

Petrochronological Constraints on the Origin of the Mountain Pass Ultrapotassic and Carbonatite Intrusive Suite, California

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ABSTRACT

Rare earth element (REE) ore-bearing carbonatite dikes and a stock at Mountain Pass, California, are spatially associated with a suite of ultrapotassic plutonic rocks, and it has been proposed that the two are genetically related. This hypothesis is problematic, given that existing geochronological constraints indicate that the carbonatite is ~15–25 Myr younger than the ultrapotassic rocks, requiring alternative models for the formation of the REE ore-bearing carbonatite during a separate event and/or via a different mechanism. New laser ablation split-stream inductively coupled plasma mass spectrometry (LASS-ICP-MS) petrochronological data from ultrapotassic intrusive rocks from Mountain Pass yield titanite and zircon U–Pb dates from 1429 ± 10 to 1385 ± 18 Ma, expanding the age range of the ultrapotassic rocks in the complex by ~20 Myr. The ages of the youngest ultrapotassic rocks overlap monazite Th–Pb ages from a carbonatite dike and the main carbonatite ore body (1396 ± 16 and 1371 ± 10 Ma, respectively). The Hf isotope compositions of zircon in the ultrapotassic rocks are uniform, both within and between samples, with a weighted mean ϵ_{Hf} of 1.9 ± 0.2 (MSWD = 0.9), indicating derivation from a common, isotopically homogeneous source. In contrast, *in situ* Nd isotopic data for titanite in the ultrapotassic rocks are variable ($\epsilon_{\text{Nd}_i} = -3.5$ to -12), suggesting variable contamination by an isotopically enriched source. The most primitive ϵ_{Nd_i} isotopic signatures, however, do overlap ϵ_{Nd_i} from monazite ($\epsilon_{\text{Nd}_i} = -2.8 \pm 0.2$) and bastnäsite ($\epsilon_{\text{Nd}_i} = -3.2 \pm 0.3$) in the ore-bearing carbonatite, suggesting derivation from a common source. The data presented here indicate that ultrapotassic magmatism occurred in up to three phases at Mountain Pass (~1425, ~1405, and ~1380 Ma). The latter two stages were coeval with carbonatite magmatism, revealing previously unrecognized synchronicity in ultrapotassic and carbonatite magmatism at Mountain Pass. Despite this temporal overlap, major and trace element geochemical data are inconsistent with derivation of the carbonatite and ultrapotassic rocks by liquid immiscibility or fractional crystallization from common parental magma. Instead, we propose that the carbonatite was generated as a primary melt from the same source as the ultrapotassic rocks, and that although it is unique, the Mountain Pass ultrapotassic and carbonatite suite is broadly similar to other alkaline silicate–carbonatite occurrences in which the two rock types were generated as separate mantle melts.

Key words: carbonatite; geochronology; mineralization; rare earth elements; titanite

INTRODUCTION

The Sulphide Queen rare earth element (REE) mine at Mountain Pass, California is the richest known source of REE ore in the USA (Long *et al.*, 2010). Since its discovery in 1949 until the late 1980s Mountain Pass was the world's foremost producer of REE commodities (Verplanck & Van Gosen, 2011). However, despite its status as an archetype for carbonatite-hosted REE deposits, the petrogenesis of the REE-bearing Mountain Pass carbonatite remains debated.

Carbonatite bodies at Mountain Pass, along with ultrapotassic, mafic to felsic, plutonic silicate rocks (shonkinite, syenite, and granite), make up the Mesoproterozoic Mountain Pass Intrusive Suite (MPIS, Fig. 1). Based on field relationships and the similar enrichment of these rocks in incompatible elements such as Sr, Ba, and light REE (LREE), previous workers have inferred that the Sulphide Queen carbonatite magma was derived from the same source as the ultrapotassic rocks and that the intrusive assemblage may represent a single suite of variably evolved alkaline igneous rocks (Woyski, 1980; Castor, 2008). This is broadly compatible with studies from a variety of locations worldwide suggesting that carbonatite and alkali-rich silicate melts can differentiate from the same parental magma, potentially by liquid immiscibility (e.g. Lee & Wyllie, 1998; Woolley, 2003; Panina & Motorina, 2008), extreme fractional crystallization of a CO₂-rich silicate melt (e.g. Bell *et al.*, 1999), or a combination of these processes (e.g. Beccaluva *et al.*, 1992).

In contrast, existing geochronological data from the MPIS suggest that the carbonatite is ~15–25 Myr younger than the ultrapotassic rocks at Mountain Pass, which yielded ages of ~1375 Ma and ~1400 Ma, respectively (DeWitt *et al.*, 1987, 2000; Premo *et al.*, 2013). Interpretation of existing data is complicated by the fact that the ages are derived from different minerals and isotopic systems in each rock type (i.e. zircon and apatite U–Pb, monazite U–Th/Pb, amphibole and biotite Ar–Ar) and are exclusively reported in conference abstracts (DeWitt *et al.*, 1987, 2000; Premo *et al.*, 2013). Thus, these ages lack the information necessary to directly compare the dates, such as which decay constants and monitor standards were used, and what sources of uncertainty are included in the quoted data. Furthermore, DeWitt *et al.* (1987) noted U–Pb discordance and 'anomalously young' dates in some samples, suggesting that age interpretation may be complicated for some rock types at Mountain Pass.

