Geological Magazine

www.cambridge.org/geo

Zircon in mantle eclogite xenoliths: a review

Aleksey E. Melnik[1,2], Nester M. Korolev[3,2], Sergey G. Skublov[2,4], Dirk Müller[5], Qiu-Li Li[1] and Xian-Hua Li[1]

[1]State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beitucheng West Road 19, Beijing 100029, China; [2]Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, nab. Makarova 2, St Petersburg 199034, Russia; [3]Saint-Petersburg State University, nab. Universitetskaya 7–9, St Petersburg 199034, Russia; [4]Saint-Petersburg Mining University, 21-ya Liniya 2, St Petersburg 199106, Russia and [5]Department for Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, Munich, Germany

Review Article

Cite this article: Melnik AE, Korolev NM, Skublov SG, Müller D, Li Q-L, and Li X-H (2021) Zircon in mantle eclogite xenoliths: a review. *Geological Magazine* **158**: 1371–1382. https://doi.org/10.1017/S0016756820001387

Received: 15 June 2020
Revised: 14 November 2020
Accepted: 27 November 2020
First published online: 21 January 2021

Keywords:
zircon; mantle eclogite; xenolith; mantle; kimberlite

Author for correspondence: Aleksey E. Melnik, Email: aleksei@mail.iggcas.ac.cn

Abstract

Very few zircon-bearing, kimberlite-hosted mantle eclogite xenoliths have been identified to date; however, the zircon they contain is crucial for our understanding of subcratonic lithospheric mantle evolution and eclogite genesis. In this study, we constrain the characteristics of zircon from mantle eclogite xenoliths based on existing mineralogical and geochemical data from zircons from different geological settings, and on the inferred origin of mantle eclogites. Given the likely origin and subsequent evolution of mantle eclogites, we infer that the xenoliths can contain zircons with magmatic, metamorphic and xenogenic (i.e. kimberlitic zircon) origins. Magmatic zircon can be inherited from low-pressure mafic oceanic crust precursors, or might form during direct crystallization of eclogites from primary mantle-derived melts at mantle pressures. Metamorphic zircon within mantle eclogites has a number of possible origins, ranging from low-pressure hydrothermal alteration of oceanic crustal protoliths to metasomatism related to kimberlite magmatism. This study outlines a possible approach for the identification of inherited magmatic zircon within subduction-related mantle eclogites as well as xenogenic kimberlitic zircon within all types of mantle eclogites. We demonstrate this approach using zircon grains from kimberlite-hosted eclogite xenoliths from the Kasai Craton, which reveals that most, if not all, of these zircons were most likely incorporated as a result of laboratory-based contamination.

1. Introduction

Mantle eclogites represent a minor component (<5 %) of the lithospheric mantle beneath cratons that is dominated by peridotitic material (e.g. Jacob, 2004). However, mantle eclogites provide unique insights into lithospheric processes given that they are thought to represent fragments of subducted oceanic crustal material. All of the rocks within the cratonic mantle can be brought to the Earth's surface (and hence can be sampled) as xenoliths entrained in volcanic rocks and as inclusions in diamonds. The most ancient mantle eclogites and eclogitic inclusions in diamonds yield late Archaean ages (3.0–2.5 Ga; Pearson *et al.* 1995; Jacob & Foley, 1999; Shirey *et al.* 2001; Jacob *et al.* 2005; Shirey & Richardson, 2011; Aulbach *et al.* 2019*a*). However, the crustal (orogenic) eclogites that crop out within orogenic belts and are thought to represent primary evidence for plate tectonics do not yield ages older than early Proterozoic (≤2.09 Ga; e.g. Boniface *et al.* 2012; François *et al.* 2018; Loose & Schenk, 2018). This means that mantle eclogite xenoliths can provide further insights into the secular evolution of the subcontinental mantle, oceanic crustal material (i.e. oceanic gabbros and basalts) and tectonic processes, at least since Archaean time.

Mantle eclogites yield a broad range of equilibration pressures that correspond to depths within the subcratonic mantle lithosphere (e.g. Schulze, 1989; Kamber & Collerson, 2000; Jacob, 2004). However, these eclogites also commonly host diamonds, indicating that they must have equilibrated at minimum pressures of 4 GPa (i.e. >120 km depth at typical cratonic conductive geotherms; e.g. Schulze, 1989; Jacob, 2004). Thermometric calculations for the majority of mantle eclogites yield equilibration temperatures of >800 °C (e.g. fig. 3 in Jacob, 2004). Residence of mantle eclogites under these elevated pressure and temperature (*P–T*) conditions for millions of years or longer, alongside the possibility of multiple metasomatic events, and the eventual influence of kimberlitic magmas could easily have perturbed the radiogenic isotope systems (e.g. Sm–Nd, Rb–Sr, Pb–Pb) of the rock-forming minerals of the eclogites, making dating of these rocks difficult (Jacob, 2004; Schmidberger *et al.* 2005; Heaman *et al.* 2006; Shu *et al.* 2014; Aulbach *et al.* 2019*a*). Bulk rock isotope analysis of mantle eclogite generally yields no reliable dates (e.g. Shu *et al.* 2014), and ages obtained from Lu–Hf dating of rock-forming minerals such as garnet and clinopyroxene (e.g. Shu *et al.* 2014) and from Re–Os dating of accessory sulfides (e.g. Aulbach *et al.* 2009) are often difficult to link with particular geological events.

© The Author(s), 2021. Published by Cambridge University Press.

CAMBRIDGE UNIVERSITY PRESS

Table 1. Available data for zircons from mantle eclogite xenoliths from kimberlites and kimberlite-like rocks

	Jericho kimberlites, Slave Craton	V. Grib kimberlite pipe, Arkhangelsk province	Kimberlite-like pipes, Colorado Plateau	Calcutteroo kimberlites, Australian Craton	Catoca and Cat-115 kimberlite pipes, Kasai Craton	Lovedale and Lace kimberlites, Kaapvaal Craton
Zircon grains in thin-sections (for at least one xenolith)	**R**	**R**	**R**	**NR**	**NR**	**NR**
Number of xenoliths with analysed zircons	5	2	6?	1	2	?
Zircon CL image	**R** (1 xenolith)	**R** (2 xenoliths)	**NR***	**NR**	**R** (2 xenoliths)	**NR**
U–Pb zircon age	**R** (5 xenoliths)	**R** (2 xenoliths)	**R** (6? xenoliths)	**R** (1 xenolith)	**R** (2 xenoliths)	**R**
Th/U in zircon	**R** (5 xenoliths)	**R** (2 xenoliths)	**NR**	**R** (1 xenolith)	**R** (2 xenoliths)	**NR**
Trace elements in zircon	**NR**	**R** (2 xenoliths)	**NR**	**NR**	**R** (2 xenoliths)	**NR**
Hf isotopes in zircon	**R** (1 xenolith)	**R** (1 xenolith)	**NR**	**NR**	**NR**	**R**
$\delta^{18}O$ in zircon	**NR**	**NR**	**NR**	**NR**	**NR**	**NR**
Reference	Heaman *et al.* 2002, 2006; Schmidberger *et al.* 2005	Skublov *et al.* 2011, 2012*b*; Shchukina *et al.* 2015, 2018	Usui *et al.* 2002, 2003; Smith *et al.* 2004	Chen *et al.* 1994	Nikitina *et al.* 2012, 2014	Schmitz *et al.* 2003
Publication type	Journal article	Journal article	Journal article	Journal article	Journal article	Conference abstract

R – reported; **NR** – not reported; ***** – an appropriate backscattered electron image has been reported for one xenolith (Usui *et al.* 2003).

However, precise dating of these rocks is vital for determining the origin of mantle eclogites and to link them with subcontinental lithospheric evolution (e.g. Usui *et al.* 2003; Shchukina *et al.* 2018; Aulbach *et al.* 2019*a*). Zircon is a promising mineral for dating mantle eclogites as it has high refractory properties (Cherniak *et al.* 1997; Whitehouse & Platt, 2003) and a U–Pb system with a relatively high closure temperature (>900 °C; Lee *et al.* 1997), and has been proven a robust geochemical tracer (Cherniak *et al.* 1997; Li *et al.* 2011). Zircon grains can record several episodes of growth (i.e. zoning) that reflect the evolution of their host rocks, which is especially typical for zircons within metamorphic and metasomatic rocks. Each of these zones can easily retain the original geochemical and some other signatures that are indicative of the conditions during the growth of that individual zone. This is true even if the U–Pb system in the zircon has been disturbed, meaning that a precise age cannot be obtained for that particular zone (e.g. Rubatto, 2017). However, zircon is not commonly found within mantle eclogite xenoliths, in contrast to the abundant zircon grains that have been identified within orogenic eclogites (Skublov *et al.* 2012*a*; Rubatto, 2017). Only a few kimberlites and kimberlite-like rocks that host zircon-bearing mantle eclogites have been identified to date, namely the Calcutteroo kimberlites of the Australian Craton (Chen *et al.* 1994), the Jericho kimberlites of the Slave Craton (Heaman *et al.* 2002, 2006; Schmidberger *et al.* 2005), kimberlite-like pipes of the Colorado Plateau (Usui *et al.* 2002, 2003; Smith *et al.* 2004), the Lovedale and Lace kimberlites of the Kaapvaal Craton (Schmitz *et al.* 2003), the V. Grib pipe of the Arkhangelsk kimberlite province (Skublov *et al.* 2011, 2012*b*; Shchukina *et al.* 2015, 2018) and the Catoca and Cat-115 kimberlite pipes of the Kasai Craton (Nikitina *et al.* 2012, 2014).

An understanding of the characteristic signatures of zircons in mantle eclogites is vital for meaningful interpretation of the ages obtained. Therefore, we use existing zircon data from these eclogites and other rocks to constrain the types of zircon that might occur in xenoliths of mantle eclogite.

2. Available zircon-bearing mantle eclogite data, associated opportunities and current barriers

Linking ages obtained during zircon U–Pb dating with specific geological events is essential, especially for those grains that record several episodes of growth (e.g. zircon grains with metamorphic rims and inherited magmatic cores). This can be achieved using zircon characteristics such as internal textures, and trace-element and further isotope compositions. Considerable quantities of data on these characteristics have been collected to date, all of which have been used to determine the origins and evolution of host rocks and/or to reconstruct and describe geological processes and settings (e.g. Belousova *et al.* 2002; Corfu *et al.* 2003; Rubatto, 2017). Zircon origins and growth conditions can be determined using variations in Th/U ratios, trace-element concentrations, and O and Hf isotope compositions alongside cathodoluminescence (CL) imaging, which allows the identification of internal zircon textures (e.g. Rubatto, 2017). However, only limited analysis has been undertaken on zircons from mantle eclogites, which presents the main barrier for the present study. To date, incomplete zircon data for only 16 mantle eclogites from five localities have been reported in peer-reviewed scientific publications (Table 1). This limited dataset is further constrained by the fact that Th/U ratios, CL images, trace-element concentrations and Hf isotope data are only available for ten, five, four and two of these eclogite xenoliths, respectively, with no O isotope analyses undertaken on any zircon from mantle eclogites to date.

