mantle source ($La/Sm_N \approx 0.4$; Fig. 5a). Although the HREE can be reproduced by 25% melting of depleted mid-ocean ridge basalt (MORB) mantle (DMM) (Fig. 5b),

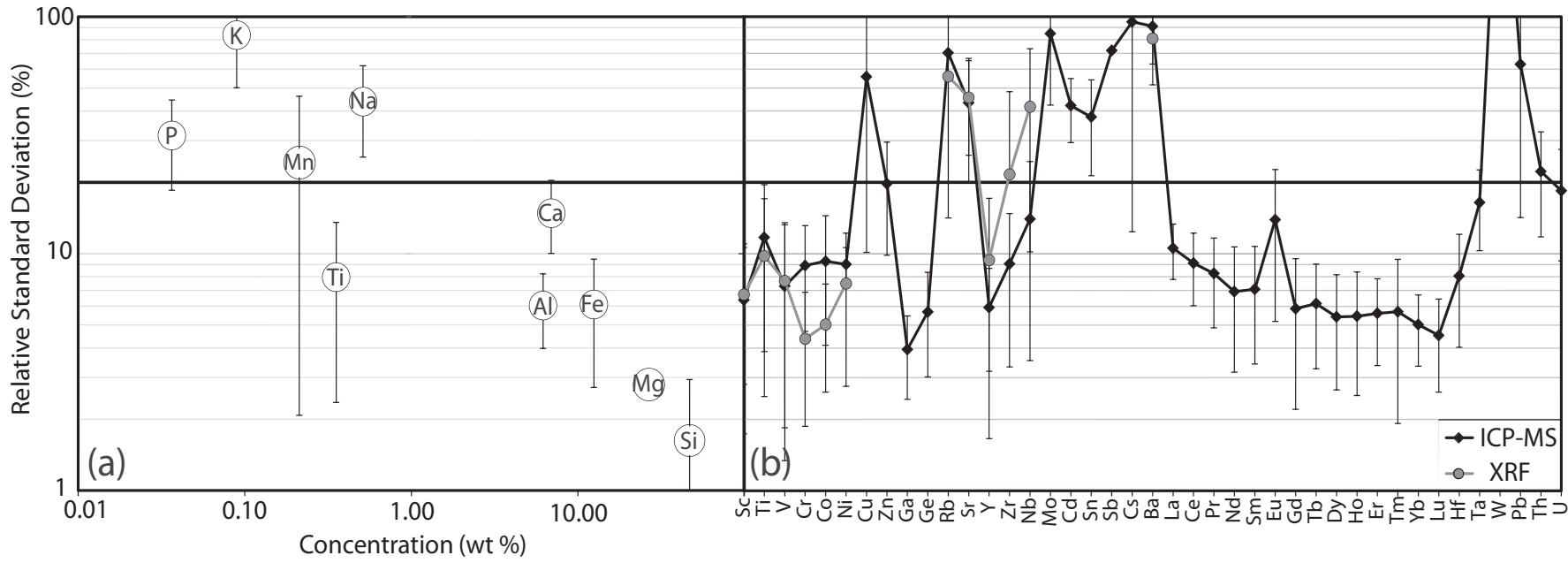


Fig. 4. Following normalisation of komatiite major and trace element data to an appropriate parental magma composition, the variability of a given element (relative standard deviation) is plotted as a function of concentration (a) and mass number (b). The bold lines (grey, XRF; black, ICP-MS) represent the average variability for the combined suites, and the horizontal line (RSD = 15%) is the threshold of uncertainty for primary values. Elements with values exceeding 15% are assumed to have been modified from their igneous concentrations.

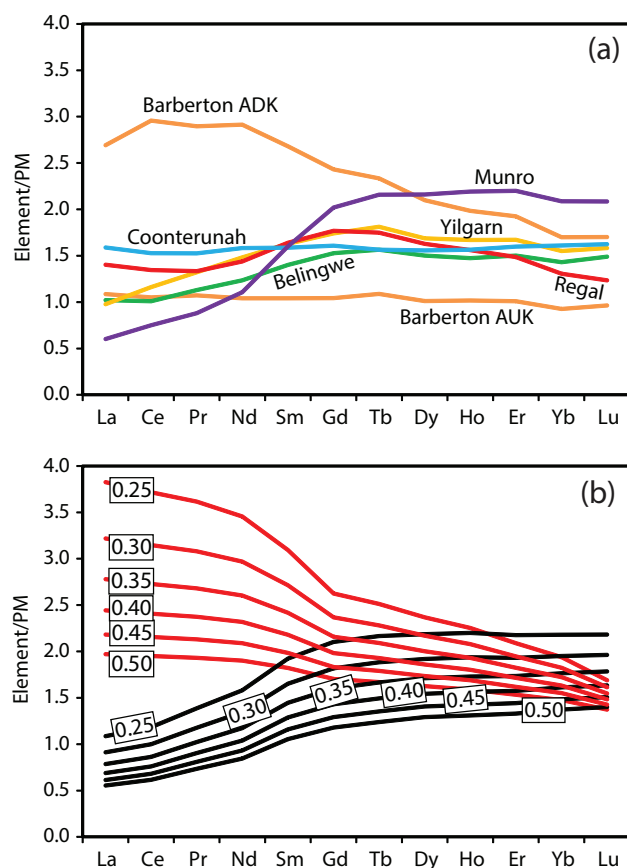


Fig. 5. (a) Primitive mantle-normalised rare earth element compositions of the calculated komatiite parental magmas. (b) Modelled batch melts of varying degree (numbers in boxes) of a primitive mantle source in the garnet stability field (red) and a depleted mantle source without garnet (black).

the strongly sloped LREE pattern requires more than one depletion event to have affected the source (Arndt *et al.*, 1977; see the section ‘Style of melting’ below). The Coonterunah and Barberton AUKs are identified by their flat PM-normalised REE patterns, and, in the case of the latter, the abundances are almost identical to primitive mantle values (Fig. 5a). Paradoxically, the melt fractions required to model these abundances for extraction from a primitive mantle source are near 90% for the Barberton AUK, and about 45% for the Coonterunah samples, which are clearly unfeasible given their major element compositions. Here, the major elements that are not appreciably affected by alteration (Al, Ti, Mg, Si and Fe) are more diagnostic as they reflect phase equilibria; these are discussed in the section on ‘Conditions of melt generation’.

Barberton ADKs have negatively sloping HREE, combined with enrichments in the LREE (Fig. 5a); 30% batch melting of a primitive mantle source containing residual garnet can produce such a pattern (Fig. 5b). The Regal–Ruth Well komatiites were derived from a slightly more depleted source, but segregated after about 35% melting in equilibrium with garnet, producing a Gd/Yb_N similar to the Barberton ADKs.

Intermediate expressions between the two extremes are also observed: Belingwe and Yilgarn both have positively sloping LREE patterns along with relatively flat HREE. Their REE spectra are a product of 35–40% melting of DMM, straddling conditions near the exhaustion of garnet that give rise to Gd/Yb_N just above unity.

A key to the interpretation of the geochemical signatures of mantle melts is discerning between the effects of partial melting (degree of melting, mechanism of melting) and source composition. Variations in source fertility can be explored through ratios of element pairs that have differing incompatibilities but otherwise behave in a similar fashion. Such a requirement is met by Nb/Zr—both are HFSE (refractory, immobile)—but Nb is roughly an order of magnitude more incompatible than Zr, and therefore is fractionated in small- to medium-degree partial melts. At high degrees of melting, variations in Nb/Zr are inherited from their mantle source, the composition of which is readily modified by extraction of even small fractions of melt. The La/Sm_N couple has similar properties, however, as $D_{\text{Nb}} < D_{\text{La}} < D_{\text{Sm}} = D_{\text{Zr}}$, it is not as sensitive to source composition. The komatiites group into clusters, defining a trend towards decreasing Nb/Zr and La/Sm_N as expected from the hierarchy of bulk D values (Fig. 6a). Modelling of a primitive mantle source (Palme & O’Neill, 2014) shows that the Nb/Zr and La/Sm_N ratios of a batch melt are ≤ 1.1 times its source value after 30% and 45% melting, respectively (Fig. 6a), suggesting that Nb/Zr and La/Sm_N in komatiites should reflect their source.

Considering this behaviour, two explanations are possible for the array shown in Fig. 6a. The preferred interpretation is that komatiite sources had experienced variable degrees of prior partial melting, with Barberton and Coonterunah komatiites coming from primitive mantle-like sources (Fig. 5a). The spread defined by the remaining komatiites may be explained by partial melting of progressively more depleted sources. If ordered according to the extent of prior melt loss, from least depleted to most depleted they vary in the range of $0\% = \text{Barberton} = \text{Coonterunah} < \text{Regal–Ruth Well} < \text{Belingwe} < \text{Yilgarn} < \text{Munro} = 4\%$ (Fig. 6a). In contrast, if the observed variation was produced solely by differing degrees of partial melting of the same source composition, the mantle source of each would necessarily be depleted, with the Munro komatiites representing the highest degree partial melts (thereby providing the closest estimate to the mantle source composition) and Barberton the lowest; such hypotheses are discrepant with their REE abundances (e.g. Fig. 5a).