Field relationships generally indicate that carbonatite is the youngest rock type in the MPIS in terms of cross-cutting relationships, but at least one study noted that a centimeter-scale vein of shonkinite appears to cut carbonatite in at least one location (Olson & Pray, 1954), inconsistent with the geochronological data. Given that fractional crystallization and liquid immiscibility processes are commonly thought to operate over time-scales $\ll$ 10 Myr (e.g. Williams *et al.*, 1986; Schmitt *et al.*, 2010), the proposed 15–25 Myr age gap is irreconcilable with the hypothesis that the carbonatite and the

ultrapotassic rocks are derived from the same parental magma or were generated during the same melting event. Thus, it has been asserted that, although these rocks are geochemically similar, the MPIS is not a simple cogenetic magma series (e.g. Haxel, 2005), and models testing the common parental magma hypothesis have not been presented.

This study utilizes titanite, zircon, and monazite U–Th/Pb geochronology, accessory-phase and whole-rock geochemistry, Nd and Hf isotope geochemistry and petrography within the context of field data to decisively resolve the temporal and petrogenetic relationships between carbonatite and ultrapotassic igneous rocks in the MPIS. A quantitative model is developed to test whether the ultrapotassic rocks and carbonatites at Mountain Pass are related by fractional crystallization or liquid immiscibility. In aggregate, these data place new constraints on existing ore genesis models for the Sulphide Queen carbonatite REE deposit, and indicate that the MPIS is the result of long-lived carbonatite–alkaline silicate magmatism in which multiple melting events of the same source produced separate carbonatite and ultrapotassic melts.

GEOLOGICAL CONTEXT

The Mountain Pass district is located in the central Mojave Desert of California, about 75 km SSW of Las Vegas, Nevada (Fig. 1). The district encompasses a topographic low between the Clark Mountain Range to the north and the Mescal Range to the south, and is primarily underlain by autochthonous, Proterozoic crystalline basement rocks that lie in the footwall of the west-dipping Keystone Thrust of the Sevier Orogen (Burchfiel & Davis, 1971; Fig. 1b). Neoproterozoic to lower Paleozoic limestone, quartzite, and shale, and Mesozoic siliciclastic and felsic volcanic rocks lie above the thrust in the Mountain Pass area (Evans, 1974). In the east, the ~7 km wide structural block of Proterozoic crystalline rocks is bound by the inferred normal-sense Ivanpah fault (Olson *et al.*, 1954). The structural block that exposes MPIS rocks is also cut by several transverse faults, none of which place the Proterozoic rocks against units of significantly different age or lithology (Olson *et al.*, 1954; Fig. 1b). Despite local faulting, decimeter- to meter-scale dike emplacement in the Cenozoic, and minor, localized hydrothermal alteration and localized deposition of Th along faults (Shawe, 1952), the Proterozoic rocks in the district are relatively well preserved and were less affected by Cenozoic extension and deformation compared with neighboring areas in the Mojave Desert (Haxel, 2005).

GEOLOGICAL UNITS AT MOUNTAIN PASS

Paleoproterozoic host rocks

The Proterozoic crystalline basement rocks that underlie most of the Mountain Pass area are part of the Mojave