Sampling and laboratory-based sample preparation can lead to the contamination of geological samples by xenogenic material (e.g. Dobrzhinetskaya *et al.* 2014; Litasov *et al.* 2019). The rare

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

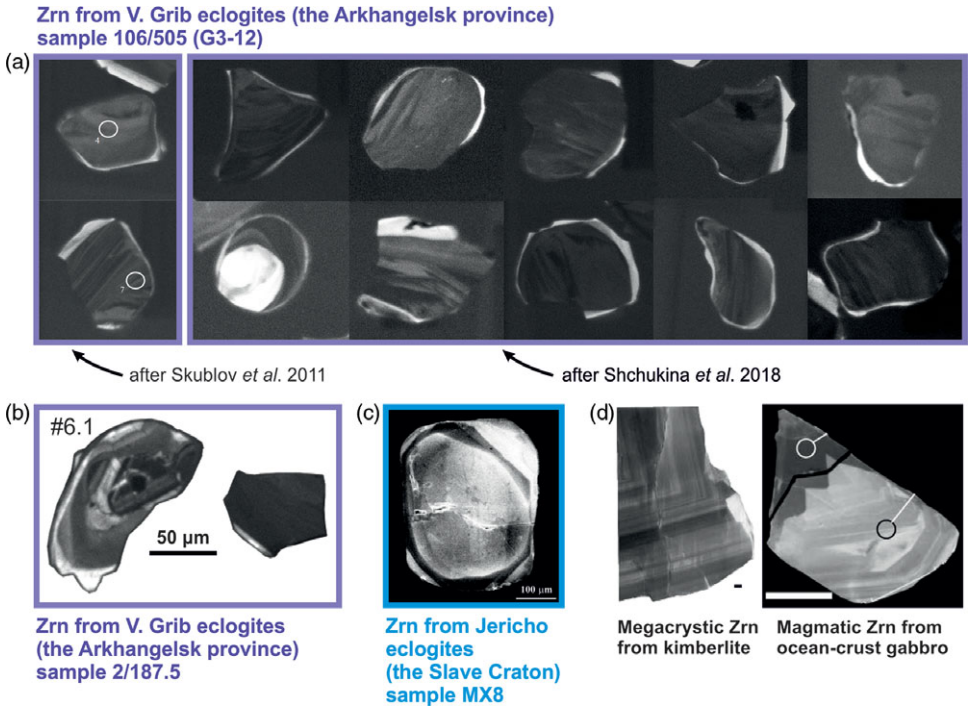


Fig. 1. (Colour online) Cathodoluminescence images for mantle eclogite-hosted, magmatic oceanic gabbro-hosted and kimberlitic zircons. (a) Zircon grains from mantle eclogite xenolith sample 106/505 (G3-12) from the V. Grib kimberlites, Arkhangelsk province (modified after Skublov *et al.* 2011 and Shchukina *et al.* 2018; note that this sample is labelled as 106/505 and G3-12 in the first and second publications on this eclogite, respectively). The zircon grains are ~100–150 μm long, and the images are reprinted by permission from Springer Nature under licences (i) 4826260699731: Springer Nature, Geochemistry International, vol. 49, fig. 1, p. 416, Geochemical characteristics of zircons from xenoliths in the V. Grib Kimberlite Pipe, Archangelsk Diamondiferous Province, Skublov *et al.*, Copyright (2011); and (ii) 4826261215178: Springer Nature, Mineralogy and Petrology, vol. 112, fig. S3-a, ESM 3, Origin of zircon-bearing mantle eclogites entrained in the V. Grib kimberlite (Arkhangelsk region, NW Russia): evidence from mineral geochemistry and the U–Pb and Lu–Hf isotope compositions of zircon, Shchukina *et al.*, Copyright (2018). (b) Zircon grains within mantle eclogite 2/187.5 from the V. Grib kimberlite (modified after Skublov *et al.* 2012*b*). Reprinted by permission from Springer Nature under licence 4826260895721: Springer Nature, Doklady Earth Sciences, vol. 444, fig. 1, p. 596, U–Pb age and geochemistry of zircons from xenoliths of the V. Grib kimberlitic pipe, Arkhangelsk diamond province, Skublov *et al.*, Copyright (2012). (c) Zircon within the MX8 mantle eclogite from the Jericho kimberlite of the Slave Craton (modified after Heaman *et al.* 2006). Reprinted by permission from Oxford University Press under licence 4850101300985: Heaman *et al.* (2006), Multi-stage modification of the northern Slave mantle lithosphere: evidence from zircon- and diamond-bearing eclogite xenoliths entrained in Jericho Kimberlite, Canada, Journal of Petrology, vol. 47, fig. 2c, p. 826. (d) Oscillatory zoning within kimberlitic zircon (modified after Corfu *et al.* 2003) and oscillatory-sector zoning within magmatic zircon from an oceanic gabbro (modified after Cavosie *et al.* 2009). Reprinted with the permission of the Mineralogical Society of America as follows: (i) from Corfu *et al.* (2003), Atlas of Zircon Textures, *Reviews in Mineralogy and Geochemistry*, vol. 53, fig. 4, p. 477; (ii) from Cavosie *et al.* (2009), Primitive oxygen-isotope ratio recorded in magmatic zircon from the Mid-Atlantic Ridge, *American Mineralogist*, vol. 94, fig. 2, p. 928.

nature of zircon within mantle eclogites indicates that the addition of contaminant zircon grains during laboratory-based mineral separation is likely. This type of contamination is especially plausible if (1) zircon grains are isolated from mantle eclogites within laboratories that routinely process zircon-rich rocks, and (2) zircon grains are not identified in thin-sections of the same mantle eclogite sample. This study, therefore, focuses on mantle eclogite suites that contain visible zircons in thin-sections. These suites of zircon-bearing mantle eclogites contain 13 xenoliths, and include eclogites of the Colorado Plateau, the Jericho eclogites of the Slave Craton and the V. Grib eclogites of the Arkhangelsk province (Table 1).

The mantle eclogites from kimberlite-like rocks of the Colorado Plateau, and the Jericho and V. Grib kimberlites contain zircon grains that record more than one episode of crystal growth as evidenced by (1) complex internal textures present in the zircons, and (2) the scattered nature of the U–Pb ages obtained from these zircon grains. Some of the zircons from these eclogites have sharp boundaries between relict cores and more recent overgrowths (i.e. rims) that are visible in CL and backscattered electron images (Fig. 1a–c; fig. 3B in Usui *et al.* 2003). The distribution of U–Pb ages obtained for zircons within a single mantle xenolith can span >500 Ma and provides evidence of multiple episodes of zircon growth (Schmidberger *et al.* 2005; Heaman *et al.* 2006; Shchukina *et al.* 2018). The presence of several episodes of zircon growth within mantle eclogites, combined with the limited range of incomplete data available to date for these zircons, mean it is not possible to determine characteristics specific to zircon that grows during the formation of the hosting mantle eclogites. However, combining existing data on the characteristics of zircon from different rocks that enable the identification of geological processes and settings with concepts relating to the origins of mantle eclogites can provide insights into the types of zircon that can be present in mantle eclogite xenoliths, and those that cannot. This study summarizes the characteristics of zircon types that may be found within zircon-bearing mantle eclogites and, therefore, provides a firm basis for future research. We also use these characteristics to determine the nature of zircon grains from the Kasai Craton eclogite xenoliths; these xenoliths were selected because they represent the only mantle eclogite samples in which zircon has not been identified in thin-sections that provide sufficient zircon data for such analysis (Table 1).

The Colorado Plateau eclogites likely formed at *c.* 80 Ma (see discussion in Usui *et al.* 2006) and represent atypical mantle eclogites as they contain lawsonite or pseudomorphs after primary lawsonite. The petrography of these eclogites and the mineral assemblages present in these samples are similar to those found

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

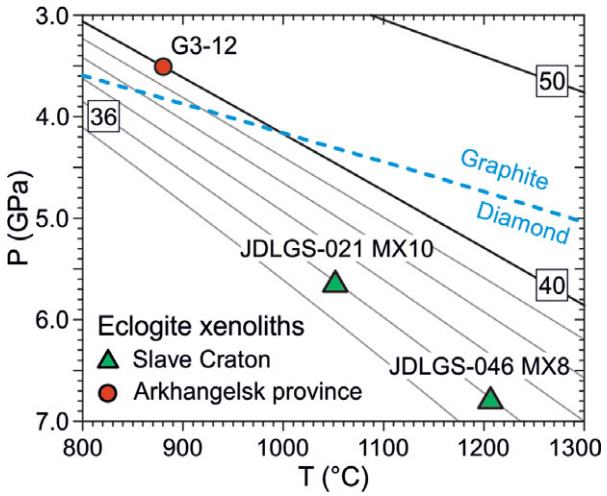


Fig. 2. (Colour online) *P–T* diagram for zircon-bearing eclogite xenoliths from kimberlites of the Slave Craton and the Arkhangelsk province, where *P–T* parameters are only calculated for xenoliths if zircon grains were observed in thin-section. Mineral chemical compositions used for *P–T* calculations are after Shchukina *et al.* (2018) and Heaman *et al.* (2006) and are given in online Supplementary Material Table S1. Numbers in boxes indicate the heat flow of the corresponding geothermal gradients, and the dashed line indicates the graphite–diamond phase boundary (Day, 2012). *P–T* conditions were estimated using garnet–clinopyroxene geothermometry (Nakamura, 2009) in combination with 40 and 36 mW/m^2 model conductive geotherms for the Arkhangelsk province (Hasterok & Chapman, 2011) and the Slave Craton (Kopylova *et al.* 1999), respectively.

in low-temperature orogenic eclogites (Usui *et al.* 2003, 2006) that formed during cold subduction, a process that commonly occurred during Phanerozoic and late Neoproterozoic times (Tsujimori *et al.* 2006; Tsujimori & Ernst, 2014). In comparison, U–Pb zircon dating of the Jericho and V. Grib eclogites yielded ages up to 2.0–1.8 Ga (Schmidberger *et al.* 2005; Heaman *et al.* 2006; Shchukina *et al.* 2018). These eclogites have a garnet + clinopyroxene + zircon ± rutile ± kyanite ± ilmenite mineral assemblage (Heaman *et al.* 2006; Shchukina *et al.* 2018) that (barring zircon) is typical for many mantle eclogites (Jacob, 2004). Determining the *P–T* conditions for the Jericho and V. Grib eclogites indicates that they formed within both the graphite and diamond stability fields (880–1210 °C, 3.5–6.8 GPa; Fig. 2; online Supplementary Material Table S1). The presence of garnet with elevated Na concentrations within some of the zircon-bearing Jericho eclogites also indicates the residence of these rocks within the diamond stability field (Heaman *et al.* 2002). The only factor that links the Colorado Plateau, Jericho and V. Grib eclogites is a proposed subducted oceanic crustal origin (Usui *et al.* 2003; Heaman *et al.* 2002; Shchukina *et al.* 2018). However, compared with zircon-free mantle eclogites, each of these zircon-bearing eclogites can have a unique petrological or geochemical signature (e.g. whole-rock compositions of the Jericho eclogites are highly enriched in high-field-strength elements; Heaman *et al.* 2002, 2006) that is not shared by any other zircon-bearing eclogite, which indicates that these unique signatures are not critical for this review.