The difference between source composition and melting effects is illustrated by a Hf/Sm_N vs La/Yb_N diagram (Fig. 6b). During melting in the spinel facies, $D_{\text{Hf}} \approx D_{\text{Sm}}$, whereas in the presence of garnet $D_{\text{Hf}} > D_{\text{Sm}}$ (Corgne *et al.*, 2012); however, as both D_{Hf} and D_{Sm} are $\ll 1$, this change influences the concentration of these elements only in the melt, not in the residue (Fig. 6b). Variations in La/Yb_N of the melt are caused by prior source depletion (low values) or melting in the garnet

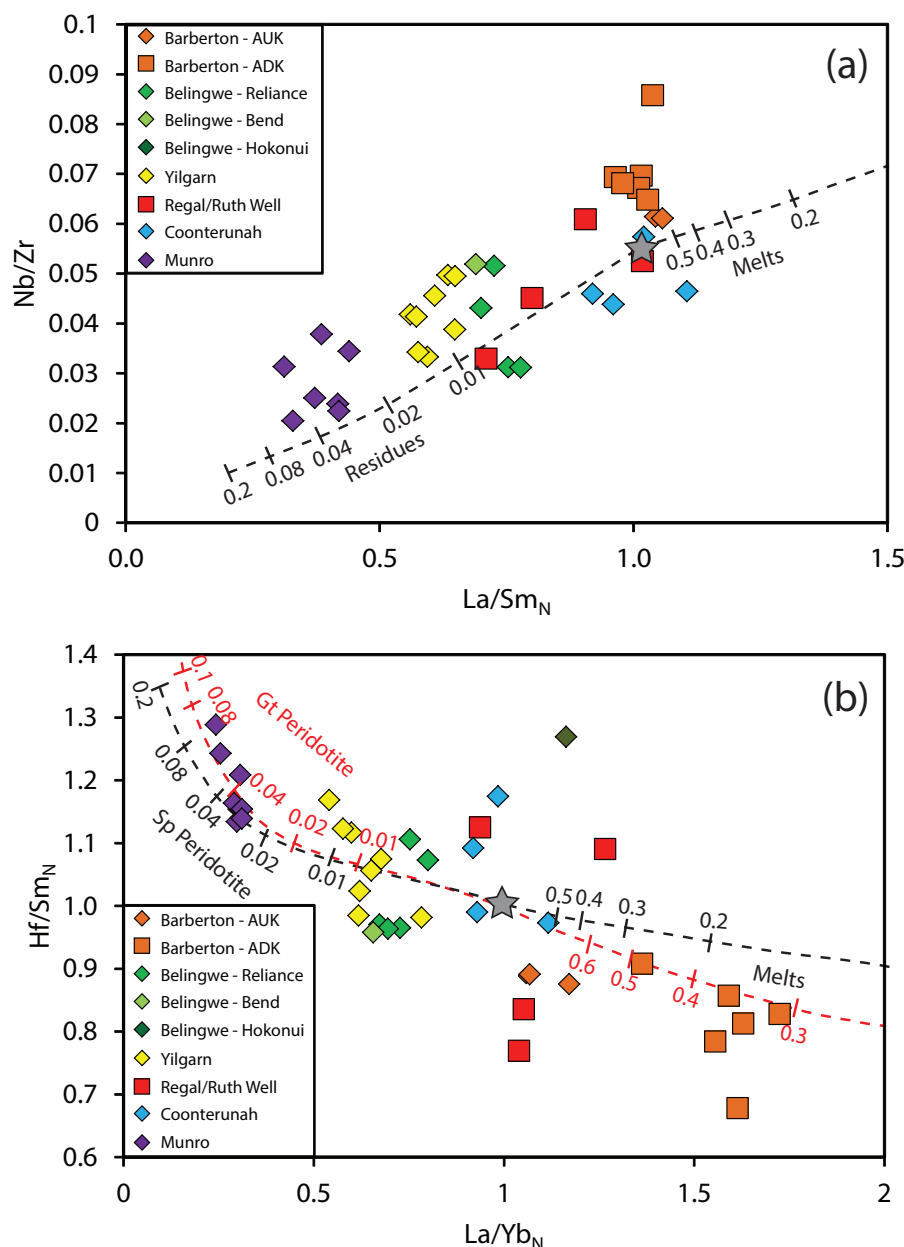


Fig. 6. Incompatible trace element ratio binary plots. As these ratios are not affected by olivine crystallisation, each komatiite sample is plotted. The grey star shows the primitive mantle. Dashed lines give the composition of the peridotite residue after melt extraction, and those of the complementary melts as labelled. (a) La/Sm normalised to primitive mantle vs Nb/Zr. (b) Primitive mantle-normalised La/Yb vs Hf/Sm.

field (high values). As in Fig. 6a, Munro and Barberton define the two end-members of the komatiite array. The Munro komatiite source has experienced 4% melt extraction from a primitive source, compared with $\approx 1\%$ in Yilgarn and Belingwe. The Coonterunah komatiites are unfractionated in both indices, suggesting derivation from a PM-like source under garnet-absent conditions. Modelling melting without garnet cannot reproduce the depletion in Hf/Sm_N with a high La/Yb_N observed in the Barberton and Regal–Ruth Well komatiites.

Variations in the highly incompatible elements Th, Nb and La should also reflect the source compositions of komatiites. These elements are plotted in a ternary

diagram (Fig. 7), following Jochum *et al.* (1991). As expected for such high-*F* melts, most komatiites plot near the primitive mantle composition. Contrary to some komatiites described by Jochum *et al.* (1991), they do not follow a trend expected from melt extraction (if $D_{Th} \approx D_{Nb} < D_{La}$). Instead, Nb–Th are decoupled in the Yilgarn and Munro komatiites, which have a positive Nb anomaly. They are displaced from the primitive mantle in a direction complementary to the Upper Continental Crust (UCC). This signature is also observed in oceanic basalts (especially the HIMU group), which, in their case, is explained by the involvement of recycled basaltic crust in their source. In light of their high *F*, this

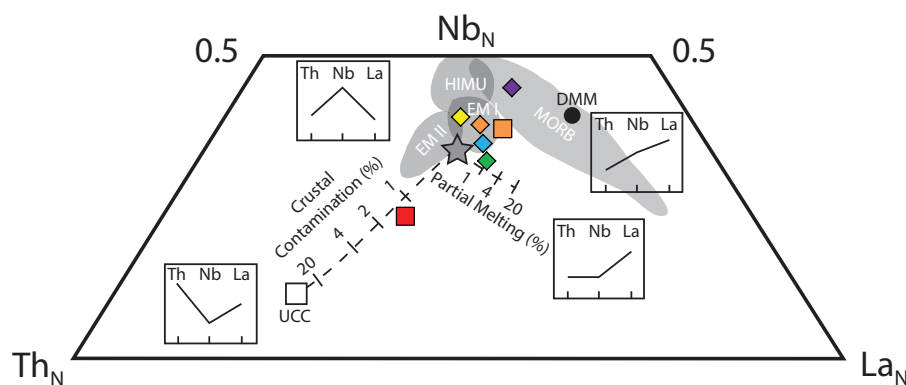


Fig. 7. Primitive mantle-normalised concentrations for calculated komatiite parent magmas (after Jochum *et al.*, 1991). The 'partial melting' model illustrates the evolution of the peridotite residue. 'Crustal contamination' shows the trend of addition of upper continental crust (Rudnick & Gao, 2014) to a model komatiite parent melt with primitive mantle-like trace element ratios. The insets are a schematic depiction of the PM-normalised trace element patterns for each apex. Symbols as in Fig. 6.

anomaly is also inherited from the komatiite source, and is observed only in the younger, more melt-depleted 2.7 Ga suites. Here, we attribute this effect to prior continental crust extraction from their sources; that is, mantle that had experienced melt extraction in the upper mantle, perhaps in a subduction-zone environment causing preferential Nb retention, the complement to the negative HFSE anomalies observed in arc magmas. In addition to source variations, the Th enrichments in the UCC relative to Nb make it ideal for investigating crustal contamination. Of the suites investigated, only the Regal–Ruth Well suite has experienced (upper) crustal contamination, of about 1%, in line with its low Nb/U ratio (≈ 15).

Conditions of melt generation

Style of melting

Trace elements preserve memories of the effects of partial melting and source composition; however, when used in tandem with radiogenic isotopes, a time-integrated history of the mantle source can be revealed. Furthermore, the concordance (or lack thereof) between trace element ratios and radiogenic isotopes facilitates interpretation of the type of melting (batch, fractional or a combination) that occurred during komatiite genesis. The observation that the $\epsilon\text{Nd}_{(i)}$ of komatiite suites show no dependence on the komatiite type (i.e. between ADKs and AUKs), implies that their sources had similar time-integrated Sm/Nd ratios, and that any fractionation in this ratio in komatiites arises from partial melting [Robin-Popieul *et al.*, 2012; although see Blichert-Toft & Arndt (1999) for a contrasting viewpoint]. This has led to the proposition that the three types of komatiite observed at Barberton and Gorgona Island could be produced in a critical melting scenario, intermediate between fractional and batch melting (Sobolev & Shimizu, 1993; Arndt *et al.*, 1997; Robin-Popieul *et al.*, 2012). In this situation, melting proceeds until some portion of the liquid is buoyant enough to escape its source; however, depending on the density contrast between liquid and solid, a certain fraction remains in the residue and

segregates at shallower depths. This gives rise to source depletion just prior to komatiite extraction, with insufficient time for the source to develop a radiogenic isotope signature, decoupling the isotopic signature from the parent–daughter element abundances. The result is that radiogenic isotope compositions in komatiites would be independent of their type or source fertility, as observed at Barberton. This discrimination is important because the style of melting affects how (particularly incompatible trace) element concentrations in partial melts vary as a function of F (e.g. Shaw, 2000).