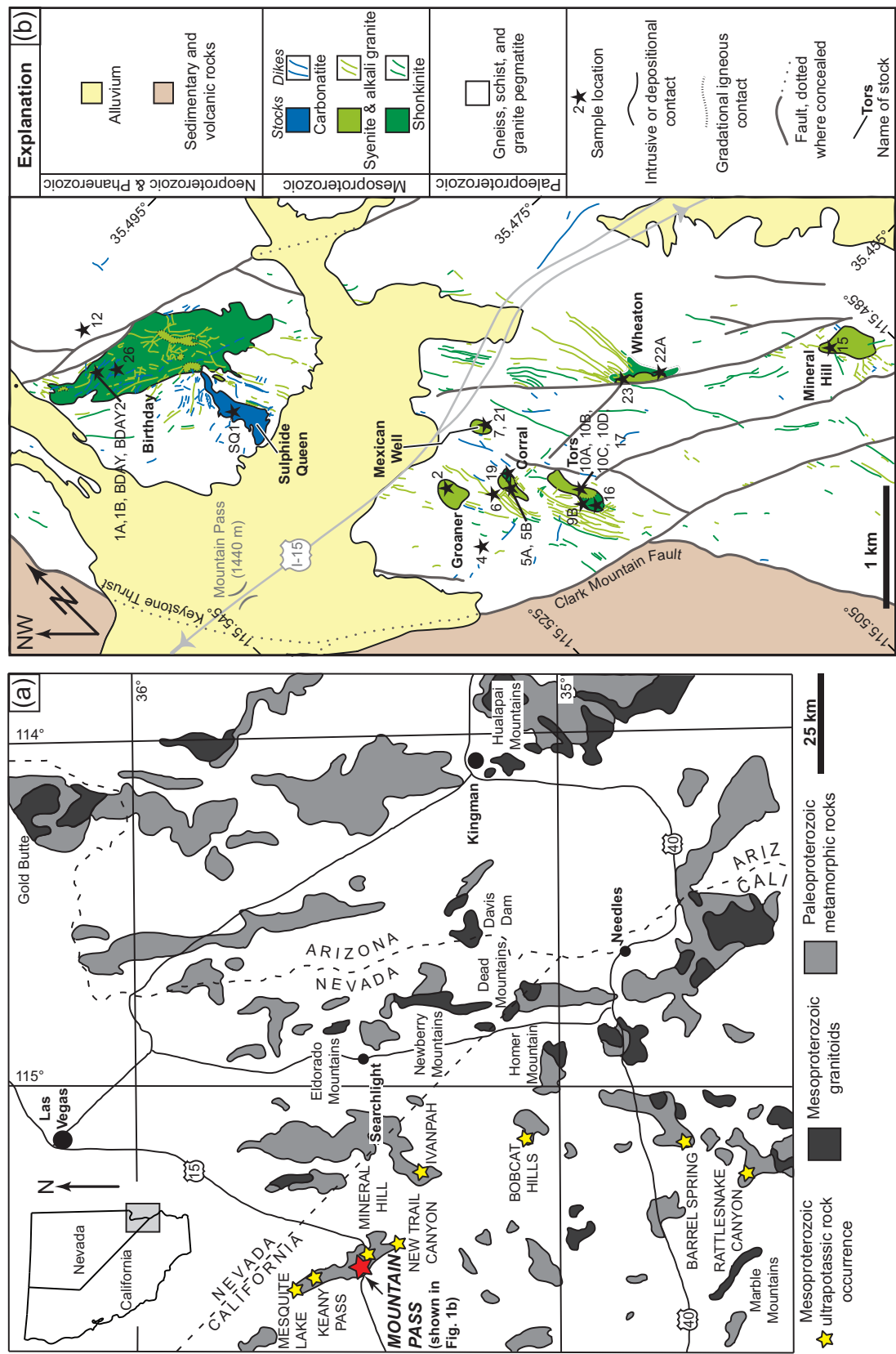


Fig. 1. (a) Map showing locations of Paleoproterozoic metamorphic rocks and Mesoproterozoic intrusive rocks in the southwestern USA. Modified from [Castor \(2008\)](#). (b) Generalized geological map of the Mountain Pass area. Alluvium contacts/exposures have been simplified for clarity. It should be noted that dike thickness is not to scale, and that north is not up. Modified from [Haxel \(2005\)](#), after [Olson & Pray \(1954\)](#), [Burchfiel & Davis \(1971\)](#) and [Evans \(1971\)](#).

Crustal Province (Wooden & Miller, 1990) and are primarily Paleoproterozoic gneiss and schist. The Paleoproterozoic rocks of the Mojave Crustal Province record a complex history of plutonism, metamorphism, and sedimentation associated with multiple orogenic events. U–Pb zircon ages from the province reported in several studies have been interpreted to indicate several discrete episodes of widespread pluton emplacement between ~1.79 and 1.64 Ga (Wooden & Miller, 1990; Barth *et al.*, 2000, 2009; Strickland *et al.*, 2013; McKinney *et al.*, 2015). Zircon and monazite U–Pb ages indicate that metamorphism also took place in several discrete episodes, occurring locally between ~1.79 and 1.65 Ga (Wooden & Miller, 1990; Barth *et al.*, 2000, 2009; Strickland *et al.*, 2013; McKinney *et al.*, 2015). The Paleoproterozoic rocks of the Mojave Crustal Province were widely intruded by 1.45–1.40 Ga granitoids throughout the southwestern USA (e.g. Anderson & Bender, 1989; McKinney *et al.*, 2015), including the Mountain Pass Intrusive Suite. The origin of the 1.45–1.4 Ga granitoids and the tectonic environment in which they were emplaced remains debated, with some workers inferring an anorogenic setting (e.g. Anderson & Bender, 1989; Hoffman, 1989), whereas others have concluded that they were emplaced during an orogenic event at ~1.49–1.35 Ga (Picuris orogeny of Daniel *et al.*, 2013; and see also Nyman *et al.*, 1994; Daniel & Pyle, 2006; Whitmeyer & Karlstrom, 2007).

In the Mountain Pass area, the Paleoproterozoic rocks are quartzofeldspathic gneiss and schist, coarse-grained to pegmatitic alkali granite dikes, and minor mafic to ultramafic rocks (this work; Olson *et al.*, 1954; Haxel, 2005; Castor, 2008; Fig. 1). K-feldspar augen gneiss and migmatitic K-feldspar + plagioclase + quartz + biotite ± garnet ± sillimanite gneiss are most common. Foliation in the gneiss and schist generally strikes north to NW and dips 45–85° to the west (this work; Olson & Pray, 1954; Olson *et al.*, 1954). Mineral ages from Paleoproterozoic rocks in the Mountain Pass area have not been reported, but are generally assumed to be similar to the rest of the Mojave Crustal Province based on their similar field relationships, lithology and close proximity to well-studied occurrences (e.g. Ivanpah Mountains, Strickland *et al.*, 2013; Fig. 1a).