3. Origins of mantle eclogites and associated zircon

The majority of mantle eclogites are thought to represent metamorphosed mafic rocks that formed from subducted oceanic crustal material and associated residues (e.g. Jacob *et al.* 1994; Jacob, 2004; Aulbach & Jacob, 2016). This hypothesis is generally accepted (e.g. Korolev *et al.* 2018 and references therein) and has been supplemented by the identification of additional eclogite formation processes. These include the reworking of primary subduction-related eclogites during mantle metasomatism (Smart *et al.* 2009; Huang *et al.* 2014; Aulbach *et al.* 2019*b*) and the ultrahigh-pressure (UHP) metamorphism of picritic cumulates that originally formed at lower pressures (1–2 GPa; Jacob, 2004). A significant amount of research supports the subduction-related hypothesis for the origin of mantle eclogite (Jacob, 2004), including the identification of Colorado Plateau eclogite xenoliths that were derived from a slab that is currently being subducted (Helmstaedt & Doig 1975; Usui *et al.* 2003). However, the other hypothesis, which indicates that mantle eclogites represent UHP cumulates formed from primary mantle-derived melts, is still being discussed and cannot, therefore, be discounted entirely (e.g. Griffin & O'Reilly, 2007).

The origin and evolution of subduction-related mantle eclogites (SM eclogites) have the following stages (see review in Korolev *et al.* 2018): (1) formation of an oceanic crust protolith (i.e. basalts and gabbros), (2) hydrothermal alteration of the oceanic crust by seawater, (3) subduction-related metamorphism, partial melting and metasomatism, (4) long-term residence in the lithospheric mantle with possible mantle metasomatism, (5) interaction with kimberlitic melt during ascent and emplacement, and (6) alteration within the hosting kimberlites after emplacement. In comparison, mantle eclogites that originate from mantle-derived melts (MDM eclogites) have different evolutionary histories (Korolev *et al.* 2018) involving (1) partial melting of mantle peridotites and melt migration, and (2) eclogite formation by crystallization from this melt at mantle pressures, followed by the same evolutionary stages as 4–6 for the SM eclogites.

The likely origin and evolution of mantle eclogites suggest that zircon within mantle eclogites can be (1) magmatic, (2) metamorphic and (3) kimberlitic. For the purposes of this study, zircon that formed during either metasomatic reworking or hydrothermal alteration of mantle eclogites and their protoliths is also considered metamorphic. Hypothetical zircon origins associated with mantle eclogites are illustrated in Figure 3.

Magmatic zircon in MDM eclogites might form during crystallization of melt at mantle depths, whereas magmatic zircon within SM eclogites is inherited from subducted oceanic basalts and gabbros. The latter process has been inferred from orogenic high-pressure (HP) and UHP rocks, including (a) the Dora–Maria whiteschists within the Western Alps that preserve relict granitic zircon, despite the fact that the protoliths of these rocks were metasomatically altered and underwent UHP metamorphism (Gauthiez-Putallaz *et al.* 2016); and (b) the Monviso orogenic eclogites (Western Alps), which contain inherited magmatic zircon derived from their oceanic gabbro protoliths, despite these eclogites having undergone HP metamorphism and extensive metasomatism within a subduction channel environment (Rubatto & Angiboust, 2015).

Metamorphic zircon may form in mantle eclogites and their protoliths as a result of (1) the low-pressure (LP) hydrothermal alteration of a mafic protolith in a mid-ocean ridge setting (i.e. the recrystallization of magmatic zircon; Spandler *et al.* 2004; Grimes *et al.* 2009); (2) the metamorphism and metasomatic alteration of subducting oceanic crustal material at crustal and mantle depths (Heaman *et al.* 2002; Schmidberger *et al.* 2005; Page *et al.* 2014; Rubatto & Angiboust, 2015; Shchukina *et al.* 2018; Aulbach *et al.* 2020), leading to possible growth of medium- to UHP zircon; (3) thermal events and associated mantle metasomatism during

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

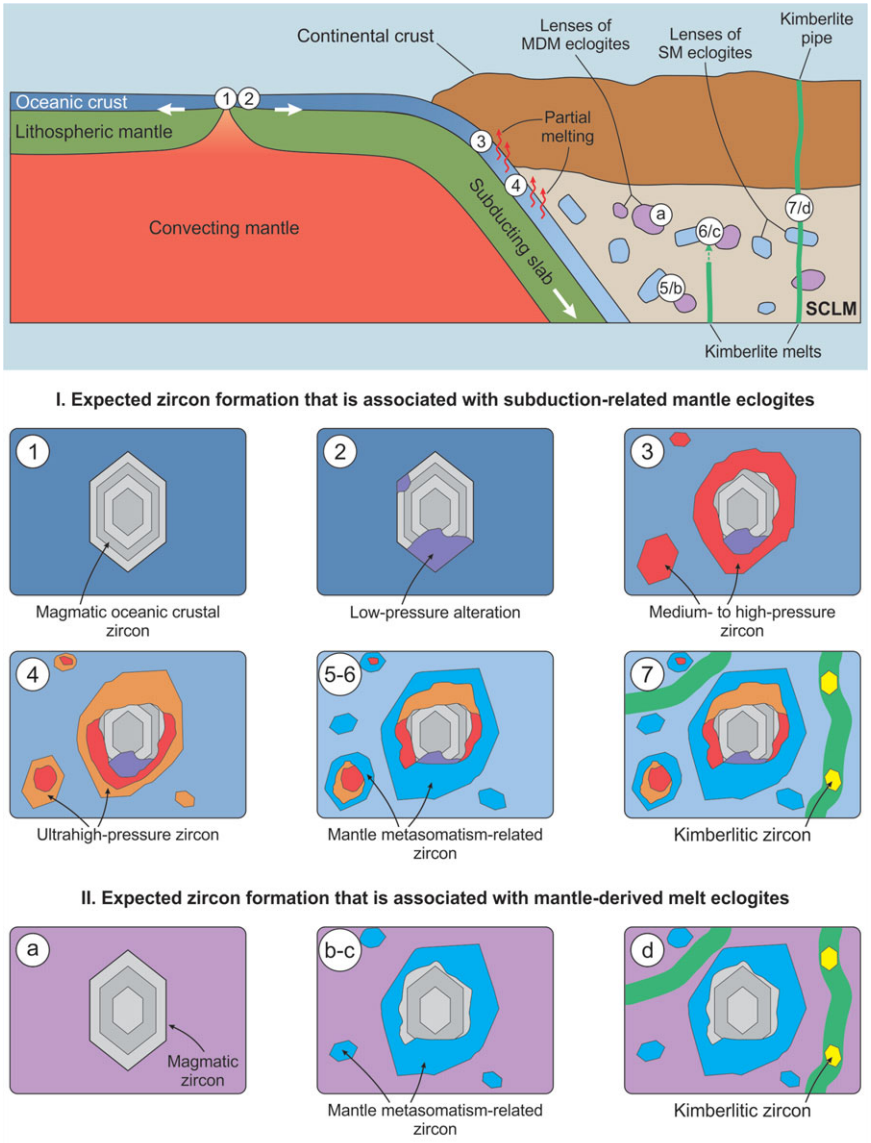


Fig. 3. (Colour online) Schematic diagram illustrating zircon formation that is associated with the origin and evolution of mantle eclogites. (1–7) Stages for subduction-related mantle (SM) eclogites and their oceanic crustal protoliths. (a–d) Stages for mantle-derived melt (MDM) eclogites. All these stages are simplified and modified after Korolev *et al.* (2018). (1) Formation of oceanic basalts and gabbros from mantle-derived melts and the crystallization of associated magmatic zircon. (2) Low-pressure seafloor hydrothermal alteration of the oceanic crust and associated partial recrystallization of magmatic zircon. (3) Medium- to high-pressure zircon growth related to metamorphism and/or metasomatism at crustal depths during subduction. (4) Ultrahigh-pressure zircon growth related to metamorphism and/or metasomatism at mantle depths during subduction. (5, 6) Long-term residence of SM eclogites in the subcratonic lithospheric mantle (SCLM) with possible mantle metasomatism and associated zircon growth. Mantle metasomatism can be linked (6) and/or not linked (5) with kimberlitic magmas. (7) Incorporation of kimberlitic zircon within xenoliths of SM eclogites during ascent within the hosting kimberlites. (a) Crystallization of eclogites from mantle-derived melts at mantle pressures and possible crystallization of associated magmatic zircon. Further stages b–d for the MDM eclogites are equivalent to stages 5–7 for the SM eclogites. Possible zircon origins for stages 1–4 are inferred from natural examples (see text for details). Hypothetical zircon origins for stages 5–7 and a–d are assumed from the likely origin and subsequent evolution of mantle eclogites (Section 3).

long-term residence in the cratonic mantle (Heaman *et al.* 2006); and (4) metamorphism or metasomatism associated with kimberlite magmatism (Usui *et al.* 2003). A combination of some or all of these events can lead to multiple periods of zircon growth, as well as various degrees of alteration, resorption, overgrowth and recrystallization of earlier-formed zircon within individual eclogite samples (stages 2–6 and b, c in Fig. 3).

Kimberlitic magmas interact directly with mantle xenoliths during magma ascent, occasionally leading to infiltration and injection of kimberlitic magma into the xenoliths. This in turn indicates that kimberlitic zircon might be incorporated within mantle eclogite xenoliths during this process (stages 7 and d in Fig. 3).

The textural relationship between accessory zircon and rock-forming minerals can provide information on the origin of the former. Zircon inclusions in garnet and clinopyroxene have been identified within mantle eclogites (Usui *et al.* 2003; Schmidberger *et al.* 2005; Heaman *et al.* 2006; Shchukina *et al.* 2018), which indicates that either all these minerals formed at the same time or the zircon pre-dates the garnet and clinopyroxene. Interstitial zircon grains provide no clear textural evidence of their origin, meaning that these grains can be inherited, can be related to eclogite formation and can be secondary. Xenogenic kimberlitic zircon may be added to mantle eclogites, which indicates these zircon grains will be either interstitial or hosted by veins that cross-cut the xenoliths.

4. Internal textures and trace-element compositions of zircon within mantle eclogites

Metamorphic and magmatic zircon can generally be distinguished by variations in internal textures and geochemical signatures, although distinguishing metamorphic zircons of particular origins may be complicated (see review in Rubatto, 2017). This suggests that it is possible to discriminate between metamorphic and magmatic zircon within mantle eclogite xenoliths, rather than to identify the specific origin of metamorphic zircons.