As a means of distinguishing between melting styles, $\epsilon\text{Nd}_{(i)}$ values taken from the literature on the komatiite suites analysed in this study are plotted versus their Gd/Yb_N and La/Sm_N ratios (Fig. 8). Globally, no correlation between komatiite petrogenetic type and radiogenic isotope composition is observed (Fig. 8a), as noted by Robin-Popieul *et al.* (2012). In contrast, the younger, 2.7 Ga komatiite suites that have more depleted trace element compositions, as quantified by La/Sm_N , tend to have more radiogenic $\epsilon\text{Nd}_{(i)}$, whereas the older examples (Barberton, Coonterunah) with primitive-mantle like La/Sm , have $\epsilon\text{Nd}_{(i)}$ near zero (Fig. 8b). This correlation implies that depletion of the sources of the younger, 2.7 Ga komatiites is ancient (Blichert-Toft & Puchtel, 2010). As such, it did not occur during melting caused by plume ascent, a process that takes <1 Myr to traverse the upper mantle (given a 0.1 m a^{-1} ascent rate), because this timescale is insufficient to generate such radiogenic values given the Sm/Nd ratios. An $\epsilon\text{Nd}_{(i)}$ of +3 corresponds to the depleted mantle (Goldstein, 1984) at 2.7 Ga, suggesting incorporation of material that has undergone prior melting at shallow depths, as supported by Nb–La–Th systematics (Fig. 7). Depending on the assumed composition of the primitive mantle, the 3.2–3.5 Ga komatiites may have undergone slight depletion from a CHUR-like mantle (see Puchtel *et al.*, 2013) or none assuming a non-chondritic source (Caro & Bourdon, 2010). Their primitive mantle-like trace elements preclude any loss of melt from the system upon ascent (i.e. prohibiting

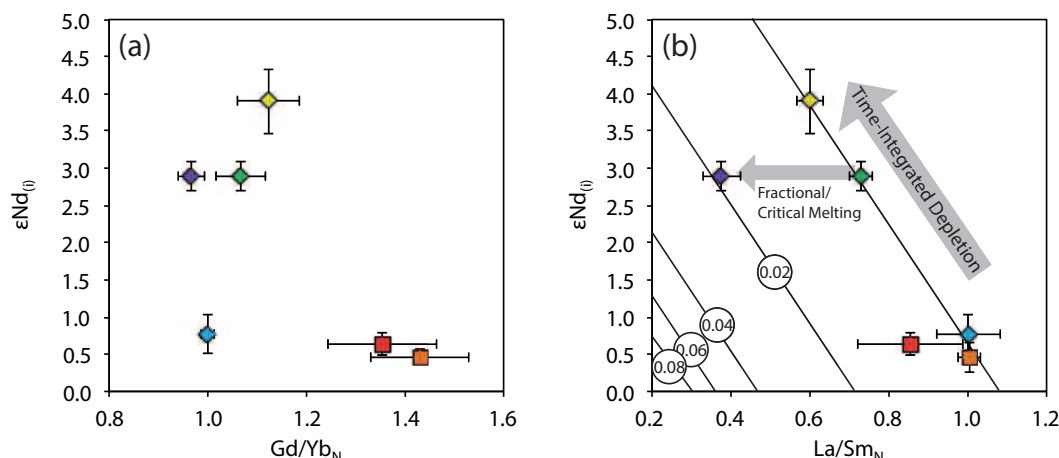


Fig. 8. Comparison between the Nd isotope composition of komatiite suites (symbols as in Fig. 6), corrected back to their age of eruption ($\epsilon\text{Nd}_{(i)}$) and their Gd/Yb_N ratio (a) and La/Sm_N ratio (b). The diagonal line in (b) represents a best fit through the data; lines to its left show the effect of additional partial melting (F values in circles) on the La/Sm_N ratio, assuming no further ingrowth of ^{143}Nd . Neodymium isotope data from Puchtel *et al.* (2013) for Barberton, Puchtel *et al.* (2009) for Munro and Belingwe, Lesher & Arndt (1995) for Yilgarn, and Arndt *et al.* (2001) for Coonterunah and Regal–Ruth Well.

fractional or critical melting), with the simplest explanation being that they represent batch melts of a near-PM source. Taken together, the komatiite suites define a trend that passes near the primitive mantle at $\epsilon\text{Nd}_{(i)} = 0$ and $\text{La}/\text{Sm}_N = 1$. However, the Munro komatiites deviate noticeably from this array, with a much lower La/Sm_N for their $\epsilon\text{Nd}_{(i)}$. This additional depletion of LREE, decoupling them from Nd isotopes, is consistent with melt extraction just prior to the formation of the Munro komatiites, as suggested by Arndt *et al.* (1977). However, this additional melt extraction is constrained to $\approx 2\%$ (Fig. 8b), meaning that the majority of the liquid stayed in contact with its residue; akin to the ‘high retention critical melting’ model of Robin-Popieul *et al.* (2012).

With the exception of the Munro komatiites, the trace element–radiogenic isotope characteristics of komatiite suites globally imply that the majority were formed by batch melting, rather than fractional melting as is typical at low pressures (McKenzie & Bickle, 1988; Asimow *et al.* 1997). However, the Munro komatiites, which are the lowest pressure komatiites, record evidence of fractional melting, an observation discussed in the section on ‘Physics of melting’. In the following sections, we attempt to better constrain melting conditions (P , T , F) using a framework of experimental data. Ensuring the method is robust depends on the following considerations.

1. Source composition. In view of the small degrees of melt extraction undergone by komatiite sources (no more than 4%; see Fig. 6a and b), the melting systematics of a single peridotite composition, the near primitive mantle KR4003 (37.3% MgO) of Walter (1998), are used to elucidate the conditions of melt generation using major elements. When considering mantle Mg# values, we make a small allowance for melt depletion in changing the Mg# of the residue

slightly, affecting the calculated $K_D^{\text{Fe–Mg}}$ to < 0.05 . The uncertainty is discussed in the section on ‘Fraction of melting’.

2. Style of melting. The lack of unequivocal signatures of significant fractional or critical melting in any of the suites (except a small amount at Munro) permits the use of batch melting experiments to constrain the petrogenetic conditions of komatiite formation. Furthermore, differences in the major element compositions of batch melts and accumulated fractional melts at the same F and P are small (Kushiro *et al.*, 1996) and exhibit identical Fe–MgO–FeO systematics (Herzberg & O’Hara, 2002), as discussed further in the section on ‘Fraction of melting’.

Pressure of melting

The frequent use of the Al/Ti ratio in conjunction with Gd/Yb_N as an indicator of the final pressure of melt extraction is based on the different partitioning of Al and Ti into (majoritic) garnet (Zhang & Herzberg, 1994) compared with spinel. In this scheme, komatiites tend to fall into two groups, ADK or AUK (Nesbitt & Sun, 1979), equated with high or moderate pressure, respectively, and hence information about subtle changes in depth are lost. The identification of komatiites with Ti enrichment in Finnish Lapland led Hanski *et al.* (2001) to develop a classification based on Al_2O_3 and TiO_2 abundances, projected from olivine, thereby distinguishing between high pressures (low Al abundance) and low degrees of melting or fertile sources (high Ti), which give similar Al/Ti ratios but result from vastly different petrogenetic conditions. Therefore Al/Ti is not simply correlative with pressure of melting, as has become the rule of thumb in komatiite research.

In an extensive series of experiments, Walter (1998) demonstrated that whereas Al is highly sensitive to pressure, Ti is not, thereby establishing a quantitative

basis for the use of Al/Ti. However, unlike Al, Ti concentration is modified by the extent of melting. As such, both P and F play a role in the resultant Al/Ti ratio of a komatiitic liquid, where increasing melt fraction has the opposite effect to increasing pressure (Fig. 9). Adopting the melting behaviour of Al and Ti from Walter (1998), a

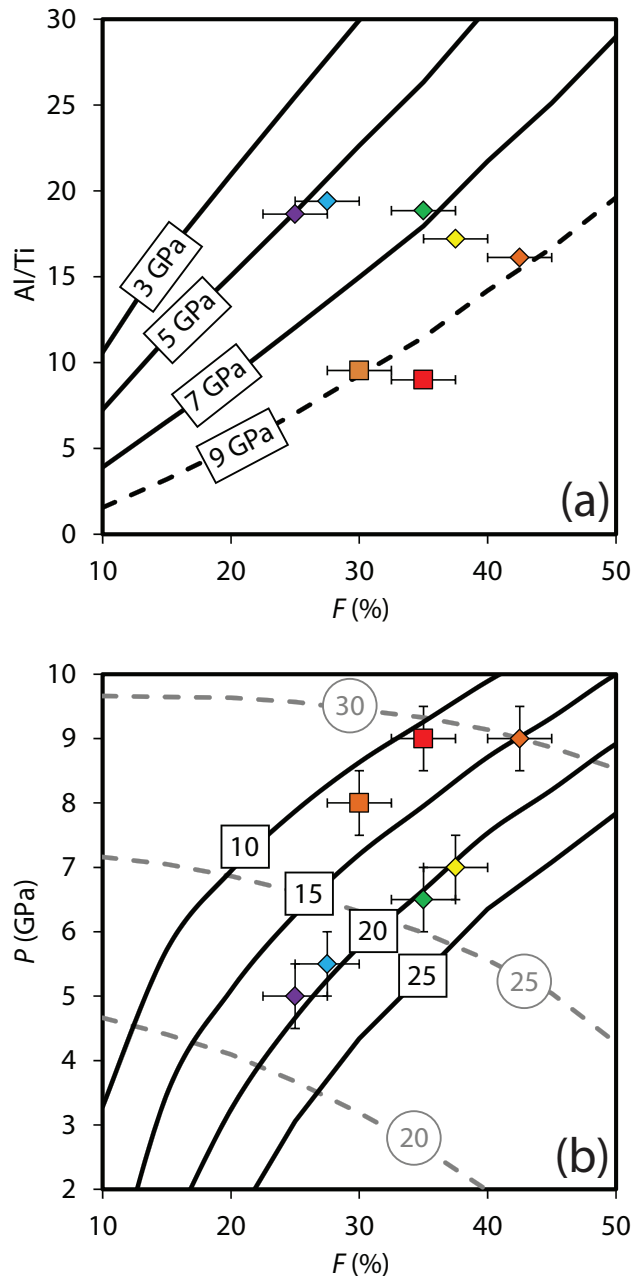


Fig. 9. Variation of Al/Ti as a function of P and F . These diagrams use the experimental data of Walter (1998), adjusted to a starting TiO_2 (wt %) content of 0.1 to make it internally consistent with komatiite data. This does not alter the trends. (a) Calculated Al/Ti ratio for a given melt fraction at different pressures. (b) Constant Al/Ti contours (values in squares) vs F and pressure. Grey dashed lines show the MgO (wt %) contents of melts produced at these conditions (numbers in grey circles). Error bars neglect uncertainty in Al/Ti ratios and are estimated for P and F based on uncertainties in the experiments. Symbols as in Fig. 6.

liquid produced at $F=0.4$ at 7 GPa is calculated to have the same Al/Ti as a 30% melt at 5 GPa (Fig. 9a and b). Hence Al abundance is a less ambiguous indicator of pressure of melting in komatiites (as Al/Ti requires knowledge of F). The disadvantage of using this proxy is that it is affected by olivine fractionation whereas Al/Ti is not (Fig. 10), necessitating accurate determination of the parental magma composition first (see 'Determination of primary magma composition'). This is readily achieved, as Al is sufficiently resistant to post-magmatic alteration (see 'Chemical effects of alteration and metamorphism') such that its concentration can be accurately calculated and is a simple linear function of MgO (Fig. 10a).