Mountain Pass Intrusive Suite

Paleoproterozoic rocks in the Mountain Pass area are intruded by hundreds of sub-meter- to meter-scale dikes and eight map-scale stocks that compose the Mountain Pass Intrusive Suite (Fig. 1b). Six of the stocks consist of shonkinite and/or syenite, one contains significant granite in addition to syenite (Mineral Hill), and the Sulphide Queen stock is carbonatite (Fig. 1b). Geochemical, mineralogical, and textural gradations between shonkinite–syenite and syenite–granite are common in single bodies. The stocks form ovoid to roughly tabular, sill-like bodies tens to hundreds of meters wide and hundreds of meters long, and occur

within a ~7 km × 2 km zone in the host gneiss. Most dikes and stocks in the MPIS are oriented roughly parallel to the regional foliation of the basement rocks (roughly north to NW), but some dikes also strike roughly NE. Dikes and stocks of both orientations cross-cut foliation on an outcrop scale and are undeformed; there does not appear to be an obvious structural reason for the two different trends. In general, cross-cutting relationships indicate that the sequence of intrusion in the MPIS was (1) shonkinite and melanosyenite, (2) syenite, (3) quartz syenite, (4) granite, (5) shonkinite dikes, and (6) carbonatite (e.g. this work, Fig. 2a–d; Olson *et al.*, 1954; Haxel, 2005; Castor, 2008). However, as stated above, a centimeter-scale shonkinite vein appears to cut carbonatite in at least one location (Olson & Pray, 1954; Haxel, 2007). Magma mingling and mixing textures are common in some areas (e.g. Tors stock, Figs 1b and 2e; Haxel, 2005), and some shonkinite dikes within syenite are discontinuous, deformed, and back-intruded by fine-grained syenite (Fig. 2f), indicating that emplacement of some of the shonkinite and syenite was synchronous (this work; Haxel, 2005). The Sulphide Queen carbonatite stock, which is the principal ore body at Mountain Pass (Fig. 1b), contains blocks of gneiss, shonkinite, syenite, and older carbonatite, the last indicating that carbonatite was not emplaced during a single event (Olson *et al.*, 1954).

The MPIS lies roughly at the northwesternmost end of a zone containing Mesoproterozoic alkaline granitoid plutons that vary in areal exposure from ~4 to 150 km², extending from southeastern California into southern Nevada and western Arizona (Haxel, 2007; Castor, 2008; Fig. 1a; also see above). Ultrapotassic rocks are known only from the western edge of this zone and form an ~130 km belt from Rattlesnake Canyon in the south to Mesquite Lake in the north (Castor, 2008; Fig. 1a), indicating that their occurrence at Mountain Pass is potentially not unique (e.g. Gleason *et al.*, 1994). However, the ultrapotassic rocks that compose the belt are not well studied outside the Mountain Pass area, with the exception of the Barrel Spring Pluton in the Piute Mountains (Gleason *et al.*, 1994; Fig. 1a). Generally, neither the relationships among ultrapotassic rock occurrences in the region nor the broader connections to Mesoproterozoic alkaline magmatism in the southwestern USA are well studied (Haxel, 2007; Castor, 2008).

Shonkinite

The most abundant intrusive rock in the study area is coarse-grained shonkinite—a distinctive, dark gray to greenish rock composed of microcline, clinopyroxene (diopside, augite, and/or aegirine–augite), and euhedral, Mg-rich biotite, with or without amphibole (riebeckite, arfvedsonite, and/or hornblende) and minor sodic plagioclase, perthite, and apatite (up to ~3%). Accessory phases include quartz, zircon, titanite, magnetite, pyrite, Fe-oxides, calcite, and fluorite. Some samples contain