Magmatic zircons from rocks of different geological settings typically have oscillatory and/or sector zoning that is visible during CL imaging (Fig. 1d), and have Th/U ratios of >0.1. These characteristics also apply to magmatic zircons from mafic oceanic

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

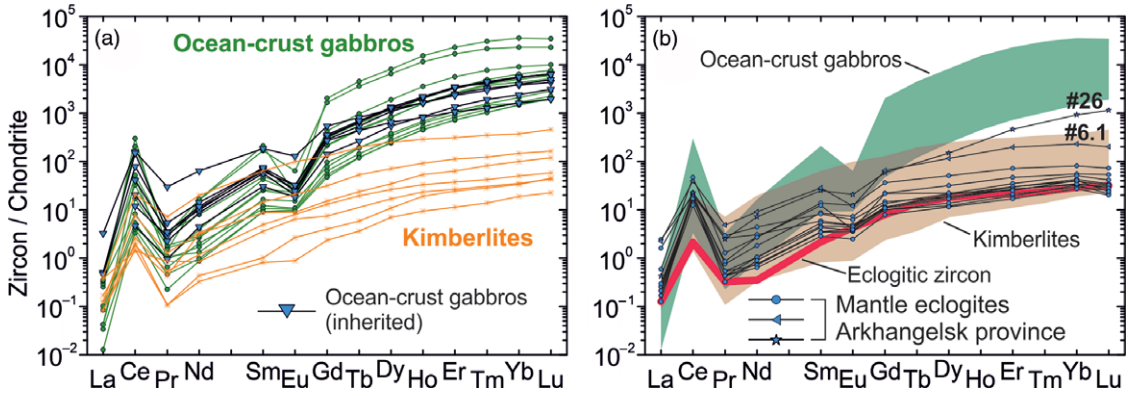


Fig. 4. (Colour online) REE_N patterns for mantle eclogite-hosted, oceanic gabbro-hosted and kimberlitic zircons. (a) REE_N patterns for representative zircons from oceanic crustal gabbros (magmatic zircon; Cavosie *et al.* 2009; Grimes *et al.* 2009) and kimberlites (Belousova *et al.* 2002; Page *et al.* 2007) along with representative REE_N patterns for inherited relict magmatic oceanic crustal gabbro zircons now hosted within orogenic metamorphic rocks (Rubatto & Hermann, 2003; Rubatto & Scambelluri, 2003; Spandler *et al.* 2004); note that the REE_N patterns of the relict zircon grains match the field defined by zircon from oceanic gabbros. (b) REE_N patterns of zircon grains from the V. Grib mantle eclogites (Skublov *et al.* 2011, 2012*b*; Shchukina *et al.* 2018) compared to REE_N patterns for metamorphic ('eclogitic') zircons from orogenic eclogites (Skublov *et al.* 2012*a*), magmatic zircons from oceanic gabbros and kimberlitic zircons. The REE data used in this figure are given in online Supplementary Material Table S2, and all REE concentrations are normalized to the CI chondrite composition of McDonough & Sun (1995).

crustal rocks and to kimberlitic zircons (Belousova *et al.* 2002; Corfu *et al.* 2003; Zartman & Richardson, 2005; Cavosie *et al.* 2009; Grimes *et al.* 2009). Relics of magmatic zircons from oceanic gabbro protoliths can potentially be inherited by SM eclogites, and would have chondrite-normalized rare earth element (REE_N) patterns (Fig. 4a) that are similar to the majority of other magmatic zircons of different origins. These patterns have a steep increase from the light REEs (LREEs, La–Nd) to the heavy REEs (HREEs, Gd–Lu), with positive Ce and negative Eu anomalies (Belousova *et al.* 2002; Hoskin & Schaltegger, 2003). Relics of magmatic zircon grains preserving all of the characteristics described above have been identified previously within HP and UHP orogenic rocks (e.g. Rubatto & Hermann, 2003; Gauthiez-Putallaz *et al.* 2016), including eclogites (or former eclogites) with oceanic crustal protoliths (Fig. 4a). Kimberlitic zircons, in contrast, have relatively flat $HREE_N$ patterns, are free of Eu anomalies (Fig. 4a) and contain lower total REE concentrations (maximum of ~650 ppm, typically <60 ppm; Belousova *et al.* 2002; Page *et al.* 2007). Kimberlitic zircon has low U concentrations (<90 ppm; Valley *et al.* 1998; Belousova *et al.* 2002; Sun *et al.* 2018), which is distinct from most magmatic crustal zircons (Belousova *et al.* 2002). The geochemical characteristics of magmatic zircons within MDM eclogites remain unknown, as no unambiguous MDM eclogite samples have been identified to date (e.g. Jacob, 2004).

Lithium concentrations can potentially be used to discriminate between magmatic zircons that formed in oceanic and continental crustal environments (Ushikubo *et al.* 2008; Bouvier *et al.* 2012). Magmatic zircon grains within rocks derived from the Mid-Atlantic Ridge, including oceanic crustal gabbros, have low Li concentrations (<<0.1 ppm, n = 39; Ushikubo *et al.* 2008; Grimes *et al.* 2011), whereas magmatic zircons formed in continental crustal settings typically contain 1–100 ppm Li, although concentrations outside this range may also be possible (Ushikubo *et al.* 2008; Barth & Wooden, 2010; Bowman *et al.* 2011; Li *et al.* 2011; Bouvier *et al.* 2012). In addition, the diffusion of Li in zircon is slow enough to preserve primary Li concentrations, even under high-grade metamorphic conditions and during anatexis (see Bouvier *et al.* 2012). This suggests that the low concentrations of Li (<<1 ppm) found in magmatic zircons that formed in oceanic crustal environments can be retained during subduction processes and eclogite formation.

Metamorphic zircon domains (e.g. metamorphic rim) and grains typically have weaker zoning visible in CL images (e.g. homogeneous, weak oscillatory, irregular, cloudy or mosaic zoning), Th/U ratios that are generally <0.1 and lower total REE concentrations relative to those found within magmatic zircons (Corfu *et al.* 2003; Hoskin & Schaltegger, 2003; Rubatto, 2017). However, these characteristics do not apply to all metamorphic zircons, with these differences potentially related to the origin of SM eclogites. For instance, oscillatory zoning has been identified within HP zircon that formed as a result of hydrothermal fluid-related processes, as is the case for orogenic eclogites with oceanic crustal protoliths. However, even these zoned metamorphic zircons have Th/U ratios of ≤0.1 (Rubatto & Hermann, 2003; Page *et al.* 2014). (U)HP metamorphic zircons can also have high Th/U ratios (see review in Rubatto, 2017). Zircon domains that formed as a result of seafloor hydrothermal alteration of magmatic zircon at low pressures (stage 2 in Fig. 3) have high Th/U ratios (>0.1) and usually have REE_N patterns that resemble those of unaltered magmatic zircon (Spandler *et al.* 2004; Grimes *et al.* 2009). Zircon grains within oceanic gabbros sometimes have relatively weak magmatic zoning, and large parts of these grains appear texturally homogeneous (Fig. 1d; fig. 2 in Cavosie *et al.* 2009), which potentially causes problems relating to the identification of relics of these zircon grains within mantle eclogites. All of these exceptions need to be considered carefully when determining the origins of zircon within mantle eclogites.

Zircon grains in the Colorado Plateau, Jericho and V. Grib eclogites vary in size from <20 μm (Usui *et al.* 2003) up to 2 mm (Schmidberger *et al.* 2005), and range in shape from anhedral to rounded (Fig. 1a–c). In addition, zircon grains from the Jericho and V. Grib eclogites have core–rim textures with cores that generally appear darker during CL imaging. The brighter and darker domains of these zircons have relatively homogeneous and patchy/mosaic zoning, respectively. This weak zoning contrasts with the regular zoning expected for magmatic and kimberlitic zircons (Fig. 1d), and suggests these zircons have a metamorphic origin. The core of zircon grain no. 6.1 from a V. Grib eclogite

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

(Fig. 1b) has oscillatory-like zoning, suggesting it is magmatic (Skublov *et al.* 2012*b*). However, this is not the case as it has a REE_N pattern (Fig. 4b) that is consistent with the majority of the other metamorphic zircons within the V. Grib eclogites.

All but one of the zircon grains from the V. Grib eclogites have flat $HREE_N$ patterns ($Lu_N/Gd_N = 1–3$) and are HREE depleted (8–229 times chondrite) relative to magmatic zircon within oceanic gabbros (Fig. 4b; online Supplementary Material Table S2). These characteristics are indicative of metamorphic zircon that formed in equilibrium with garnet that sequestered HREEs (Rubatto, 2017). Only one zircon grain from the V. Grib eclogites (no. 26 in Fig. 4b) is relatively enriched in the HREEs (up to 1142 times chondrite) and has a steeply inclined REE_N pattern ($Lu_N/Gd_N = 19$), which suggests this zircon has a distinct origin. However, this remains uncertain as this zircon has no associated CL image or reported U–Pb data. All of the zircon grains from the V. Grib eclogites have negative Eu anomalies ($Eu/Eu^* = 0.24–0.65$). The presence of a negative Eu anomaly in metamorphic zircons from mafic rocks is indicative of the formation of zircon together with plagioclase that preferentially sequesters Eu or is indicative of the presence of a significant bulk rock Eu anomaly (Rubatto, 2017). The fact that the bulk composition of the V. Grib eclogites is free of any significant Eu anomaly ($Eu/Eu^* = 0.8$; Shchukina *et al.* 2015, 2018) suggests that these zircons formed as a result of subduction-related metamorphism under crustal conditions where garnet and plagioclase are both stable (e.g. amphibolite-facies conditions). In addition, the REE_N patterns of these zircon grains are inconsistent with those expected for eclogitic zircon within HP orogenic rocks. The latter are characterized by flat $HREE_N$ patterns and are free of Eu anomalies (Fig. 4b), which reflects the presence of garnet and the absence of plagioclase within orogenic eclogites (Rubatto, 2002, 2017; Skublov *et al.* 2012*a*). The zircon within the V. Grib eclogites cannot have formed during the generation of an eclogite-facies assemblage at crustal or mantle depths, given the lack of plagioclase in both cases. It has been concluded previously that the V. Grib eclogite zircon could have formed just before, but in association with, the formation of these eclogites (Shchukina *et al.* 2018). Our interpretation suggests that the zircon should have formed prior to the eclogite-facies conditions at crustal depths (e.g. amphibolite-facies subduction-related metamorphism), which improves upon the previous conclusion.

Metamorphic zircons within HP rocks that formed at subsolidus (i.e. 'cold') temperatures, including orogenic eclogites, have Th/U values that are generally <0.1, but vary between 0.001 and 0.6 (Rubatto, 2017). Zircon grains from the Jericho eclogites have Th/U ratios of 0.05–0.37 (n = 19; Heaman *et al.* 2006) that are indistinguishable from the zircons found within 'cold' orogenic eclogites. These zircon grains also contain low concentrations of U (9–62 ppm; Heaman *et al.* 2006) that is consistent with the U concentrations of metamorphic zircons within a wide range of orogenic eclogites (Skublov *et al.* 2012*a*). The zircon grains within the V. Grib eclogites have higher Th/U ratios (0.26–0.99; online Supplementary Material Table S2). The low Th/U ratios (<0.1) of metamorphic zircons generally reflect the partitioning of Th between zircon and Th-rich phases such as monazite and allanite; however, the latter two minerals (1) might not have formed during metamorphism as a result of the bulk composition of the rock, or (2) can also be removed during melting under ultrahigh temperature conditions (UHT, >900 °C; Rubatto, 2017). Ti-in-zircon thermometry yielded temperatures of 707–769 °C for the formation of the V. Grib eclogite zircon (Skublov *et al.* 2011, 2012*b*; Shchukina *et al.* 2018). This temperature range indicates that the high Th/U ratios of zircon grains from the V. Grib eclogites reflect the specific bulk composition of these rocks, rather than zircon growth under UHT conditions. These temperatures also suggest that the zircon grains formed before garnet–clinopyroxene equilibration within the V. Grib eclogites at higher temperatures and mantle depths (880 °C; Fig. 2; online Supplementary Material Table S1).