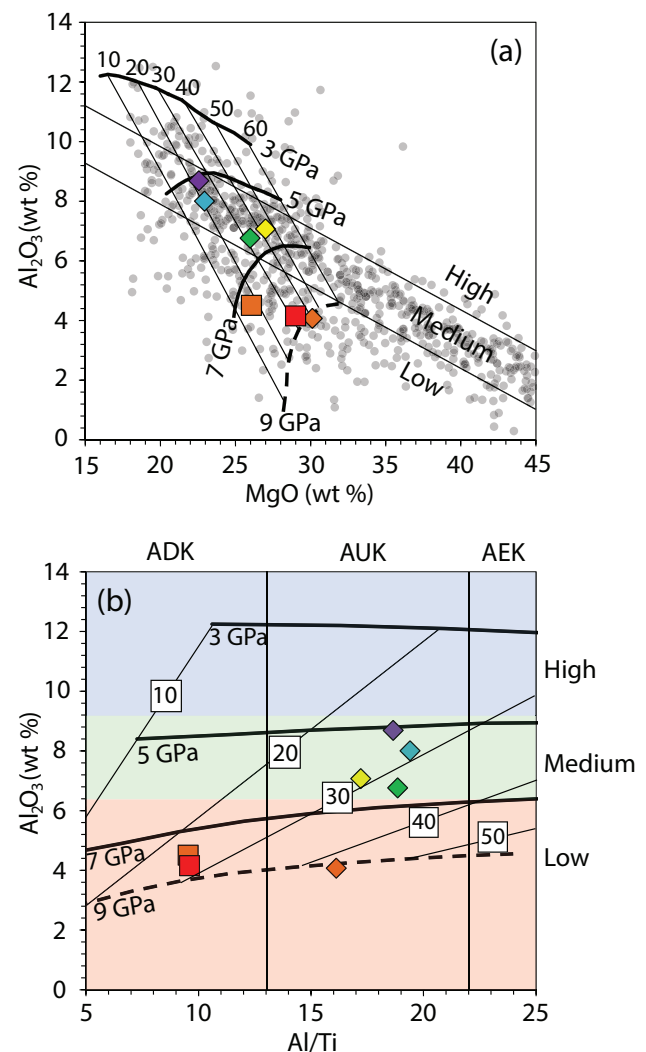


Fig. 10. Chemical discrimination of komatiite types. Grey symbols correspond to a global dataset of komatiite analyses (Barnes & Fiorentini, 2012). Melting contours are taken from Walter (1998). (a) Co-variation of Al_2O_3 (wt %) with MgO (wt %). Natural komatiites follow olivine control lines, the slope of which defines the boundaries between the Low-, Medium- and High-Al komatiite classes. (b) The complementary nature of the Al/Ti and Al_2O_3 classification—the curves for the latter are calculated at 25 wt % MgO and parallel pressure contours (melt fraction contours are shown in lighter lines).

Exploiting these systematics, a new classification of komatiites with a view to constraining pressures of magma generation is proposed using their Al contents (Fig. 10b). A compilation of 786 global komatiite analyses (Barnes & Fiorentini, 2012), highlights that a bimodal distribution is present, though not pronounced, in a plot of MgO vs Al_2O_3 (Fig. 10a). A subdivision between the newly classified ‘Low-Aluminium Komatiites’ and ‘Medium-Aluminium Komatiites’ can be quantified as a function of MgO given the stoichiometry of olivine addition assuming Al is perfectly incompatible. From a komatiite liquid with 25% MgO, crystallisation of Fo_{90} gives a slope of Al_2O_3 (wt %) = -0.27MgO . Adopting this slope, the y-intercepts are 13.25 and 15.25 for the Low–Medium and Medium–High Al boundaries, respectively. These boundaries are subparallel to melt fractions where the melting stoichiometry is dominated by olivine (3 GPa), but become increasingly perpendicular to them at higher pressures.

The complementarity with the Al/Ti discrimination is illustrated in Fig. 10b. Low-, Medium- and High-Al komatiite boundaries calculated at 25 wt % MgO are parallel to melts formed at constant pressure (Walter, 1998). Here, the Low-Al type corresponds to partial fusion pressures above 7 GPa, Medium-Al pertains to between 5 and 7 GPa, and High-Al komatiites to less than 5 GPa. Contours of melt fraction flatten with increasing degree of melting, whereas the Al/Ti classification is independent of Al content. The Al classification makes no judgement as to the character of the mantle source, in contrast to the Al/Ti classification in which the ‘undepleted’ definition signifies chondritic Al/Ti. This is a misnomer, because the source of ‘undepleted’ komatiites is often depleted with respect to major and trace elements (Figs 6 and 7). Therefore, whereas Al/Ti ratios in komatiites are best utilised to assess the presence or absence of garnet in the residue, their Al contents are more faithful determinants of melting pressure. Together, estimates of both P and F are readily obtained.

Figure 5 of Walter (1998) illustrates the dependence of various major elements on pressure and melt fraction, and, of these, Al, Mg and Fe are critical to constraining P and F . A similar exercise was undertaken by Herzberg (1992), who projected experiments from the CMAS system into FCMAS (encompassing 98% of the elements in a natural peridotite) to calculate the compositions of partial melts of peridotite up to 10 GPa and obtained very similar results to the experiments on natural peridotite. The combination of all three oxides, Al_2O_3 , $\text{Fe}_2\text{O}_3^{(\text{T})}$ and MgO, in the experimental melts is depicted in Fig. 11, contoured for P and F . Superimposed on this plot are the calculated primary komatiite liquids. The projected compositions define a clear trend perpendicular to the pressure contours. Suites produced by the lowest degrees of melting (Munro and Coonerunah) also record the lowest pressures (near or just above 5 GPa). Both Belingwe and Yilgarn have Al contents that suggest a pressure of melting close to 7 GPa, a result in line with their weakly

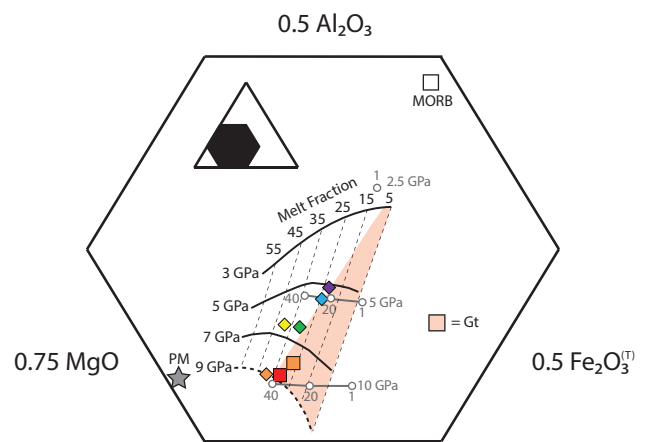


Fig. 11. Modified ternary plot with apices of MgO , Al_2O_3 and $\text{Fe}_2\text{O}_3^{(\text{T})}$. The curves for melt fraction and pressure are parameterised from the data of Walter (1998) in black and Herzberg (1992) in grey. The calculated komatiite parent magmas, the primitive mantle (PM) and MORB (Workman & Hart, 2005) are plotted for reference. The shaded pale red area shows the stability of garnet. Symbols as in Fig. 6.

fractionated HREE abundances and estimates from Herzberg & O'Hara (2002). Unsurprisingly, the ADKs of Barberton and Regal–Ruth Well indicate pressures above 7 GPa—extrapolation of the Walter (1998) trends might suggest a P of 8 and 9 GPa, respectively. The Barberton ADKs plot to a lower melt fraction as a consequence of their lower MgO contents. The AUKs of Barberton record very high pressures (comparable with Regal–Ruth Well ~ 9 GPa) at high melt fractions ($\geq 40\%$; see ‘Fraction of melting’), implying very high mantle potential temperatures. Their Al/Ti ratio ranges between 16 and 18 (Nesbitt & Sun, 1976; Robin-Popieul *et al.*, 2012), placing them close to the AUK field. In this scenario, the high extents of melting have offset the very high pressures, resulting in the exhaustion of garnet, which gives rise to moderate Al/Ti ratios. In fact, Al_2O_3 is lower than in their ADK counterparts (~ 4 wt % vs ~ 4.5 wt %), coupled with much lower TiO_2 (0.22 vs 0.42 wt %), a relic of higher F .

Fraction of melting

In interpreting the conditions of partial melting, mineral–liquid equilibria provide tighter constraints than elemental ratios or abundances. Such an assessment is afforded through the comparable ionic properties of Fe^{2+} and Mg^{2+} , which result in near-ideal mixing in olivine solid solutions. The Fe/Mg ratio of the Earth's mantle is well constrained ($\text{Mg}\# = 89$) and cannot have changed appreciably since the cessation of core formation (O'Neill & Palme, 1998; Delano, 2001). Additionally, the Fe/Mg of the parental komatiite melts is also known to $\pm 5\%$ relative (Table 2), making the application of $K_D^{\text{Fe–Mg}}$ exchange between olivine and liquid possible (Rajamani *et al.*, 1993). The thermodynamic underpinning of this exchange reaction is determined up to 2073 K and 7 GPa (Toplis, 2005), covering the eruptive conditions and the majority of P and T values previously posited for the

generation of komatiites. A favourable property of $K_D^{\text{Fe-Mg}}$ is that it is relatively independent of P and T , but a strong function of composition, and is therefore sensitive to differences in the chemistry of komatiite liquids.