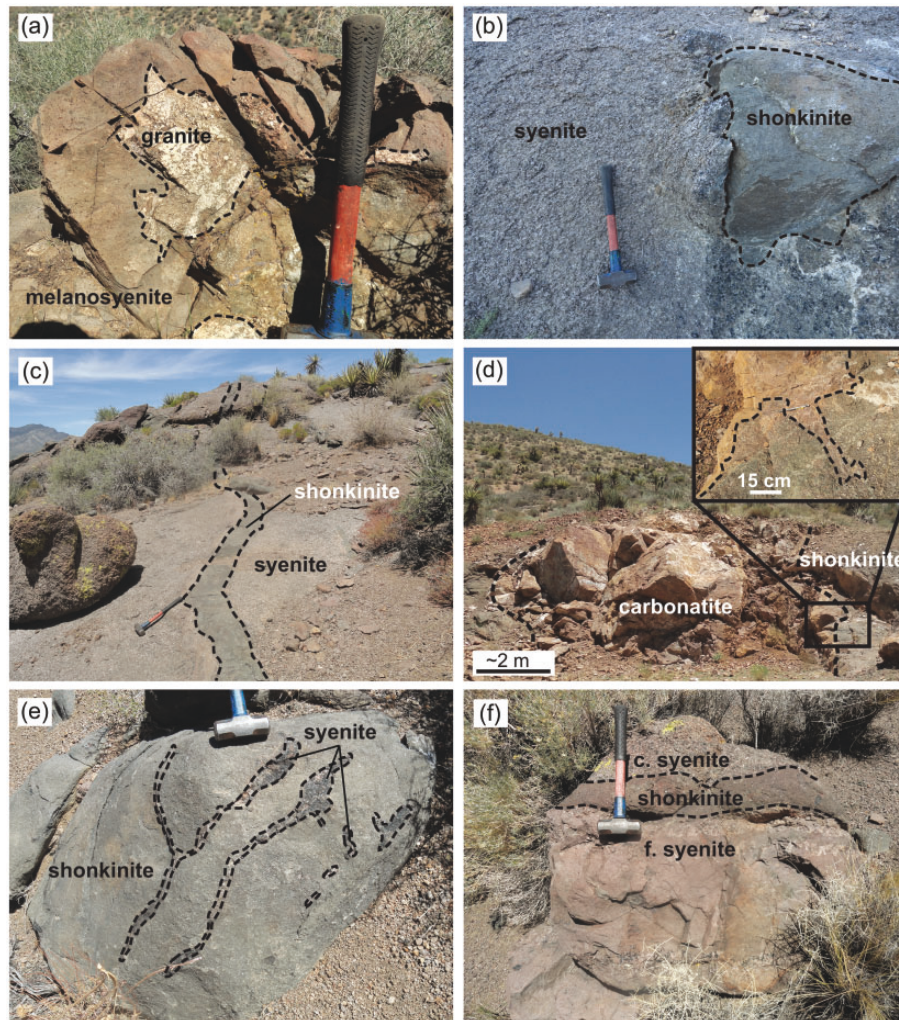


Fig. 2. Examples of cross-cutting relationships within the MPIS. Contacts are indicated by dashed lines for clarity. (a) Granite xenoliths in melanosyenite dike (MP-P0913-6) just west of Corral stock. (b) Porphyritic shonkinite enclave (MP-P0914-10A) in coarse syenite (MP-P0913-10B) in Tors stock. (c) Porphyritic shonkinite dike (e.g. MP-P0913-10C) in coarse syenite (MP-P0913-10B) in Tors stock. (d) Bastnäsite–barite carbonatite dike (MP-L0613-BDAY2; Birthday Vein) that cuts coarse shonkinite (MP-L0613-BDAY, MP-P0913-1A) in Birthday stock. (e) Diffuse syenite inclusions in shonkinite at Tors stock. (f) Shonkinite dike that cuts coarse syenite and is back-intruded by fine-grained syenite (MP-P0714-17) in Tors stock (*ex situ*). c, coarse; f, fine.

micrometer-scale veins composed primarily of barite, quartz, and Fe-oxide with minor monazite. Based on mineralogy, the rock is a melanosyenite; however, the name shonkinite is used here to maintain continuity with previous work and to describe the most mafic rocks consisting of K-feldspar + biotite + clinopyroxene $\pm$ amphibole. Melanosyenite is used for rocks that are transitional from shonkinite–syenite and contain ~ 40 – 55% mafic minerals. The shonkinite has $\text{MgO} > 3\text{ wt } \%$, $\text{K}_2\text{O} > 3\text{ wt } \%$, and $\text{K}_2\text{O}/\text{Na}_2\text{O} > 2$, and is therefore considered ultrapotassic based on the criteria of [Foley *et al.* \(1987\)](#). Some shonkinite is peralkaline [highest $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{Al}_2\text{O}_3 \sim 1.1$], but most samples are metaluminous. Sample petrographic descriptions and photographs of representative hand samples are provided in [Supplementary Data Electronic Appendices 1 and 2](#), respectively ([supplementary data are available for downloading at http://www.petrology.oxfordjournals.org](http://www.petrology.oxfordjournals.org)).

Syenite, quartz syenite, and granite

Syenite is the second most common intrusive rock type at Mountain Pass, occurring as a pinkish to purple to brick-red rock that consists mostly of K-feldspar with variable amounts of biotite, sodic amphibole (riebeckite and/or arfvedsonite) and quartz, with minor sodic plagioclase, clinopyroxene, and Fe-oxides. Accessory minerals include apatite, zircon, titanite, pyrite, fluorite, calcite, thorite, and galena. Rutile, epidote, monazite, and trace barite are present in some samples, but textural relationships suggest that these phases are secondary. Monazite and barite primarily occur in veins, as fine, disseminated grains (this work; [Stoeser, 2013](#)), or as fine aggregates, and are most abundant in samples with pervasive rust-colored stains along grain boundaries and fractures (see [Supplementary Data Electronic Appendix 1](#)). Based on these textures, we consider samples with abundant veins and/or fine, disseminated monazite and barite

grains to be altered (see also [Stoeser, 2013](#)). Leucosyenite, quartz syenite, and granite occur as dikes and pods in shonkinite or syenite, although the Mineral Hill stock ([Fig. 1b](#)) contains significant granite. The mineralogy of these rock types differs from that of syenite only in the relative proportions of K-feldspar and quartz. Some syenite and all leucosyenite at Mountain Pass is potassic rather than ultrapotassic (see criteria above); however, we use the term ultrapotassic here to refer to all K-rich igneous rocks for brevity.

Carbonatite

Carbonatite at Mountain Pass varies in appearance, but is generally porphyritic with centimeter-size barite phenocrysts in a matrix of calcite, dolomite, quartz, Fe-oxide, and bastnäsite ($[\text{LREE}]\text{CO}_3\text{F}$). Synchysite ($\text{Ca}[\text{LREE}](\text{CO}_3)_2\text{F}$), parisite ($\text{Ca}[\text{LREE}]_2(\text{CO}_3)_3\text{F}_2$), ankerite, siderite, monazite, thorite, zircon, strontianite, celestite, apatite, an unidentified Th-carbonate, and at least two unidentified REE-bearing phases are common as minor, accessory, or trace phases. The most abundant types of carbonatite are bastnäsite–barite beforosite (dolomite-dominated) and bastnäsite–barite dolomitic sövite (calcite-dominated with significant dolomite), but sövite (calcite-dominant) and silicio-carbonatite are also common ([Castor, 2008](#)).