5. Expected range of O isotope compositions for mantle eclogite-hosted zircon

The O isotope composition of zircon within mantle eclogites can be constrained using O isotope data for mantle-derived rocks and orogenic eclogites. Mantle and primary mantle-derived materials have uniform O isotope compositions. For example, garnet within mantle peridotites has $\delta^{18}O$ values of 5.42 ± 0.5 ‰ (Wang *et al.* 2011), whereas fresh modern mid-ocean ridge basalts have $\delta^{18}O$ values of 5.25–5.85 ‰ (Harmon & Hoefs, 1995; Eiler, 2001; Cooper *et al.* 2009). Kimberlitic (i.e. mantle) zircon yields an average $\delta^{18}O$ value of 5.3 ± 0.6 ‰ (2SD; Valley *et al.* 1998), which is indistinguishable from the O isotope composition of magmatic zircon from different rocks (including gabbros) within the oceanic crust (5.3 ± 0.8 ‰, 2SD; Cavosie *et al.* 2009; 5.2 ± 0.5 ‰, 2SD; Grimes *et al.* 2011). This suggests that magmatic zircon within SM eclogites and, probably, within MDM eclogites is likely to have mantle-like O isotope signatures within a narrow range of 4.5–6.1 ‰. The initial mantle-like $\delta^{18}O$ values for relics of the magmatic zircon within SM eclogites are likely to be preserved during the sub-solidus alteration of the oceanic crust (Cavosie *et al.* 2009), as well as during metamorphism and metasomatic reworking within subduction zone environments (Rubatto & Angiboust, 2015).

Hydrothermal alteration by seawater can shift the primary mantle-like bulk O isotope composition of the oceanic crust considerably, yielding a range of $\delta^{18}O$ values between 0 and 15 ‰, depending on temperature (references in Korolev *et al.* 2018). This means that zircon that forms during closed-system metamorphism within a subduction zone environment will inherit this bulk O isotope composition, as is the case for zircon within orogenic eclogites with oceanic crustal protoliths (Page *et al.* 2014; Rubatto & Angiboust, 2015). Within subduction channel environments, an influx of external fluids can cause the metasomatism of subducting oceanic crustal material, and zircon that forms during this process inherits the O isotope compositions of the associated fluids (Page *et al.* 2014; Rubatto & Angiboust, 2015). These external fluids contrast with the uniform O isotope composition of the mantle materials, in that these fluids can be isotopically lighter or heavier, depending on the nature of a given fluid-derived source (i.e. isotopically lighter serpentinized or heavier sedimentary rocks) within the mantle wedge (Errico *et al.* 2013; Rubatto & Angiboust, 2015). This means that metamorphic or metasomatic subduction-related zircons within mantle eclogites are likely to have variable (likely between 0 and 15 ‰) O isotope compositions compared with magmatic zircons that have mantle-like (4.5–6.1 ‰) O isotope compositions. A comparison of the $\delta^{18}O$ values of coexisting zircon and garnet within mantle eclogites could address the issue of the relative origins of these minerals, given that the O isotopic equilibrium between them in orogenic eclogites is a robust indication that they formed simultaneously (Page *et al.* 2014; Rubatto & Angiboust, 2015).

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

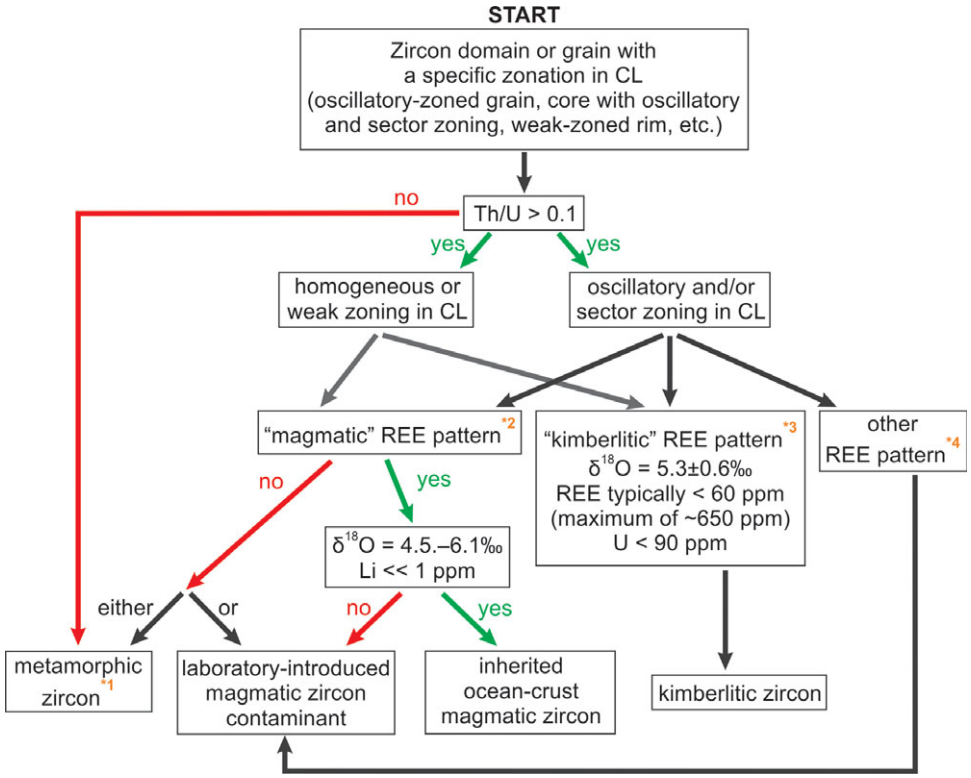


Fig. 5. (Colour online) Flowchart for an algorithm for the identification of kimberlitic and inherited ocean-crust magmatic zircon within mantle eclogite xenoliths. This algorithm allows the discrimination of these zircons from (i) magmatic zircon contaminants that can be introduced to mantle eclogite samples during laboratory-based mineral separation, and (ii) metamorphic zircon. However, this algorithm does not consider magmatic zircon of MDM eclogites and zircon that originated from low-pressure alteration of ocean-crust magmatic zircon. *1 – The metamorphic zircon represents different 'metamorphic' origins (including metasomatic) and does not provide information on its relationship with mantle eclogite samples (i.e. 'metamorphic' zircon of most origins is meant here, including laboratory-induced metamorphic zircon contaminants). *2 – 'Magmatic' REE_N patterns that increase rapidly from the LREEs to the HREEs, with positive Ce and negative Eu anomalies, are generally indicative of magmatic zircon (Belousova *et al.* 2002; Hoskin & Schaltegger, 2003), including magmatic zircons that form within oceanic gabbros (Fig. 4a). *3 – Kimberlitic zircon has flat $HREE_N$ patterns, positive Ce (but no Eu) anomalies and overall depleted REE concentrations relative to magmatic oceanic crust-derived zircon (Fig. 4a); the range of $\delta^{18}O$ (2SD) is after Valley *et al.* (1998). Note that HP (eclogitic) zircon has low U and REE concentrations (Skublov *et al.* 2012*a*) and can have REE_N patterns that overlap those of kimberlitic zircon (Fig. 4b). In cases when this HP zircon has Th/U >0.1, it, therefore, can be mistaken for those kimberlitic zircons whose primary zoning has been erased. In this case, the kimberlitic zircon can be identified by the U–Pb age it yields that should be equal to the emplacement age of the hosting kimberlite pipe in most cases (Page *et al.* 2007). *4 – 'Other REE pattern' refers to magmatic zircons that have different REE_N patterns from those of kimberlitic and typical magmatic zircons. These zircons are exemplified by zircon grains from syenites that have REE_N patterns that increase rapidly from the LREEs to the HREEs, and have positive Ce but no Eu anomalies (Belousova *et al.* 2002), and by zircon 5.1 in Figure 6b.

6. Identification of zircon associated with mantle eclogites

6.a. An algorithm for identification of these zircons

As discussed in Sections 2–4 above, the zircon grains in the Jericho and V. Grib eclogites represent very few specific examples of zircon growth. Therefore, these zircons cannot be considered representative examples of the metamorphic zircon expected to be present in all types of mantle eclogites. It is also likely that metamorphic zircons within mantle eclogites undergo multiple episodes of growth during the formation and evolution of these rocks. This means that the lack of available data for these metamorphic zircons, combined with their highly variable O isotope compositions (discussed in Section 5 above), highlights the absence of a reliable framework for the identification of specific metamorphic zircons associated with mantle eclogites. However, magmatic zircons within oceanic gabbros and kimberlites have well-investigated and particular zoning patterns, Th/U ratios, and trace-element and O isotope characteristics that can be used for identification purposes. This enabled the construction of an algorithm (Fig. 5) that allows the identification of inherited oceanic crust-derived and xenogenic kimberlitic zircons that may be present in mantle eclogite xenoliths. This algorithm can also be used for the identification of metamorphic zircons (albeit of unknown origin and unknown relation to mantle eclogite samples) and magmatic zircon contaminants added to samples during laboratory-based mineral separation processes. This application is especially useful for testing zircon grains isolated from mantle eclogite xenoliths that contain no zircons in their thin-sections. Although magmatic zircons within MDM eclogites should theoretically have magmatic (i.e. oscillatory and/or sector) zoning that is visible in CL images, in addition to Th/U ratios of >0.1 and mantle-like $\delta^{18}O$ compositions, the characteristics of these magmatic zircons remain unknown, which means that they cannot be assessed using our algorithm. Recrystallized domains of oceanic magmatic zircons that formed as a result of LP hydrothermal alteration (stage 2 in Fig. 3) cannot be correctly assessed using this approach, owing to the geochemical affinity with the magmatic zircon (discussed in Section 4 above). However, these altered domains have distinctive chaotic or perturbed zoning in CL images and contain multiple pores and Th- and Y-rich inclusions (Spandler *et al.* 2004; Grimes *et al.* 2009), which could be indicative of their origin in combination with the geochemical characteristics.

We suggest that inherited magmatic zircons derived from oceanic crust are likely to be present either as relics (e.g. magmatic

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

cores overgrown by metamorphic rims) or as zircon grains with evidence of alteration, as is the case in some HP orogenic rocks (e.g. fig. 1a, b, e in Rubatto & Hermann, 2007). This parameter was not included in our algorithm; however, the algorithm does account for some other possible challenges: (1) despite the fact that kimberlitic zircons generally have oscillatory zoning that is visible in CL images (Page *et al.* 2007), this primary zoning can be erased during later processes in some grains (Corfu *et al.* 2003); and (2) zoning in either magmatic zircon relics or fragments can be relatively weak (e.g. the homogeneous darker sectors of the oceanic crust-derived zircon shown in Fig. 1d).