One atmosphere liquidus temperatures were calculated according to the Nisbet (1982) calibration (based on MgO– T correlations for the melt) and the olivine–liquid geothermometer of Ford *et al.* (1983). An intermediate, best-fit value was taken, ameliorating any bias between the two determinations. Using these temperatures, taking the pressure estimates from the ‘Pressure of melting’ section, and compositions from Table 2, the $K_D^{\text{Fe-Mg}}$ can be determined at the P and T conditions of magma formation using the parameterisation of Toplis (2005). The calculated $K_D^{\text{Fe-Mg}} = 0.35 \pm 0.02$ (1SD) depends on composition; higher temperature, higher pressure liquids (Barberton AUK) have higher $K_D^{\text{Fe-Mg}}$, whereas the opposite is true for the Munro komatiites (Table 3). Melt fraction can be solved for considering the equations below.

$$M_r = \frac{M_i - M_l F_M}{1 - F_M} \quad (2)$$

where M is Fe or Mg, and i , r and l denote the concentration in the initial peridotite, residual peridotite, and

komatiite liquid, respectively. With the constraints that $F_{\text{Mg}} = F_{\text{Fe}}$ and that $K_D^{\text{Fe-Mg}} \approx 0.35$

$$\left(\frac{\text{Mg}_l}{\text{Fe}_l}\right) / \left(\frac{\text{Mg}_r}{\text{Fe}_r}\right) = 0.35. \quad (3)$$

Substituting equation (2) into equation (3) yields the F for the komatiite liquid. These equations are summarised graphically in Fig. 12 for $K_D^{\text{Fe-Mg}} = 0.35$ (Bickle *et al.*, 1977) and assuming a primitive mantle starting composition (M_i). Overlain on these melt fraction contours are those for fractional melting (Herzberg & O’Hara, 1998) and pressure contours for KR4003 from Walter (1998). These sets of contours are perpendicular to one another, where, with increasing F at constant P , a small increase in MgO is accompanied by an appreciable decrease in Fe. Conversely, to higher pressures at constant F , both MgO and FeO increase in tandem. The pressure estimates derived from this method are not independent, as pressure is an input parameter for $K_D^{\text{Fe-Mg}}$. As such, this representation is only semi-quantitative, owing also to subtle changes in the calculated $K_D^{\text{Fe-Mg}}$ and the starting source composition (M_i) that affect the melt fraction. These considerations are taken into account, by adjusting M_i (the Fe/Mg ratio) for

Table 3: Parameters for $K_D^{\text{Fe-Mg}}$ modelling

Suite	$K_D^{\text{Fe-Mg}}$	Source (M_i)	F (batch)	1SD	F (fractional)	1SD
Barberton AUK	0.36	PM	0.41		0.50	
Barberton ADK	0.37	PM	0.30	0.04	0.41	0.08
Belingwe	0.35	0.3PM:0.7DMM	0.34	0.03	0.44	0.05
Yilgarn	0.36	0.3PM:0.7DMM	0.38	0.05	0.50	0.09
Regal–Ruth Well	0.36	0.7PM:0.3DMM	0.35	0.07	0.45	0.11
Coonterunah	0.36	PM	0.27	0.12	0.34	0.15
Munro	0.33	DMM	0.26	0.03	0.29	0.05

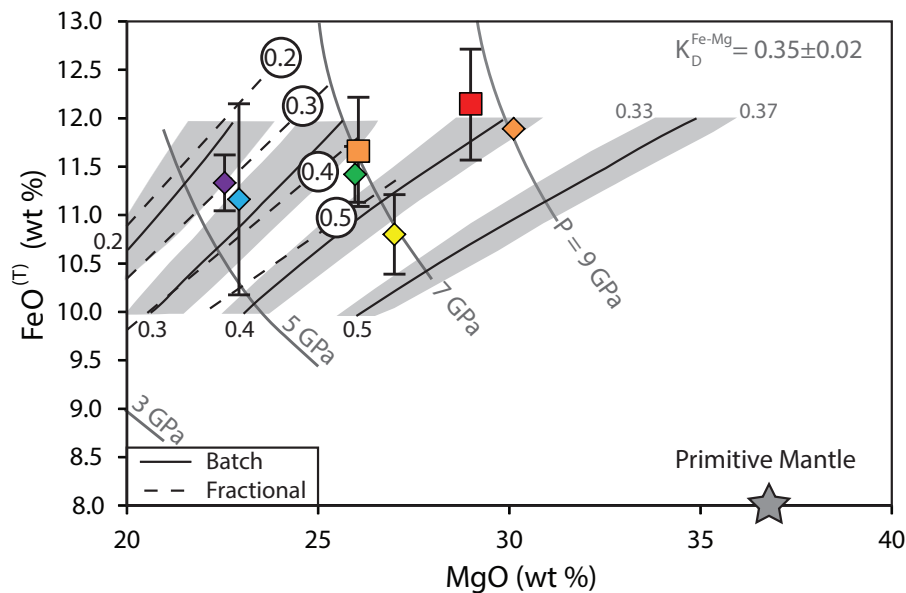


Fig. 12. MgO vs $\text{FeO}^{(T)}$ for the calculated komatiite parental magmas. Shown are the modelled melt fractions calculated for batch melting for $K_D^{\text{Fe-Mg}} = 0.35$, with an uncertainty of ± 0.02 shown by the grey envelopes, for a primitive mantle source (see ‘Fraction of melting’). The dashed lines show the same calculation for fractional melting (Herzberg & O’Hara, 2002). Overlain are the experimentally determined pressure contours of Walter (1998). Symbols as in Fig. 6.

each suite according to its source fertility (see Fig. 6), as detailed in Table 3. The 1SD uncertainty is calculated assuming the bulk of the error comes from the scatter in primary magma $\text{FeO}^{(\text{T})}$ contents. We assume that difference between the Fe^{3+} content of the mantle and that of komatiite liquids is within uncertainty of their known concentration (e.g. Table 2), such that no correction for Fe^{3+} is made.

Regardless of whether pure batch or pure fractional melting is modelled, estimates for P and F increase together, such that the hottest magmas also segregate at the highest pressures. For batch melting, komatiites from Munro and Coonterunah record similar conditions, near 5 GPa and 25% melting. The ADKs of Barberton can be modelled by $30 \pm 4\%$ melting, slightly lower than the Belingwe komatiites at $\approx 34 \pm 3\%$ and the Yilgarn komatiites at $\approx 38 \pm 5\%$.

Fractional melts are typified by systematically higher $\text{FeO}^{(\text{T})}$ contents than batch melts for a given melt fraction, particularly at high F (Herzberg & O'Hara, 2002; Fig. 12). As a result, calculated degrees of melting for komatiites are higher, ranging from 30% for the Munro komatiites to 50% for the Barberton AUKs. Because the range in Fe and Mg spanned by fractional melts is smaller than for batch melts, the uncertainties in F are systematically higher, such that the estimates between fractional and batch overlap (Fig. 12; Table 3). However, it is emphasised that melt fraction and pressure contours in Fe–Mg space are independent of melting style, and hence the relative hierarchy of P and F values calculated for each suite remain unchanged in both scenarios. Considering the uncertainty in initial komatiite FeO and MgO contents, and in the K_D values themselves (grey fields in Fig. 12) the differences in major element composition arising from batch and fractional melting are unresolvable for most suites. Following the reasoning in the 'Style of melting' section, and as will be shown quantitatively in the 'Physics of melting' section, batch melting is probably the dominant form of melting that occurs to produce komatiites, and accordingly these estimates of F are preferred.

Mechanisms of komatiite formation

Mantle potential temperatures

The mantle potential temperature (T_p) is the temperature a parcel of mantle peridotite would have at the surface if it were to adiabatically decompress without melting (e.g. Cawthorn, 1975; McKenzie & Bickle, 1988). The projection of this curve with depth can be estimated as a function of the temperature (T), the coefficient of thermal expansion (α), the mean density (ρ) and the heat capacity at a given pressure (C_p):

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T\alpha}{\rho C_p}. \quad (4)$$

In reality, the trajectory of the convective adiabat in P – T space is curved, as α , $C_p = f(T, P)$. Shockwave

experiments (Miller *et al.*, 1991) account for this curvature by correcting the high-pressure bulk modulus using a Mie–Grüneisen term, and we adopt their expressions here. Under the simplified assumption that a mantle plume ascends at constant velocity, the additional gravitational potential energy means that entropy increases (an irreversible process) during decompression (Ramberg, 1971). A thermodynamic expression to account for this effect on the isentropic gradient was put forth by Ganguly (2005), in his equation (17):

$$\left[\frac{dT}{dZ}\right]_{Q(\text{ir})} = \frac{\rho_r}{\rho} \left[\frac{dT}{dZ}\right]_s + \frac{g}{C_p} \left(1 - \frac{\rho_r}{\rho}\right) - \frac{u}{C_p} \left(\frac{d}{dZ}\right) \quad (5)$$

where Z is the distance (in metres), ρ_r and ρ are the densities of ambient mantle and plume mantle, respectively, g is the acceleration due to gravity (9.81 m s^{-2}), C_p is the heat capacity at constant pressure (in $\text{J g}^{-1} \text{ K}^{-1}$) and u is the acceleration of the plume (in m s^{-2}). As the potential energy of a rising plume is always higher than that of the ambient mantle ($\rho < \rho_r$), the dT/dP slope is 15% lower in the irreversible as opposed to the isentropic case for a parcel of rock that has $\approx 99\%$ the density of ambient mantle, a value typical of purely thermal plumes (see Supplementary Data Appendix C).

When peridotite begins to melt, energy is used to convert solid to liquid, and, consequently, a drop in the temperature of the system occurs, concomitant with the amount of melt produced (F) and the latent heat of fusion (ΔH_{fus}). This effect is quantified by the equation

$$\Delta T_{\text{fus}} = F \frac{\Delta H_{\text{fus}}}{C_p}. \quad (6)$$

The uncertainty in F is the main source of error, and although both ΔH_{fus} and C_p change with temperature, the changes are small, so modelling their temperature dependence is unnecessary (Putirka, 2005; Putirka *et al.*, 2007). Values for ΔH_{fus} and C_p are calculated for a peridotite composition of 60% olivine, 30% pyroxene and 10% garnet yielding 125 J mol^{-1} and $227 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively (Richet & Bottinga, 1986; Téqui *et al.*, 1991; Richet *et al.*, 1993). The fraction of melting is well known for each komatiite parent magma (see the section 'Fraction of melting'), with an average uncertainty of ± 0.05 (Table 3), corresponding to $\pm 30 \text{ K}$.