SUMMARY OF PREVIOUS GEOCHEMICAL, GEOCHRONOLOGICAL, AND ISOTOPIC WORK AT MOUNTAIN PASS

Previous workers generally agreed that the MPIS carbonatite and ultrapotassic rocks are genetically related based on field relationships and similar geochemical characteristics (e.g. [Olson et al., 1954](#); [Woyski, 1980](#); [Haxel, 2005, 2007](#); [Castor, 2008](#)). [Haxel \(2005, 2007\)](#) proposed that a small degree (~ 0.01 – 0.1%) of partial melting of highly enriched lithospheric mantle source produced the shonkinite magma. In this model, shonkinite is the parental magma that evolved to the more silicic rock types in the complex (syenite, quartz syenite, granite). [Crow \(1984\)](#) showed that the syenite could be produced by $\sim 20\%$ crystal fractionation of the shonkinite. The relatively high abundance of compatible elements (e.g. Cr, Ni) but distinctively lower contents of Al, Ca, and Na in the shonkinite in comparison with other primitive mafic rocks was interpreted to indicate derivation from harzburgitic peridotite that had previously been depleted in Al, Ca, and Na through extraction of basaltic magma ([Haxel, 2007](#)). These geochemical characteristics coupled with extreme enrichment in incompatible elements (i.e. K, Ba, LREE) in the MPIS rocks require that the depleted source was metasomatically re-enriched ([Haxel, 2007](#)). The model of [Haxel \(2005\)](#) did not consider derivation of the carbonatite from a shonkinite parental magma, partially owing to the implications of the geochronological data reported by [DeWitt et al. \(1987, 2000\)](#). Conversely, [Castor \(2008\)](#) viewed the

spatial association and similar geochemistry of the ultrapotassic rocks and carbonatites as evidence for a common parental magma.

Available geochronological data do not support the notion that the ultrapotassic rocks and carbonatites may have differentiated from a common parental magma. Early attempts to determine ages of the MPIS yielded data that were too imprecise to critically evaluate the absolute timing of the various intrusive phases (i.e. [Jaffe, 1955](#); [Lanphere, 1964](#)). More recent studies by [DeWitt et al. \(1987, 2000\)](#) reported $^{40}\text{Ar}/^{39}\text{Ar}$ dates of 1400 ± 8 Ma and 1403 ± 7 Ma from phlogopite in shonkinite and arfvedsonite in syenite, respectively; apatite from shonkinite yielded a U–Pb date of 1410 ± 2 Ma; monazite from carbonatite yielded a Th–Pb date of 1375 ± 7 Ma. Zircons from the syenite were reportedly highly discordant with respect to U–Pb. Bastnäsite and parisite from carbonatite contained abundant common Pb—both yielding dates of ~ 1330 Ma and younger, which [DeWitt et al.](#) considered ‘anomalously young’ based on the monazite Th–Pb date of 1375 ± 7 Ma for the same rock type. [DeWitt et al. \(1987, 2000\)](#) interpreted these dates as indicating emplacement of carbonatite ~ 25 Myr after crystallization of the ultrapotassic intrusive rocks.

[Premo et al. \(2013\)](#) reported zircon U–Pb secondary ionization mass spectrometry dates from shonkinite, syenite, and granite that overlap within uncertainty between 1410 and 1422 Ma, supporting the interpretations of [DeWitt et al. \(1987, 2000\)](#), but did not specify whether there was a statistically distinguishable age difference between rock types.

[DeWitt et al. \(1987, 2000\)](#) and [Premo et al. \(2013\)](#) also reported Pb, Sr, and Nd isotopic data for the MPIS. Common Pb isotopic ratios from galena in carbonatite and K-feldspar in the ultrapotassic rocks are as follows: $^{204}\text{Pb}/^{206}\text{Pb} = 1:16.08$, $^{204}\text{Pb}/^{207}\text{Pb} = 1:15.32$, $^{204}\text{Pb}/^{208}\text{Pb} = 1:35.61$ ([DeWitt et al., 1987](#)). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from 0.7046 to 0.7072 ([DeWitt et al., 2000](#)). [Premo et al. \(2013\)](#) reported a slightly smaller range of whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7045–0.7068) and whole-rock ϵ_{Nd} values ranging from -1.5 to -6 for the ultrapotassic rocks and carbonatite. [DeWitt et al. \(2000\)](#) interpreted their Pb, Sr, and Nd isotope data to indicate derivation of the carbonatite magma from a hybrid source, produced by mixing of 1.4 Ga mantle and 1.75 Ga mantle or enriched lower crust. [DeWitt et al. \(2000\)](#) also noted that only the youngest shonkinite dikes at Mountain Pass have the same Nd isotopic signature as the carbonatite.

Based on their U–Th/Pb data, [DeWitt et al. \(1987, 2000\)](#) and [Premo et al. \(2013\)](#) concluded that, although the various intrusive phases in the MPIS appear to be closely related based on petrological and geochemical evidence, the different rock types of the MPIS were not contemporaneous.

ANALYTICAL METHODS

Here, we report new U–Th/Pb, trace element, isotopic, and/or textural data for a suite of U- and/or Th-bearing

accessory minerals from 22 Mountain Pass shonkinite, syenite, and carbonatite samples and three host-rock samples. Additionally, whole-rock geochemical data are reported for 14 ultrapotassic rock samples and one carbonatite sample. Three to four kilograms of each sample was collected from suitable outcrops (e.g. Fig. 2), and representative samples were selected for mineral analysis based on cross-cutting relationships, lithology, and spatial context (see Table 1 for summary of samples and sample locations). Zircon, titanite, monazite, apatite, bastnäsite and rutile were analyzed, but the measured concentrations of U in the last three minerals were too low to provide reliable U–Pb dates; therefore only zircon, titanite, and monazite data are utilized for geochronology in this study. Bastnäsite and apatite are employed only for Nd isotopic data and trace element data, respectively. Accessory mineral U–Th/Pb isotopes and trace elements were measured by laser ablation split-stream inductively coupled plasma mass spectrometry (LASS-ICP-MS), accessory mineral Nd and Hf isotopes were measured by laser ablation multi-collector (LA-MC)-ICP-MS, and whole-rock geochemistry was measured by X-ray fluorescence spectrometry (XRF) and laser ablation quadrupole (LA-Q)-ICP-MS. Detailed analytical methods are presented in the Appendix, and representative SEM images of sample grains with labeled spot analyses are provided in Supplementary Data Electronic Appendix 3 (supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>).