The algorithm suggests that the V. Grib eclogite zircon grains have metamorphic origins in that they have Th/U values >0.1, contain only weak zoning visible during CL imaging and have REE_N patterns that do not match those of typical magmatic zircons that formed in different environments (for REE_N patterns in typical magmatic zircons, see Belousova *et al.* 2002; Hoskin & Schaltegger, 2003). The Jericho eclogite zircon grains that have Th/U values <0.1 are also classified as metamorphic by our algorithm, whereas those with Th/U values >0.1 cannot be assessed using this approach, owing to the lack of other necessary data (e.g. no REE compositions are available to date).

6.b. Case study of zircon from the Kasai mantle eclogites

Zircon grains isolated from the Kasai eclogite xenoliths represent a good case study for testing the effectiveness of the algorithm developed during this study as (1) no zircon grains have been identified in thin-sections of these xenoliths, and (2) CL imaging, Th/U values and trace-element data have been reported previously for zircon grains isolated from these xenoliths (Nikitina *et al.* 2012, 2014). Importantly, these eclogites are also thought to have formed as a result of the subduction of oceanic crust or by the recrystallization of SM eclogites within the mantle (Nikitina *et al.* 2014, 2017; Korolev *et al.* 2017; N. M. Korolev *et al.* submitted). The O isotope compositions of the Kasai eclogite zircon grains cannot be considered as no data have been reported.

Four zircon grains were separated from two Kasai eclogite xenoliths. These zircon grains yield U–Pb ages that range between 2799 and 430 Ma (Fig. 6a), all of which are older than the timing of emplacement of the hosting kimberlites (118 ± 1 Ma; Robles-Cruz *et al.* 2012) and are thought to record different stages of the evolution of the Kasai eclogites within the upper lithospheric mantle (Nikitina *et al.* 2012, 2014, 2017).

Two zircon grains from low-Mg mantle eclogite sample Cat-11 have similar internal textures (Fig. 6a) where cores with oscillatory zoning are overgrown by weak, patchy-zoned rims. Classifying these zircon grains with our algorithm suggests that the weak, patchy zoning of both rims, coupled with their low Th/U values (0.05–0.06), is indicative of a metamorphic origin. The cores have magmatic-like REE_N patterns that are similar to those present in zircon from the oceanic crust (Fig. 6b), as well as oscillatory zoning that is visible during CL imaging, and Th/U values >0.1, all of which are indicative of a magmatic origin. However, these cores also have high Li contents (2–13 ppm) that are indicative of formation in a continental crustal setting. This suggests that both of the zircon grains isolated from mantle eclogite sample Cat-11 are contaminants that were most likely introduced during laboratory-based mineral separation.

The two zircon grains from high-Mg mantle eclogite sample Cat-2 are magmatic, indicated by their Th/U values of >0.1 and distinct oscillatory zoning visible during CL imaging (Fig. 6a), as

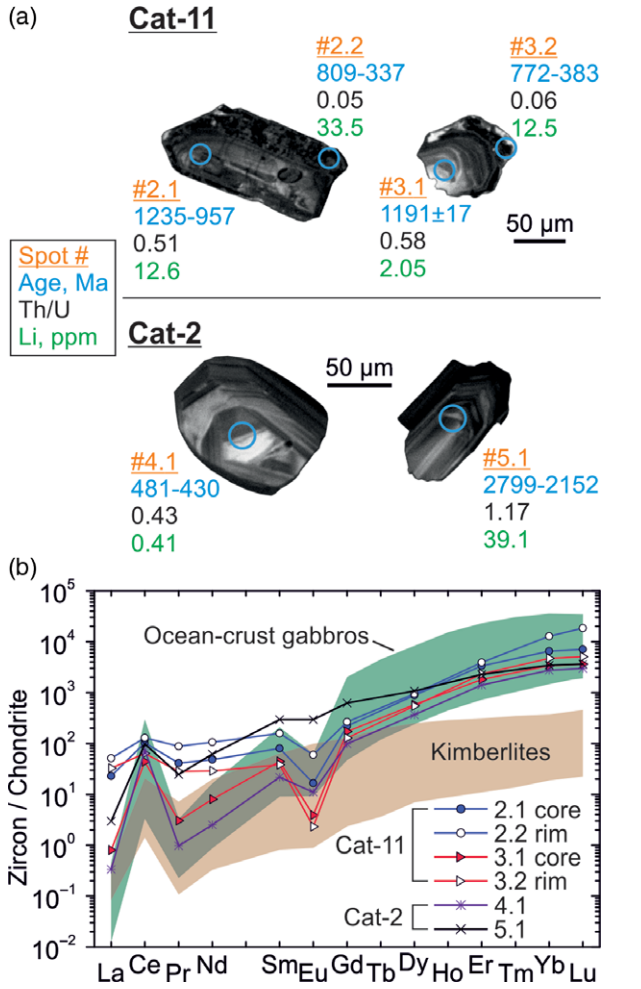


Fig. 6. (Colour online) (a) Cathodoluminescence images of zircon grains from low-Mg (Cat-11) and high-Mg (Cat-2) mantle eclogite xenoliths from kimberlites of the Kasai Craton (modified after Nikitina *et al.* 2012). Images of these grains are reprinted by permission from Springer Nature under licence 4826261015582: Springer Nature, Doklady Earth Sciences, vol. 445, fig. 1, p. 841, U–Pb age and geochemistry of zircon from mantle xenoliths of the Katoka and Kat-115 kimberlitic pipes (Republic of Angola), Nikitina *et al.*, Copyright (2012). Ages (Ma ± 1σ for concordant analyses, ^{207}Pb–^{206}Pb and ^{206}Pb–^{238}U ages (Ma) for discordant analyses), Th/U ratios, Li concentrations and analysis numbers are from Nikitina *et al.* (2012, 2014), and are indicated by different colours. The diameter of the blue circles is ~20 µm, and each circle indicates the approximate location of the U–Pb and trace-element ion microprobe analyses of these zircon grains. (b) REE_N patterns of zircons from the Cat-11 and Cat-2 mantle eclogites compared to zircon REE_N patterns for oceanic gabbros and kimberlites (Fig. 4a). REE concentrations are normalized to the CI chondrite composition of McDonough & Sun (1995), and the trace-element data used in (a) and (b) are given in online Supplementary Material Table S2.

well as REE_N patterns that are distinct from those of kimberlitic zircon (Fig. 6b). Zircon grain 5.1 has a weaker Eu anomaly than that expected for oceanic crust-derived zircons (Eu/Eu* = 0.69 and 0.03–0.45, respectively; online Supplementary Material Table S2), and is relatively enriched in the REEs from Pr to Gd (Fig. 6b). This REE composition differs from typical magmatic patterns and is related to the 'other REE pattern' classification within our algorithm (Fig. 5). This indicates that zircon 5.1 is most likely another laboratory-introduced contaminant. The high Li content (39 ppm) of this zircon grain is also indicative of a contaminant origin. Zircon grain 4.1 has a REE_N pattern that is similar to that expected for typical magmatic zircon and contains a low concentration of Li (0.4 ppm), suggesting it might have formed in an

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

oceanic crustal setting and could have been inherited subsequently by the eclogite. However, this grain represents a fragment of zircon that has distinct magmatic zoning visible during CL imaging and records no textural evidence of alteration. Preservation of grains of inherited oceanic crustal zircon that have no overgrown rims or other textural records of metamorphic alteration (e.g. partial resorption, recrystallization along fractures) is highly unlikely, considering the evolutionary history of mantle eclogites and previous examples of inherited magmatic zircon grains or magmatic zircon relics within (U)HP orogenic rocks (e.g. Rubatto & Hermann, 2007; Gauthiez-Putallaz *et al.* 2016). Therefore, it is likely that zircon grain 4.1 also represents a laboratory-introduced contaminant.

7. Suggestions for future research

We suggest that two main reasons may lead to the scarcity of zircon within mantle eclogites in contrast with zircon-rich orogenic eclogites: (1) it is unlikely that individual samples of mantle eclogites would contain accessory zircon, because these kimberlite-hosted mantle-derived xenoliths are relatively small in size (typically <100 mm); (2) the majority of mantle eclogites underwent higher rates of partial melting that, therefore, makes it more possible for accessory zircon to be removed from these rocks during this process. However, mantle eclogites of all types may theoretically contain accessory zircons related to one or several origins (Fig. 3). To make progress with the proper identification of zircon-bearing mantle eclogites, and with the linking of the U–Pb ages of the zircons they contain with particular geological events, it will be useful to:

(a) search for zircon grains within thin-sections only. This approach enables the avoidance of possible contamination of mantle eclogite samples during laboratory-based mineral separation. It also should be considered that, as an accessory mineral, zircon may not be observed in every single thin-section. Therefore, an investigation of several thin-sections of each mantle eclogite xenolith should increase the probability of finding zircons.
(b) fully characterize zircon from mantle eclogites to utilize its outstanding potential to date and identify processes that affected these rocks and their precursors. Th/U ratios, trace-element concentrations (at least REE, Y, Hf, U, Th and Li), O and Hf isotope compositions, internal zircon textures (CL imaging) and textural relationships with other minerals are the most critical characteristics of mantle eclogite-derived zircons in addition to the U–Pb ages they yield.
(c) compare the $\delta^{18}O$ values of coexisting zircon and garnet within mantle eclogites. This approach could be a robust proxy for the identification of the relative origins of these minerals as it has been demonstrated for orogenic eclogites (Page *et al.* 2014; Rubatto & Angiboust, 2015).