Based on the major and trace element systematics of komatiites, it is clear that they segregated from their mantle sources at mean depths equivalent to pressures $> 3 \text{ GPa}$ (Nisbet *et al.*, 1993; Herzberg, 1995; Herzberg & O'Hara, 2002; Arndt *et al.*, 2008; see section on 'Pressure of melting'). Therefore, their 1 atm liquidus temperatures are not indicative of their temperature of formation, and must therefore be corrected upwards for pressure. For this purpose, we use the equation of Herzberg & O'Hara (2002), which is calibrated based on 322 data points between 0.2 to 7 GPa and 1100 and 1950°C :

$$T^{\circ}C_{\text{atP}} = T^{\circ}C_{1\text{atm}} + 54P - 2P^2. \quad (7)$$

Herzberg & O'Hara (2002) considered a temperature uncertainty of $\pm 31^{\circ}\text{C}$ up to 7 GPa at the 1σ level. Uncertainty in the pressure of formation by 1 GPa results in a similar error, of the order of $\pm 32^{\circ}\text{C}$. The potential temperature of the mantle source of the komatiite liquid is then given by

$$T_p = T_{\text{atP}} + F \frac{\Delta H_{\text{fus}}}{C_p} - \left(\frac{\partial T}{\partial P} \right)_{Q(\text{ir})}. \quad (8)$$

Input parameters and calculated T_p for each of the calculated primary magmas for the komatiite suites are given in Table 4. Previous estimates place the T_p for the Barberton komatiites at 1900°C (Herzberg, 1992; Nisbet *et al.*, 1993), using the more magnesian 49J sample (Barberton AUK). To put these calculations into geodynamic perspective, the liquidus and solidus curves for typical mantle peridotite have been constructed for $0 < P$ (GPa) < 29 (Fig. 13a), adopting the values of Takahashi (1986) Zhang & Herzberg (1994), Walter (1998) and Hirschmann (2000) below 10 GPa. Over the pressure range of formation of most komatiites (5–9 GPa), the solidus temperatures of Walter (1998) are used to maintain consistency with estimates of the pressure and degree of melting. Above 10 GPa, we plot the solidus and liquidus boundaries of Litasov & Ohtani (2002), with the appropriate effect of phase transitions on the solidus as given by Herzberg *et al.* (2000).

Melt production as a function of T and P is difficult to parameterise because mantle melting is non-modal, such that it depends on the type and number of phases present, which also changes with pressure (see Supplementary Data Appendix B). To remain internally consistent, an empirical fit to the melting relations from Walter (1998), as described by the following equation, are plotted in Fig. 13b:

$$F(P, T) = 2 \cdot 33 \times 10^{-4} T - 1 \cdot 507 P + 1 \cdot 07 \times 10^{-3} P T - 6 \cdot 38 \times 10^{-2} P^2. \quad (9)$$

This equation is calibrated for the range $3 < P$ (GPa) < 7 , $1515 < T$ ($^{\circ}\text{C}$) < 1850 and $0.09 < F < 0.66$, with an average melt fraction misfit of 0.04. As the liquidus

and solidus converge at high pressures, melt production occurs over a smaller temperature interval, necessitating a second-order polynomial fit. Melting at a given pressure and phase assemblage can be approximated as a linear function of temperature, but melt productivity is tempered following phase exhaustion (Asimow *et al.*, 1997; Hirschmann *et al.*, 1999).

Importantly, temperatures calculated for komatiites at their source region are consistent with the degrees of melting based on the experimental data of Walter (1998). Taking the Munro komatiites as an example, they represent a 25% melt at 5 GPa, according to the major element trends. At 23% MgO, they have a 1 atm liquidus of about 1475°C , which, corrected up to 5 GPa [equation (7)], yields 1695°C , with the model predicting $\approx 1700^{\circ}\text{C}$ (Fig. 13b).

Physics of melting

In the infancy of komatiite research, it was postulated that such magnesian magmas could represent near-complete partial melts of the source at low pressure or small-degree melts at high pressure (e.g. Green, 1981). It is clear, from the discussion above, that komatiites are produced under both high- F and high- P melting conditions, a conclusion reached by a number of other researchers (e.g. Herzberg, 1992; Nisbet *et al.*, 1993; Herzberg & O'Hara, 2002; Arndt, 2003).

This combination of both high F and high P necessitates an exceedingly high T_p if the source is nominally anhydrous, as suggested by Berry *et al.* (2008). Estimates for the evolution of ambient mantle T_p , from and within the Archean, converge on a temperature excess of no more than 300°C compared with contemporary mantle (closer to 200°C at 2.5 Ga; Pollack, 1997; Davies, 1998). However, the MgO contents of Archean basalts, assuming that they are products of adiabatic decompression of ambient mantle, suggest that potential temperatures were only marginally (~ 100 – 150°C) higher than at present (Campbell & Jarvis, 1984; Abbott *et al.*, 1994; Herzberg & Rudnick, 2012). If the present-day T_p is $\approx 1350^{\circ}\text{C}$ in passive upwelling settings (McKenzie & Bickle, 1988; Lee *et al.*, 2009), then the Archean ambient mantle had a T_p of 1450 – 1550°C . The lowest calculated T_p , 1750°C , required to produce the Munro komatiites exceeds these estimates by at least

Table 4: Summary of average melt fractions, pressures, and temperatures (in $^{\circ}\text{C}$); at 1 atm, at pressure of melting and the mantle potential temperature (T_p)

	F	P (GPa)	$T_{1\text{ atm}}$ (Ford)	$T_{1\text{ atm}}$ (Nisbet)	$T_{1\text{ atm}}$	$T_{\text{at P}}$	$T_{\text{ad at P}}$	T_p
Barberton ADK	0.3	8	1506	1520	1510	1814	2014	1830
Belingwe	0.34	6.5	1512.5	1519	1510	1792	2019	1850
Yilgarn	0.38	7	1531.5	1540	1530	1810	2064	1900
Barberton AUK	0.41	9	1568.5	1600	1575	1900	2174	1950
Regal–Ruth Well	0.35	9	1549	1580	1560	1884	2118	1915
Munro	0.25	5	1477.5	1460	1475	1695	1862	1740
Coonterunah	0.27	5.5	1458	1460	1460	1697	1877	1740

$T_{\text{ad at P}}$ is $T_{\text{adiabat at P}}$.

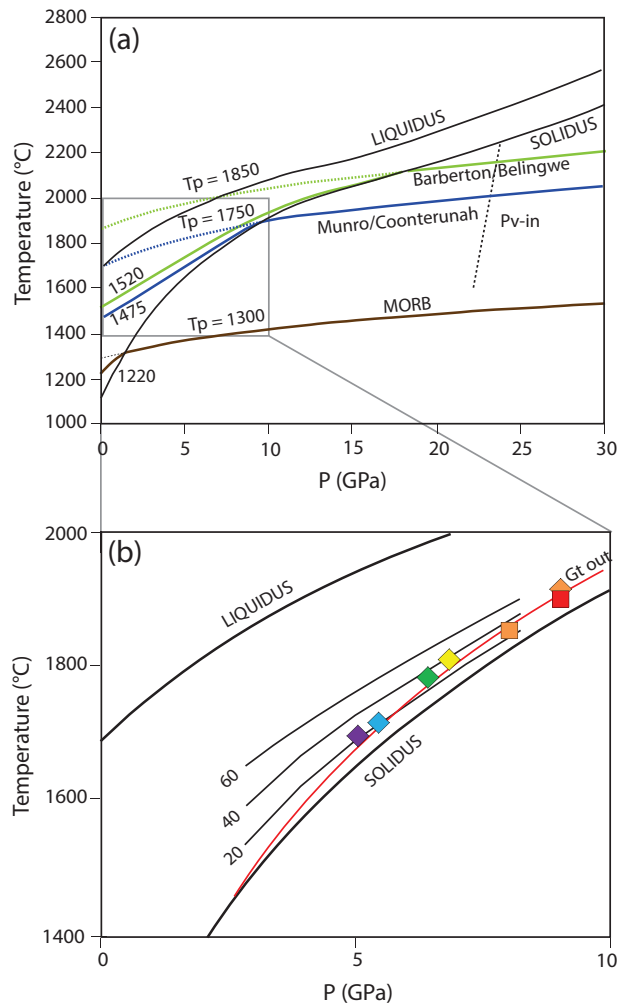


Fig. 13. (a) Adiabatic gradients, calculated according to Miller *et al.* (1991) and modified for gravitational potential energy after Ganguly (2005), for different mantle potential temperatures. Eruptive temperatures (T_{atm}), P , and T at P are given in Table 4. Solidus and liquids of peridotite modelled after the experimental data of Litasov & Ohtani (2002) for $P > 10$ GPa and after Takahashi (1986), Herzberg (2000) and Hirschmann (2000) below 10 GPa. For clarity, phase boundaries are not shown. (b) Enlargement of the area indicated in (a). Melt fraction contours calculated according to equation (9) and the calculated P and T of generation for each komatiite suite are plotted (Table 4). Symbols as in Fig. 6.

200°C. Such a thermal anomaly is an expression of heat sourced from the core–mantle boundary, which physically manifests itself in the form of a mantle plume (Campbell *et al.*, 1989; Davies & Davies, 2009; Campbell & Griffiths, 2014). It thus appears that plumes are required to generate komatiites (Arndt *et al.*, 2008).

Upwelling mantle at a T_P of $\approx 1850^\circ\text{C}$ will intersect its solidus at ~ 15 GPa (Fig. 13a). The very low dT/dP slope of the solidus at high pressures ($\approx 25^\circ\text{C GPa}^{-1}$ vs $\approx 120^\circ\text{C GPa}^{-1}$ at low pressure) leads to a phenomenon in which the adiabat ‘skims’ the solidus at an acute angle (Fig. 13a), giving rise to the production of small-degree melts (Nisbet, 1982). The chemical systematics of komatiites (see ‘Style of melting’) require that the

melt has been in equilibrium with the solid since its inception (i.e. a batch melt). This depends on (1) the capacity for the melt to mix and homogenise and (2) its ability to remain in the proximity of the solid.