RESULTS

Whole-rock geochemistry

Geochemical data for ultrapotassic rock samples are shown on variation diagrams in Fig. 3, and presented in full in Table 2. TiO_2 , Fe_2O_3 , MnO , MgO , CaO , and P_2O_5 , compatible trace elements (e.g. Cr, V), and incompatible trace elements (e.g. Sr, Ba, LREE) decrease in abundance with increasing silica content; Al_2O_3 and Na_2O contents increase with increasing silica content; K_2O , high-field-strength elements (HFSE; e.g. Zr, Nb, and Ta), heavy rare earth elements (HREE), and actinides (Th, U) do not show demonstrable trends. The ultrapotassic rocks are enriched in LREE by ~ 500 – 1000 times chondritic values, and in HREE by ~ 10 – 50 times chondritic values (Fig. 4). They display chondrite-normalized REE patterns with steep negative slopes (La/Yb ranging from 18 to 174), and without a significant Eu anomaly. Carbonatite from the MPIS is highly enriched in LREE, containing $\sim 500\,000 \times$ chondritic values, with a La/Yb ratio of $\sim 15\,000$ (Fig. 4). MPIS carbonatite whole-rock data are provided in Supplementary Data Electronic Appendix 4.

Titanite textures, U–Pb, trace elements, and Nd isotopes

Titanite is present in most fresh ultrapotassic rock samples collected at Mountain Pass as translucent, euhedral

to subhedral, dark brown to golden crystals up to ~ 2 mm (Fig. 5a and b). Interstitial grains are common in coarse-grained samples, and euhedral matrix grains are typical in fine-grained samples (Fig. 5a and b). Titanite is absent in most samples that contain significant monazite and rutile (e.g. MP-P0913-2), with one exception (MP-P0913-10B). Titanite grains in some samples contain inclusions of clinopyroxene or apatite (Fig. 5a and b) and small ($\leq 2\,\mu\text{m}$) inclusions of monazite (Fig. 5c); monazite inclusions are most common in samples that appear to have undergone alteration (see above description of alteration textures in syenite). Grains with small monazite inclusions were typically avoided for analysis. Titanite in most samples appears unzoned in BSE images, but some grains appear to be weakly zoned (Fig. 5d). Where identified, specific zones were targeted for U–Pb, trace element and Nd isotopic analysis, but no consistent age, trace element, or isotopic pattern with respect to zonation was observed. Similarly, core and rim regions of grains are indistinguishable in terms of their age, trace element, and Nd isotopic composition.

Representative titanite geochronology data are presented in Table 3, and complete titanite LASS-ICP-MS data (including trace element data) are reported in Supplementary Data Electronic Appendix 5. LASS-ICP-MS U–Pb data from 10 titanite samples yielded single population [i.e. mean square weighted deviation (MSWD) ~ 1] isochrons ranging from 1429 ± 10 to 1385 ± 18 Ma (Fig. 6). MP-P0714-17 has relatively little spread in U/Pb and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, leading to a relatively imprecise isochron age of 1358 ± 71 Ma. Two samples have MSWD = 1.7, larger than expected for a single age population, and yield apparent ‘errorochrons’ of 1410 ± 17 and 1367 ± 9 Ma (MP-P0714-16 and MP-P0714-26). Subdividing the analyses into two single populations based on their relative ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ date yields dates that broadly overlap within uncertainty for MP-P0714-16, and yields dates of 1410 ± 17 ($n=8$, MSWD = 0.3) and 1363 ± 7 Ma ($n=27$, MSWD = 1.0) for MP-P0714-26 (Fig. 6). In general, the position of each analysis in Tera–Wasserburg space correlates with U content (Fig. 6), suggesting that the degree of discordance in single analyses is due to the radiogenic Pb/common Pb ratio, as opposed to inheritance.

Chondrite-normalized REE profiles for titanite are characterized by LREE enrichment, with a negative LREE to HREE slope and no notable Eu anomaly (Fig. 7a). Zr-in-titanite apparent temperatures form single populations in only three samples (MP-P0913-10C weighted mean = $859 \pm 9^\circ\text{C}$; MP-P0714-17 weighted mean = $875 \pm 8^\circ\text{C}$; MP-P0714-23 weighted mean = $806 \pm 16^\circ\text{C}$) (Ti and Si activities assumed to be 0.8 and unity, respectively; see the Appendix for analytical details). Apparent temperatures in other samples range from ~ 950 – 850 to 700 – 650°C (Fig. 7b). There is no consistent correlation observed between apparent Zr-in-titanite temperature and either the trace element

Table 1: Summary of sample lithology, location, geochronology data, Nd and Hf isotope data