8. Conclusions

(1) The supposed origins and evolutionary histories of mantle eclogites suggest that xenoliths of these rocks can contain several types of zircon: (a) magmatic zircon within MDM eclogites that formed during melt crystallization, (b) magmatic zircon within SM eclogites that was inherited from mafic rocks that formed within oceanic crustal settings, (c) metamorphic zircon (including metasomatic), and (d) xenogenic kimberlitic zircon. Zircon types (c) and (d) can occur within all types of mantle eclogites.
(2) The specific characteristics of magmatic zircon within MDM eclogites and metamorphic zircon within all mantle eclogites remain unknown. However, the magmatic zircon derived from mafic rocks formed in oceanic crustal environments and kimberlitic zircon have distinctive trace-element and O isotope compositions. Kimberlitic and magmatic oceanic crust-derived zircons generally have oscillatory and/or sector zoning that is visible in CL images, Th/U values >0.1 and mantle-like $\delta^{18}O$ values that range generally between 4.5 and 6.1 ‰. These oceanic crust-derived zircons have 'magmatic' REE_N patterns that increase rapidly from the LREEs to HREEs with positive Ce and negative Eu anomalies. They are also depleted in Li (<<1 ppm). Kimberlitic zircons have flat $HREE_N$ patterns, are free of Eu anomalies, are depleted in U (<90 ppm) and typically contain <60 ppm (maximum of ~650 ppm) REEs. These data allow the construction of an algorithm for the identification of inherited magmatic zircons derived from oceanic crust and xenogenic kimberlitic zircons within mantle eclogite xenoliths (Fig. 5). This algorithm can also be used to identify metamorphic zircons, albeit without specifying their origins and relation to mantle eclogites (including laboratory-based metamorphic zircon contaminants), and magmatic zircon contaminants that have been introduced to mantle eclogite samples during laboratory-based mineral separation, but does not consider the magmatic zircon of MDM eclogites.
(3) The algorithm has been applied to mantle eclogite xenoliths from kimberlites of the Kasai Craton, as these eclogites have a primary subduction-related origin and contain zircon grains that have not been identified within thin-sections (Nikitina *et al.* 2012, 2014). This analysis indicates that at least three of the four zircon grains isolated from these xenoliths most likely represent contaminants that were introduced to these mantle eclogite samples during laboratory-based mineral separation.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1017/S0016756820001387

Acknowledgements. We thank Jin-Xiang Huang for constructive comments that helped to improve the manuscript, and Alexey G. Goncharov for discussions on an earlier version of the manuscript. We are thankful to Sonja Aulbach and an anonymous referee for their very constructive comments and criticisms. This study was funded by the National Key R&D Program of China (grant 2016YFE0203000); the National Natural Science Foundation of China (grant 41811530083); and the Russian Foundation of Basic Research (RFBR), research projects No. 18-55-53022 and 16-35-60092 mol_a_dk. This study was conducted under state contract No. 0153-2019-0002 of the Institute of Precambrian Geology and Geochronology of the Russian Academy of Sciences. A.E. Melnik acknowledges the awarding of a postdoctoral fellowship under the President's International Fellowship Initiative (PIFI) of the Chinese Academy of Sciences (grant 2019PC0100). We acknowledge the permission from Springer Nature, Oxford University Press and the Mineralogical Society of America to reproduce images herein (details are given in the captions for Figures 1 and 6).

References

Aulbach S, Creaser RA, Pearson NJ, Simonetti SS, Heaman LM, Griffin WL and Stachel T (2009) Sulfide and whole rock Re–Os systematics of eclogite and pyroxenite xenoliths from the Slave Craton, Canada. *Earth and Planetary Science Letters* **283**, 48–58.

Aulbach S, Heaman LM, Jacob DE and Viljoen KS (2019a) Ages and sources of mantle eclogites: ID-TIMS and in situ MC-ICPMS Pb–Sr isotope systematics of clinopyroxene. *Chemical Geology* **503**, 15–28.

Aulbach S, Höfer HE and Gerdes A (2019b) High-Mg and low-Mg mantle eclogites from Koidu (West African Craton) linked by Neoproterozoic ultramafic melt metasomatism of subducted Archaean plateau-like oceanic crust. *Journal of Petrology* **60**, 723–54.

Aulbach S and Jacob DE (2016) Major- and trace-elements in cratonic mantle eclogites and pyroxenites reveal heterogeneous sources and metamorphic processing of low-pressure protoliths. *Lithos* **262**, 586–605.

Aulbach S, Massuyeau M, Garber JM, Gerdes A, Heaman LM and Viljoen KS (2020) Ultramafic carbonated melt- and auto-metasomatism in mantle eclogites: compositional effects and geophysical consequences. *Geochemistry, Geophysics, Geosystems* **21**, e2019GC008774. doi: 10.1029/2019GC008774.

Barth AP and Wooden JL (2010) Coupled elemental and isotopic analyses of polygenetic zircons from granitic rocks by ion microprobe, with implications for melt evolution and the sources of granitic magmas. *Chemical Geology* **277**, 149–59.

Belousova EA, Griffin WL, O'Reilly SY and Fisher NI (2002) Igneous zircon: trace element composition as an indicator of source rock type. *Contributions to Mineralogy and Petrology* **143**, 602–22.

Boniface N, Schenk V and Appel P (2012) Paleoproterozoic eclogites of MORB-type chemistry and three Proterozoic orogenic cycles in the Ubendian Belt (Tanzania): evidence from monazite and zircon geochronology, and geochemistry. *Precambrian Research* **192–195**, 16–33.

Bouvier AS, Ushikubo T, Kita NT, Cavosie AJ, Kozdon R and Valley JW (2012) Li isotopes and trace elements as a petrogenetic tracer in zircon: insights from Archean TTGs and sanukitoids. *Contributions to Mineralogy and Petrology* **163**, 745–68.

Bowman JR, Moser DE, Valley JW, Wooden JL, Kita NT and Mazdab FK (2011) Zircon U–Pb isotope, $\delta^{18}O$ and trace element response to 80 m.y. of high temperature metamorphism in the lower crust: sluggish diffusion and new records of Archean craton formation. *American Journal of Science* **311**, 719–72.

Cavosie AJ, Kita NT and Valley JW (2009) Primitive oxygen-isotope ratio recorded in magmatic zircon from the Mid-Atlantic Ridge. *American Mineralogist* **94**, 926–34.

Chen YD, O'Reilly SY, Kinny PD and Griffin WL (1994) Dating lower crust and upper mantle events: an ion microprobe study of xenoliths from kimberlitic pipes, South Australia. *Lithos* **32**, 77–94.

Cherniak DJ, Hanchar JM and Watson EB (1997) Diffusion of tetravalent cations in zircon. *Contributions to Mineralogy and Petrology* **127**, 383–90.

Cooper KM, Eiler JM, Sims KWW and Langmuir CH (2009) Distribution of recycled crust within the upper mantle: insights from the oxygen isotope composition of MORB from the Australian–Antarctic discordance. *Geochemistry, Geophysics, Geosystems* **10**. doi: 10.1029/2009GC002728.

Corfu F, Hanchar JM, Hoskin PWO and Kinny P (2003) Atlas of zircon textures. *Reviews in Mineralogy and Geochemistry* **53**, 469–500.

Day HW (2012) A revised diamond-graphite transition curve. *American Mineralogist* **97**, 52–62.

Dobrzhinetskaya L, Wirth R and Green H (2014) Diamonds in Earth's oldest zircons from Jack Hills conglomerate, Australia, are contamination. *Earth and Planetary Science Letters* **387**, 212–18.

Eiler JM (2001) Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Reviews in Mineralogy and Geochemistry* **43**, 319–64.

Errico JC, Barnes JD, Strickland A and Valley JW (2013) Oxygen isotope zoning in garnets from Franciscan eclogite blocks: evidence for rock-buffered fluid interaction in the mantle wedge. *Contributions to Mineralogy and Petrology* **166**, 1161–76.

François C, Debaille V, Paquette JL, Baudet D and Javaux EJ (2018) The earliest evidence for modern-style plate tectonics recorded by HP–LT metamorphism in the Paleoproterozoic of the Democratic Republic of the Congo. *Scientific Reports* **8**, 15452. doi: 10.1038/s41598-018-33823-y.

Gauthiez-Putallaz L, Rubatto D and Hermann J (2016) Dating prograde fluid pulses during subduction by in situ U–Pb and oxygen isotope analysis. *Contributions to Mineralogy and Petrology* **171**, 1–20.

Griffin WL and O'Reilly SY (2007) Cratonic lithospheric mantle: is anything subducted? *Episodes* **30**, 43–53.

Grimes CB, John BE, Cheadle MJ, Mazdab FK, Wooden JL, Swapp S and Schwartz JJ (2009) On the occurrence, trace element geochemistry, and crystallization history of zircon from in situ ocean lithosphere. *Contributions to Mineralogy and Petrology* **158**, 757–83.

Grimes CB, Ushikubo T, John BE and Valley JW (2011) Uniformly mantle-like $\delta^{18}O$ in zircons from oceanic plagiogranites and gabbros. *Contributions to Mineralogy and Petrology* **161**, 13–33.

Harmon RS and Hoefs J (1995) Oxygen isotope heterogeneity of the mantle deduced from global ^{18}O systematics of basalts from different geotectonic settings. *Contributions to Mineralogy and Petrology* **120**, 95–114.

Hasterok D and Chapman DS (2011) Heat production and geotherms for the continental lithosphere. *Earth and Planetary Science Letters* **307**, 59–70.

Heaman LM, Creaser RA and Cookenboo HO (2002) Extreme enrichment of high field strength elements in Jericho eclogite xenoliths: a cryptic record of Paleoproterozoic subduction, partial melting, and metasomatism beneath the Slave craton, Canada. *Geology* **30**, 507–10.

Heaman LM, Creaser RA, Cookenboo HO and Chacko T (2006) Multi-stage modification of the northern Slave mantle lithosphere: evidence from zircon- and diamond-bearing eclogite xenoliths entrained in Jericho Kimberlite, Canada. *Journal of Petrology* **47**, 821–58.

Helmstaedt H and Doig R (1975) Eclogite nodules from kimberlite pipes of the Colorado Plateau – samples of subducted Franciscan-type oceanic lithosphere. *Physics and Chemistry of the Earth* **9**, 95–111.

Hoskin PWO and Schaltegger U (2003) The composition of zircon and igneous and metamorphic petrogenesis. *Reviews in Mineralogy and Geochemistry* **53**, 27–62.

Huang JX, Griffin WL, Gréau Y, Pearson NJ, O'Reilly SY, Cliff J and Martin L (2014) Unmasking xenolithic eclogites: progressive metasomatism of a key Roberts Victor sample. *Chemical Geology* **364**, 56–65.

Jacob DE (2004) Nature and origin of eclogite xenoliths from kimberlites. *Lithos* **77**, 295–316.

Jacob DE, Bizimis M and Salters VJ (2005) Lu–Hf and geochemical systematics of recycled ancient oceanic crust: evidence from Roberts Victor eclogites. *Contributions to Mineralogy and Petrology* **148**, 707–20.

Jacob DE and Foley SF (1999) Evidence for Archean ocean crust with low high field strength element signature from diamondiferous eclogite xenoliths. *Lithos* **48**, 317–36.

Jacob D, Jagoutz E, Lowry D, Mattey D and Kudrjavtseva G (1994) Diamondiferous eclogites from Siberia: remnants of Archean oceanic crust. *Geochimica et Cosmochimica Acta* **58**, 5191–207.

Kamber BS and Collerson KD (2000) Role of 'hidden' deeply subducted slabs in mantle depletion. *Chemical Geology* **166**, 241–54.

Kopylova MG, Russell JK and Cookenboo H (1999) Petrology of peridotite and pyroxenite xenoliths from the Jericho Kimberlite: implications for the thermal state of the mantle beneath the Slave Craton, Northern Canada. *Journal of Petrology* **40**, 79–104.

Korolev NM, Melnik AE, Li X-H and Skublov SG (2018) The oxygen isotope composition of mantle eclogites as a proxy of their origin and evolution: a review. *Earth-Science Reviews* **185**, 288–300.

Korolev NM, Nikitina LP, Goncharov A, Dubinina EO, Melnik AE, Müller D, Chen Y-X, and Zinchenko VN (submitted) Origin of mantle eclogites from the Catoca pipe (Kasai Craton, Western Africa): three eclogite lithologies from two layers of oceanic crust. *Journal of Petrology*.