The low viscosity of Mg-rich melts (Bottinga & Weill, 1972; Nisbet, 1982; Giordano *et al.*, 2008) promotes chemical homogenisation of the melt by diffusion, satisfying the first requirement. The potential for a melt to escape its solid reservoir is given by

$$V = \frac{k\Delta\rho g}{\eta} \quad (10)$$

where V is the melt velocity, $\Delta\rho$ is the density difference between melt and solid, g the acceleration due to gravity, η the melt viscosity and k the reservoir permeability, which has been demonstrated, theoretically and experimentally, to conform to a power-law relationship with melt fraction (McKenzie, 1984; Zhu *et al.*, 2011; Miller *et al.*, 2014):

$$k = \frac{F^n d^2}{C} \quad (11)$$

where F is melt fraction (n is an exponent that is close to three), d is the grain size and C is a constant ranging between 10 and 270. The high compressibility of silicate liquids relative to solids means that $\Delta\rho$ decreases with increasing pressure (Stolper *et al.*, 1981). Komatiitic melt becomes denser than α -olivine at about 8 GPa (Miller *et al.*, 1991; Agee, 1998) until its transformation to wadsleyite at ≈ 15 GPa (at $T_P = 1850^\circ\text{C}$).

To map the trajectory of komatiitic melts within an ascending plume, numerical solutions to equations (10) and (11) are computed for F of 0.1, 0.2 and 0.3, assuming $\eta = 1$ Pa s (Nisbet, 1982; Huppert *et al.*, 1984), $d = 0.005$ m, $C = 200$, and $n = 2.5$, yielding melt ascent rates by porous flow. The velocity is calculated for different melt fractions and plotted versus the pressure in Fig. 14; during adiabatic decompression the melt fraction will increase with decreasing pressure, cross-cutting the contours (dashed curve in Fig. 14). At very high pressures where the solid mantle crosses its solidus, melt fractions are vanishingly small such that melt escape probably does not occur owing to lack of interconnectivity; however, experimental data on melt wetting behaviour at such high pressures are lacking. Upon continued decompression, a peridotite containing 60% olivine, 30% clinopyroxene and 10% garnet, using the equations of state of Li & Neuville (2010) and Agee (1998) for diopside and majoritic garnet, respectively, will have a density equivalent to a komatiitic melt at ~ 11 GPa (Fig. 14). Hence melts formed between 11 and 15 GPa would have a tendency to sink, if not for the competing effect of surface tension and matrix stiffness, which act to keep small melt fractions at low $\Delta\rho$ (< -0.1) in contact with their solid residue (Stolper *et al.*, 1981).

The point of neutral buoyancy is a function of the composition of the residual peridotite; this shifts to lower pressures as it becomes more dunitic (Fig. 14). The

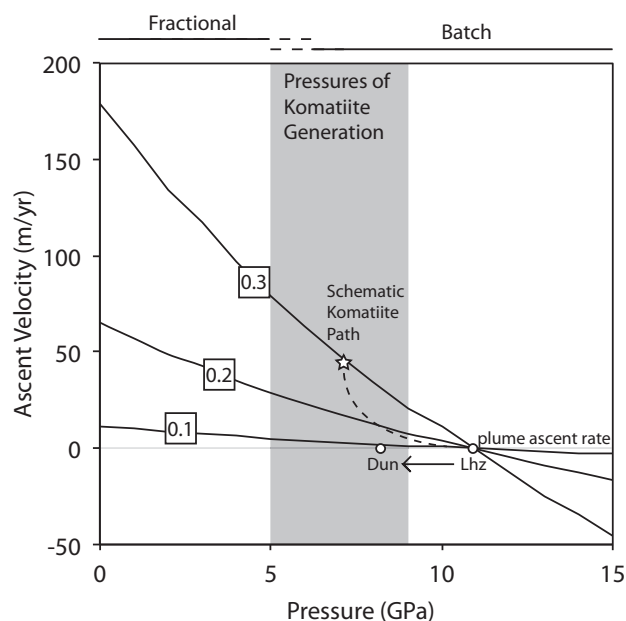


Fig. 14. Calculated melt ascent velocities [equations (10) and (11); see 'Physics of melting'] for three melt fractions ($F = 0.1$, 0.2 , 0.3) as a function of pressure. The dashed line represents a hypothetical komatiite ascent path, with the star indicating the point of segregation, near $F = 0.3$. The open circle corresponds to the point of neutral buoyancy, and how it shifts with the mineralogy of the residue from lherzolite (Lhz) to dunite (Dun).

inability of a komatiitic liquid to leave its source is overcome by $\Delta\rho$ and F , both of which increase with decreasing pressure, owing to the steeper dT/dP of the solidus, leading to higher melt productivity, as well as the structural relaxation of the silicate melt, meaning that melt escape is exponentially enhanced (Fig. 14). At pressures lower than the point of neutral buoyancy, the large melt fractions present are ostensibly readily able to escape, with ascent velocities of the order of metres per year, compared with centimetres per year for plume ascent. In this case, komatiites should have all formed at 8–9 GPa pressures, which is not observed (see 'Pressure of melting'), suggesting that matrix stiffness plays a role in preventing melt escape. This condition is favoured at high pressures and low melt fractions, where diapirs of melt are small, on the scale of kilometres. An interesting observation is that calculated melt fractions for komatiite parent magmas are often very close to 30% (Table 3). If $F \geq 0.3$, then melt interconnectivity is independent of the interfacial energies of the crystals (Shante & Kirkpatrick, 1971; Stolper *et al.*, 1981; Toramaru & Fujii, 1986), forming a suspension, and melt is then able to segregate regardless of $\Delta\rho$. At lower melt fractions, melt ascent can only occur once the barriers of interfacial energy and matrix stiffness are overcome (Stolper *et al.*, 1981). However, as the diapir containing partial melt grows and the density contrast increases at lower pressures, calculated ascent velocities become very high (Fig. 14) and this factor becomes less important. As a consequence, the dominant type of melting probably changes from batch to fractional in this interval. It is therefore more

difficult to preserve high melt fractions at lower pressures; for example, the Munro komatiites, which do show evidence for fractional melting, equilibrated at the lowest pressures (~ 5 GPa) and formed at the lowest $F \approx 25\%$ (Fig. 12), which is also below the threshold value of 0.3. On the other hand, the garnet signature recorded in ADK komatiites is often associated with high pressures (see 'Pressure of melting'). Because garnet remains in the restite of ADKs, the peridotite is denser than a garnet-free residue, thereby increasing the density contrast between melt and solid, promoting melt segregation at deeper levels. Hence the ADK signature is a natural consequence of the physical properties of garnet-bearing residues.

Melting in a model plume

To better combine the temperature and pressure constraints for komatiite genesis with their physical expression in the structure of a mantle plume, a numerical model using the Fluidity computational framework (Davies *et al.*, 2011) was employed. A purely thermal plume is initiated by a 50 km radius perturbation at the core–mantle boundary, causing it to rise through a mantle with Earth-like properties under a 100 km thick lithosphere (Supplementary Data Appendix C). Melt fraction in the plume as a function of T and P was calculated using equation (9). The plume head is typified by a more homogeneous temperature distribution, giving rise to highly pressure-dependent melting. After lateral movement of the head away from the tail, continual rise of hot material produces a strong horizontal temperature gradient in the plume tail (Fig. 15), such that contours of melt fraction taper into the tail. The hottest material resides at its core, with temperature decaying radially towards adjacent, ambient mantle. Contours of Al/Ti parallel those of melt fraction, implying that both T and P control the distribution of AUKs and ADKs within the plume. That is, ADKs can form at equivalent or lower pressures compared with AUKs, if they are sourced from the cooler, distal fringes of the plume. However, the lower degrees of melting needed to produce ADKs means that they form at greater depths for a given cross-section (a vertical line in Fig. 15) and are the first type of komatiite produced in an upwelling plume. If, however, the liquid is unable to escape from its residue, then melting continues and the melt becomes more AUK-like (higher Al/Ti).

The presence of both AUKs and ADKs in the same formation at the Komati type section in the Barberton Greenstone Belt, combined with their chemical characteristics, implies that both types are formed within the same plume. At Barberton, the ADK type predominates, and preserves evidence of lower pressure and melt fraction than its AUK counterpart (Figs 9–12), and thus a lower T_p (Table 4). Instead of ADKs pre-dating AUKs as predicted in the model plume (Fig. 15), AUKs are the earliest-produced komatiites at Barberton, perhaps suggestive of a temporal dimension in komatiite