Korolev NM, Nikitina LP, Melnik AE and Zinchenko VN (2017) Origin of upper mantle eclogites from the Catoca pipe (N.-E. Angola). International Kimberlite Conference: Extended Abstracts 11, doi: 10.29173/ikc3911.

Lee JKW, Williams IS and Ellis DJ (1997) Pb, U and Th diffusion in natural zircon. *Nature* **390**, 159–62.

Li XH, Li QL, Liu Y and Tang GQ (2011) Further characterization of M257 zircon standard: a working reference for SIMS analysis of Li isotopes. *Journal of Analytical Atomic Spectrometry* **26**, 352–8.

Litasov KD, Kagi H, Voropaev SA, Hirata T, Ohfuji H, Ishibashi H, Makino Y, Bekker TB, Sevastyanov VS, Afanasiev VP and Pokhilenko NP (2019) Comparison of enigmatic diamonds from the Tolbachik arc volcano (Kamchatka) and Tibetan ophiolites: assessing the role of contamination by synthetic materials. *Gondwana Research* **75**, 16–27.

Loose D and Schenk V (2018) 2.09 Ga old eclogites in the Eburnian–Transamazonian orogen of southern Cameroon: significance for Palaeoproterozoic plate tectonics. *Precambrian Research* **304**, 1–11.

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press

McDonough WF and Sun SS (1995) The composition of the Earth. *Chemical Geology* **120**, 223–53.

Nakamura D (2009) A new formulation of garnet-clinopyroxene geothermometer based on accumulation and statistical analysis of a large experimental data set. *Journal of Metamorphic Geology* **27**, 495–508.

Nikitina LP, Bogomolov ES, Krymsky RS, Belyatsky BV, Korolev NM and Zinchenko VN (2017) Nd–Sr–Os systems of eclogites in the lithospheric mantle of the Kasai Craton (Angola). *Russian Geology and Geophysics* **58**, 1305–16.

Nikitina LP, Korolev NM, Zinchenko VN and Felix JT (2014) Eclogites from the upper mantle beneath the Kasai Craton (Western Africa): petrography, whole-rock geochemistry and UPb zircon age. *Precambrian Research* **249**, 13–32.

Nikitina LP, Marin YB, Skublov SG, Korolev NM, Saltykova AK, Zinchenko VN and Chissupa HM (2012) U–Pb age and geochemistry of zircon from mantle xenoliths of the Katoka and Kat-115 kimberlitic pipes (Republic of Angola). *Doklady Earth Sciences* **445**, 840–4.

Page FZ, Essene EJ, Mukasa SB and Valley JW (2014) A garnet-zircon oxygen isotope record of subduction and exhumation fluids from the Franciscan complex, California. *Journal of Petrology* **55**, 103–31.

Page FZ, Fu B, Kita NT, Fournelle J, Spicuzza MJ, Schulze DJ, Viljoen F, Basei MAS and Valley JW (2007) Zircons from kimberlite: new insights from oxygen isotopes, trace elements, and Ti in zircon thermometry. *Geochimica et Cosmochimica Acta* **71**, 3887–903.

Pearson DG, Snyder GA, Shirey SB, Taylor LA, Carlson RW and Sobolev NV (1995) Archaean Re–Os age for Siberian eclogites and constraints on Archaean tectonics. *Nature* **374**, 711–3.

Robles-Cruz SE, Escayola M, Jackson S, Galí S, Pervov V, Watangua M, Gonçalves A and Melgarejo JC (2012) U–Pb SHRIMP geochronology of zircon from the Catoca kimberlite, Angola: implications for diamond exploration. *Chemical Geology* **310–311**, 137–47.

Rubatto D (2002) Zircon trace element geochemistry: partitioning with garnet and the link between U–Pb ages and metamorphism. *Chemical Geology* **184**, 123–38.

Rubatto D (2017) Zircon: the metamorphic mineral. *Reviews in Mineralogy and Geochemistry* **83**, 261–95.

Rubatto D and Angiboust S (2015) Oxygen isotope record of oceanic and high-pressure metasomatism: a P–T–time–fluid path for the Monviso eclogites (Italy). *Contributions to Mineralogy and Petrology* **170**, 44. doi: 10.1007/s00410-015-1198-4.

Rubatto D and Hermann J (2003) Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): implications for Zr and Hf budget in subduction zones. *Geochimica et Cosmochimica Acta* **67**, 2173–87.

Rubatto D and Hermann J (2007) Zircon behaviour in deeply subducted rocks. *Elements* **3**, 31–5.

Rubatto D and Scambelluri M (2003) U–Pb dating of magmatic zircon and metamorphic baddeleyite in the Ligurian eclogites (Voltri Massif, Western Alps). *Contributions to Mineralogy and Petrology* **146**, 341–55.

Schmidberger SS, Heaman LM, Simonetti A, Creaser RA and Cookenboo HO (2005) Formation of Paleoproterozoic eclogitic mantle, Slave Province (Canada): insights from in-situ Hf and U–Pb isotopic analyses of mantle zircons. *Earth and Planetary Science Letters* **240**, 621–33.

Schmitz M, Shirey S and Carlson R (2003) High-precision U–Pb geochronology and Lu–Hf isotopic systematics of zircons in southern African cratonic mantle eclogites and implications for subcontinental lithospheric mantle evolution and metasomatism. *International Kimberlite Conference: Extended Abstracts* **8**, doi: 10.29173/ikc3160.

Schulze DJ (1989) Constraints on the abundance of eclogite in the upper mantle. *Journal of Geophysical Research* **94**, 4205–12.

Shchukina EV, Agashev AM, Golovin NN and Pokhilenko NP (2015) Equigranular eclogites from the V. Grib kimberlite pipe: evidence for Paleoproterozoic subduction on the territory of the Arkhangelsk diamondiferous province. *Doklady Earth Sciences* **462**, 497–501.

Shchukina EV, Agashev AM and Zedgenizov DA (2018) Origin of zircon-bearing mantle eclogites entrained in the V. Grib kimberlite (Arkhangelsk region, NW Russia): evidence from mineral geochemistry and the U–Pb and Lu–Hf isotope compositions of zircon. *Mineralogy and Petrology* **112**, 85–100.

Shirey SB, Carlson RW, Richardson SH, Menzies A, Gurney JJ, Pearson DG, Harris JW and Wiechert U (2001) Archean emplacement of eclogitic components into the lithospheric mantle during formation of the Kaapvaal Craton. *Geophysical Research Letters* **28**, 2509–12.

Shirey SB and Richardson SH (2011) Start of the Wilson Cycle at 3 Ga shown by diamonds from subcontinental mantle. *Science* **333**, 434–6.

Shu Q, Brey GP, Gerdes A and Hoefer HE (2014) Mantle eclogites and garnet pyroxenites – the meaning of two-point isochrons, Sm–Nd and Lu–Hf closure temperatures and the cooling of the subcratonic mantle. *Earth and Planetary Science Letters* **389**, 143–54.

Skublov SG, Berezin AV and Berezhnaya NG (2012a) General relations in the trace-element composition of zircons from eclogites with implications for the age of eclogites in the belomorian mobile belt. *Petrology* **20**, 427–49.

Skublov SG, Nikitina LP, Marin YB, Levskii LK and Guseva NS (2012b) U–Pb age and geochemistry of zircons from xenoliths of the V. Grib kimberlitic pipe, Arkhangelsk diamond province. *Doklady Earth Sciences* **444**, 595–600.

Skublov SG, Shchukina EV, Guseva NS, Mal'kovets VG and Golovin NN (2011) Geochemical characteristics of zircons from xenoliths in the V. Grib Kimberlite Pipe, Archangelsk Diamondiferous Province. *Geochemistry International* **49**, 415–21.

Smart KA, Heaman LM, Chacko T, Simonetti A, Kopylova M, Mah D and Daniels D (2009) The origin of high-MgO diamond eclogites from the Jericho Kimberlite, Canada. *Earth and Planetary Science Letters* **284**, 527–37.

Smith D, Connelly JN, Manser K, Moser DE, Housh TB, McDowell FW and Mack LE (2004) Evolution of Navajo eclogites and hydration of the mantle wedge below the Colorado Plateau, southwestern United States. *Geochemistry, Geophysics, Geosystems* **5**, Q04005. doi: 10.1029/2003GC000675.

Spandler C, Hermann J and Rubatto D (2004) Exsolution of thortveitite, yttrialite, and xenotime during low-temperature recrystallization of zircon from New Caledonia, and their significance for trace element incorporation in zircon. *American Mineralogist* **89**, 1795–806.

Sun J, Tappe S, Kostrovitsky SI, Liu CZ, Skuzovatov SY and Wu FY (2018) Mantle sources of kimberlites through time: a U–Pb and Lu–Hf isotope study of zircon megacrysts from the Siberian diamond fields. *Chemical Geology* **479**, 228–40.

Tsujimori T and Ernst WG (2014) Lawsonite blueschists and lawsonite eclogites as proxies for palaeo-subduction zone processes: a review. *Journal of Metamorphic Geology* **32**, 437–54.

Tsujimori T, Sisson VB, Liou JG, Harlow GE and Sorensen SS (2006) Very-low-temperature record of the subduction process: a review of worldwide lawsonite eclogites. *Lithos* **92**, 609–24.

Ushikubo T, Kita NT, Cavosie AJ, Wilde SA, Rudnick RL and Valley JW (2008) Lithium in Jack Hills zircons: evidence for extensive weathering of Earth's earliest crust. *Earth and Planetary Science Letters* **272**, 666–76.

Usui T, Kobayashi K and Nakamura E (2002) U–Pb isotope systematics of microzircon inclusions: implications for the age and origin of eclogite xenolith from the Colorado Plateau. *Proceedings of the Japan Academy* **78**, 51–6.

Usui T, Nakamura E and Helmstaedt H (2006) Petrology and geochemistry of eclogite xenoliths from the Colorado Plateau: implications for the evolution of subducted oceanic crust. *Journal of Petrology* **47**, 929–64.

Usui T, Nakamura E, Kobayashi K, Maruyama S and Helmstaedt H (2003) Fate of the subducted Farallon plate inferred from eclogite xenoliths in the Colorado Plateau. *Geology* **31**, 589–92.

Valley JW, Kinny PD, Schulze DJ and Spicuzza MJ (1998) Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts. *Contributions to Mineralogy and Petrology* **133**, 1–11.

Wang Z, Bucholz C, Skinner B, Shimizu N and Eiler J (2011) Oxygen isotope constraints on the origin of high-Cr garnets from kimberlites. *Earth and Planetary Science Letters* **312**, 337–47.

Whitehouse MJ and Platt JP (2003) Dating high-grade metamorphism – constraints from rare-earth elements in zircon and garnet. *Contributions to Mineralogy and Petrology* **145**, 61–74.

Zartman RE and Richardson SH (2005) Evidence from kimberlitic zircon for a decreasing mantle Th/U since the Archean. *Chemical Geology* **220**, 263–83.

https://doi.org/10.1017/S0016756820001387 Published online by Cambridge University Press