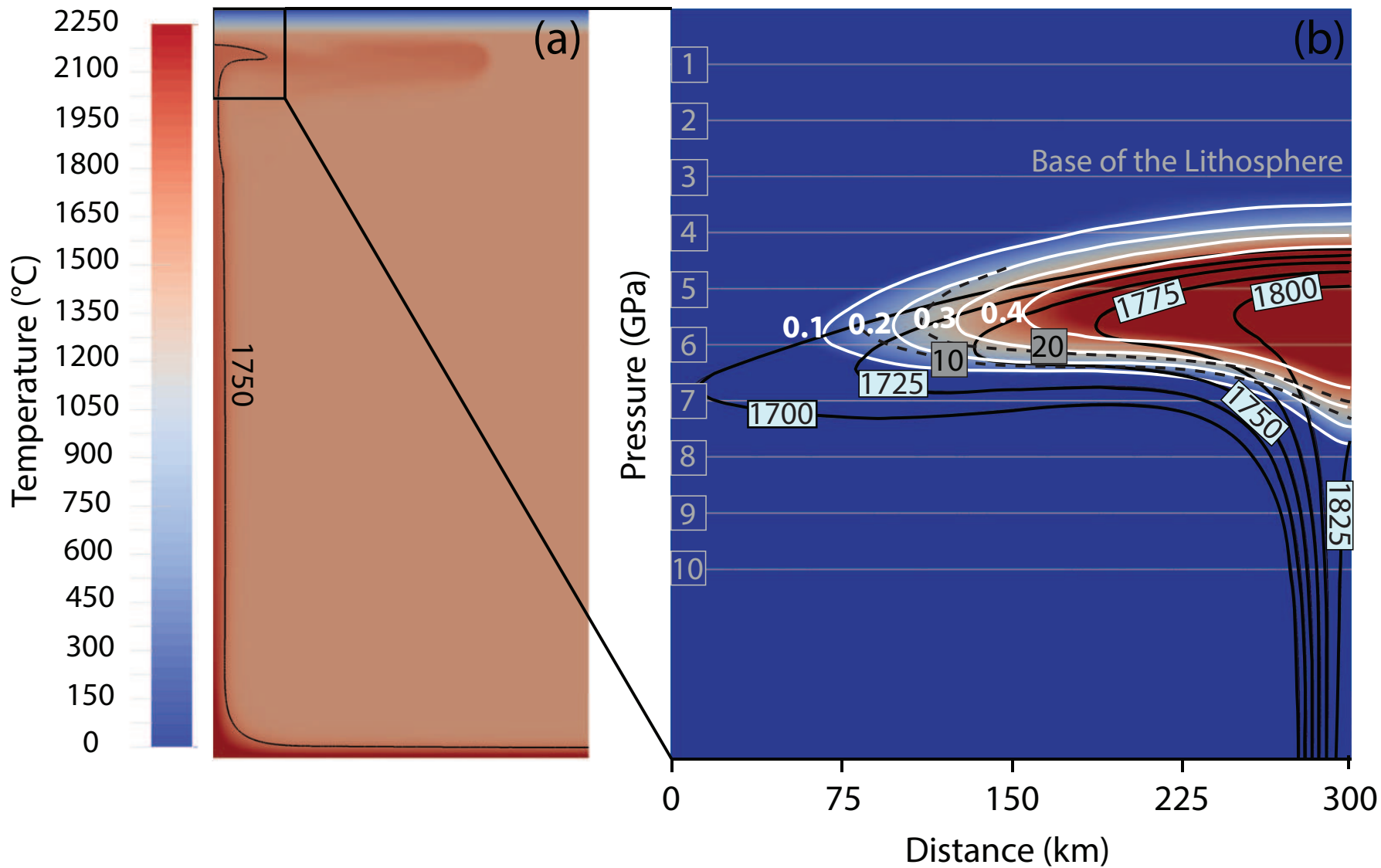


Fig. 15. (a) Temperature (°C, colour contours) in an Archean plume tail; (b) magnification of the black rectangle in which temperature (°C, black lines) and melt fraction (colour contours, emphasised at each 0.1 melt fraction by white lines) are shown as a function of pressure (GPa, grey horizontal lines), calculated using the Fluidity framework (Davies *et al.*, 2011) (see [Supplementary Data Appendix C](#) for details on the model parameters). Melt fraction (white lines) and Al/Ti contours (dashed lines) are calculated using [equation \(9\)](#) (see [Supplementary Data Appendix B](#) for details). (See the 'Melting in a model plume' section for discussion.)

production, such as critical melting (Robin-Popieul *et al.*, 2012). It might be envisaged that ADKs were indeed produced first, but were unable to escape. Only at much higher degrees of melting (~40%) was the now AUK-like melt able to escape to the surface. After this initial melt (heat) loss, the plume would have cooled over time. As a result, the peridotite in the plume would have melted to lower extents, meaning the melt needed a greater density contrast (lower pressure) to escape, forming the ADKs. However, the primitive-mantle-like trace element characteristics of both petrogenetic types preclude extraction of the ADKs from an already melt-depleted source. Therefore, rather than a critical melting scenario, it is more likely that the ADKs were derived from an off-axis zone of the tail, where potential temperatures were lower but the source composition was identical to that of the AUKs (Fig. 6). It is noteworthy that other komatiite sequences, such as those at Forresteria (Perring *et al.*, 1996) and at the Newton Township, Ontario (Cattell & Arndt, 1987) show the expected progression, in which ADKs underlie AUKs.

Archean geodynamics

Two difficulties arise in reconciling the high-pressure formation of komatiites with their extrusion onto the surface of the Earth, 150–250 km from the point of segregation from their mantle source. The first paradox to resolve is that of decompression melting. If plumes ascend towards the base of the lithosphere, why do they not continue to melt at much lower pressures? The second question regards the problem of physical transportation of these melts to the surface without undergoing chemical modification via reaction with surrounding mantle or crust.

Mantle in upwelling plumes loses its partial melt fraction in the 5–9 GPa region (see ‘Physics of melting’), leaving the residual peridotite highly refractory and infusible except at unrealistically high temperatures. Liquid extraction is associated with advective heat loss owing to the latent heat of fusion [equation (6)], producing a temperature decrease in the residue of about 200°C for $F=0.3$. Therefore, the remaining depleted material cannot melt again except at very low pressures where it can intersect the shallow dT/dP area of the mantle solidus, which is also displaced to higher temperatures with respect to fertile mantle.

Preserved komatiites erupted onto pre-existing continental crust (e.g. Nisbet, 1982; Van Kranendonk *et al.*, 2002, 2007; Bolhar *et al.*, 2003), which is almost certainly a question of preservation, as no Archean oceanic crust is preserved. Nevertheless, komatiite eruptions on continental crust show continental-scale distribution depending on the age of the overlying crust in the Yilgarn and Superior cratons (Barnes *et al.*, 2012; Mole *et al.*, 2014). In the Yilgarn Craton, komatiitic magmatism is more voluminous and AUK-dominated where the crust is more juvenile ($\epsilon\text{Hf}=0$ to $+4$), around the margins of cratonic nuclei (Mole *et al.*, 2014). In contrast, under

cratonic keels in the Yilgarn, ADKs predominate. This behaviour is as also observed at Barberton, where the komatiites were erupted onto the Ancient Gneiss Complex (3.65 Ga; Compston & Kröner, 1988). If the degree of crustal reworking, reflected in ϵHf , is directly proportional to the crustal thickness, then AUK production is promoted under thinner, more juvenile crust, whereas ADKs are favoured where the crust (and underlying lithosphere) is thicker, preventing further decompression. However, this picture is complicated by progressive injection of mantle-derived magma prior to komatiite eruption, which then remelts and mixes with older crust, in some cases as old as 3.45 Ga (Claoué-Long *et al.*, 1988), to create somewhat primitive ϵHf signatures (e.g. $+4$), noting the absence of a truly juvenile signature in the pre-existing crust that would imply its derivation from the depleted mantle. Indeed, a similar situation is recorded in the Pilbara Craton, where in some regions extensive crustal contamination of komatiitic magmas occurred to produce strongly negative Nd isotope signatures consistent with assimilation of much older, Hadean crust (Van Kranendonk *et al.*, 2002; Tessalina *et al.*, 2010). This process is also time-dependent, with the degree of crustal melting increasing as the crust heats up through radioactive heating and continued input of mafic magma. Evidence for such secular evolution is found in the igneous rocks themselves: magmas at Kambalda become more contaminated over time (Leshner & Arndt, 1995), a tendency that holds for the Yilgarn Craton on a broader scale (Bateman *et al.*, 2001). Therefore, whereas the lithospheric architecture may control komatiite magmatism on a broad scale, correlations between komatiites and their underlying sequences are not as systematic on a local scale. The final distribution of komatiites in the crust is likely to be influenced by both the lithospheric structure and temperature, in addition to plume conditions.

In continental crustal settings the presence of refractory lithosphere above komatiite plume sources would prevent further ascent of plume material above the mechanical boundary (Leitch & Davies, 2001; Campbell, 2003; Fig. 15). Although the lithosphere was not as extensive as is currently observed (Carlson *et al.*, 2005), the presence of crustal lithologies pre-dating komatiite extrusion necessitates the existence of complementary lithospheric mantle to satisfy isostatic balance. In any case, a komatiitic liquid from the plume–lithosphere boundary would then pass through the lithosphere rather than the asthenosphere to reach the surface. The melt is likely to travel through olivine-rich lithologies, as the large dihedral angles between pyroxene and melt result in low interconnectivity (Toramaru & Fujii, 1986; Holness, 2006). For example, an increase of 15% clinopyroxene would reduce permeability by one-third (Riley & Kohlstedt, 1991). Owing to the low viscosity of komatiite melts and their tendency to ascend via channel as opposed to porous flow, in addition to ever-increasing $\Delta\rho$, ascent velocities in the upper 100 km of the mantle are rapid (hundreds of metres per year). As it

ascends, given the increasing primary phase volume of olivine with decreasing pressure, the melt would tend to dissolve pyroxenes and precipitate olivine. Although the latter would shift the liquid along olivine control lines and therefore be undetectable, melting of trace element-laden pyroxenes at low pressures is capable of altering the trace element characteristics of komatiites; something that is not observed for the rocks in this study, although it may be a plausible mechanism to explain highly depleted radiogenic isotope signatures (Nebel *et al.*, 2013; Puchtel *et al.*, 2013). The lower temperatures that help to stabilize the lithospheric mantle also reduce the likelihood of contamination of rising mafic magmas with respect to the convecting mantle. Therefore, the combination of cold, highly refractory, olivine-rich lithosphere and its favourable melt passage properties allowed komatiites to ascend rapidly and with minimal change in chemical composition from their high-pressure origin (Green, 1991).

SUMMARY

A total of 38 predominantly spinifex-textured komatiites from five Archean cratons reveal that these magmas have diverse chemical characteristics that can be related to their source composition and P and T of origin. The primary magma MgO contents range from 23 to 30 wt %, corresponding to eruption temperatures of ~ 1470 – 1575°C . Aluminium concentration is shown to be a robust indicator of pressure of melt extraction. Melts of ADK composition can be converted to AUK compositions with increasing degrees of melting. The degree of melting was calculated using $K_D^{\text{Fe-Mg}}$ estimated from the Mg# of calculated parental komatiite melts, most of which were formed by $\sim 30\%$ partial melting, the point at which the peridotite matrix–melt system becomes a suspension and facilitates melt escape. However, a range from 25% melting at 5 GPa to $\sim 40\%$ melting at 9 GPa for the komatiites analysed in this study implies mantle potential temperatures between 1750 and 1950°C , 400 – 600°C hotter than present-day ambient mantle, requiring that melting in Archean plumes commenced in the mantle Transition Zone. The faithful retention of high-pressure melting chemistry in komatiites suggests minimal interaction with the lithospheric mantle as they ascended. Incompatible trace elements show that the mantle sources of komatiites from Munro, Yilgarn, Belingwe and Regal–Ruth Well have experienced varying extents of prior melt extraction from $\sim 4\%$ to less than 1% (in that order) where the involvement of depleted upper mantle material in their plume sources is plausible. This is supported by the presence of positive Nb anomalies and radiogenic Nd isotope compositions in some komatiite suites, hinting at the presence in the plume of peridotite that had previously undergone continental crust extraction.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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