Sample	Rock type	Location	Coordinates	Field context	Titanite age (Ma)	Zircon age (Ma)	Monazite Th–Pb age (Ma)	Accessory mineral $\varepsilon_{\text{Nd}_i}$ (mean)	Zircon $\varepsilon_{\text{Hf}_i}$ (mean)
MP-L0613-BDAY	biotite	Birthday mine	35.48916 N, 115.53627 W	massive body	—	1425 ± 5*	—	—	1.6 ± 0.5
MP-L0613-BDAY2	shonkinite–bastnäsite–barite	Birthday mine	35.48916 N, 115.53627 W	dike in shonkinite	—	—	1396 ± 16†	—	—
MP-P0913-SQ1	carbonatite	Sulphide Queen (parking lot near mine entrance)	35.46971 N, 115.52961 W	massive body (?)	—	—	1371 ± 10	–2.9 ± 0.13 (monazite & bastnäsite)	—
MP-P0913-1A	carbonatite	Birthday mine	35.48911 N, 115.53628 W	massive body	—	—	—	—	—
MP-P0913-1B	shonkinite	Birthday mine	35.48916 N, 115.53627 W	dike in shonkinite	—	discordant	—	—	—
MP-P0913-2	carbonatite	Groaner stock	35.46479 N, 115.52261 W	massive body	—	discordant	1376 ± 36†	—	—
MP-P0913-4	amphibole syenite	~170 m SW of Groaner stock	35.46244 N, 115.52376 W	host rock	—	~1800–1660	1693 ± 8 (mean $^{207}\text{Pb}/^{206}\text{Pb}$ age)	—	—
MP-P0913-5A	garnet–biotite–sillimanite gneiss	Corral stock	35.46213 N, 115.52045 W	massive body	1406 ± 24	1416 ± 9*	—	–9.6 ± 1† (titanite)	1.9 ± 0.7
MP-P0913-5B	leucosyenite	Corral stock	35.46213 N, 115.52045 W	m-scale host rock xenolith	—	~1820–1640	—	—	—
MP-P0913-6	granite	dike ~50 m W of Corral stock	35.46218 N, 115.52153 W	dike in host rock	1429 ± 10	1423 ± 7†	—	–5.8 ± 0.9† (titanite)	2 ± 0.5
MP-P0913-7	melanosyenite	Mexican Well stock	35.46608 N, 115.51612 W	massive body	—	discordant	1401 ± 32†	—	—
MP-P0913-9B	syenite	dike at W edge of Tors stock	35.45592 N, 115.51462 W	dike in host rock	—	discordant	—	—	—
MP-P0913-10A	leucosyenite	Tors stock	35.45634 N, 115.51416 W	enclave in syenite	1402 ± 13	discordant	—	—	—
MP-P0913-10B	biotite	Tors stock	35.45634 N, 115.51416 W	massive body	1398 ± 14	1411 ± 8†	—	–4.7 ± 0.4 (titanite)	1.2 ± 2.3†
MP-P0913-10C	shonkinite	Tors stock	35.45636 N, 115.51418 W	dike in syenite	1385 ± 18	1458 ± 7†	—	–4 ± 0.4 (titanite)	3 ± 0.9
MP-P0913-10D	biotite–amphibole syenite	Tors stock	35.45636 N, 115.51418 W	enclave in shonkinite dike	1401 ± 12	—	—	–4.1 ± 0.5 (titanite)	—

(continued)

Table 1: Continued

Sample	Rock type	Location	Coordinates	Field context	Titanite age (Ma)	Zircon age (Ma)	Monazite Th–Pb age (Ma)	Accessory mineral ε_{Nd} (mean)	Zircon ε_{Hf} (mean)
MP-P0913-12	feldspar augen gneiss	host rock ~360 m NNW of Birthday mine	35.49240 N, 115.53518 W	host rock	—	~1820–1765	—	—	—
MP-P0714-15	quartz syenite	Mineral Hill stock	35.45159 N, 115.48979 W	massive body	—	discordant	—	—	—
MP-P0714-16	biotite shonkinite	Tors stock	35.45551 N, 115.51433 W	massive body	1413 ± 16	—	—	–7.3 ± 1.3† (titanite)	—
MP-P0714-17	leucosyenite	Tors stock	35.45664 N, 115.51430 W	dike intruding shonkinite dike in syenite	1358 ± 71	—	—	–5.5 ± 0.6† (titanite)	—
MP-P0714-19	biotite shonkinite	Corral stock	35.46223 N, 115.51896 W	massive body	1414 ± 19	discordant	—	–4.2 ± 0.5† (titanite)	—
MP-P0714-21	biotite–amphibole melanosyenite	Mexican Well stock	35.46631 N, 115.51594 W	enclave in syenite	—	1407 ± 11*	—	—	0.8 ± 0.9
MP-P0714-22A	biotite–amphibole shonkinite	Wheaton stock	35.46063 N, 115.50265 W	massive body	1404 ± 12	—	—	–4.6 ± 0.7† (titanite)	—
MP-P0714-23	leucosyenite	Wheaton stock	35.46153 N, 115.50457 W	massive body	1406 ± 26	discordant	—	—	—
MP-P0714-26	biotite shonkinite	Birthday stock	35.48844 N, 115.53650 W	massive body	1410 ± 17	1434 ± 10‡	—	–5.6 ± 1.7† (titanite)	2.2 ± 1

*U–Pb concordia age.

†MSWD $\gg 1$.‡Mean $^{207}\text{Pb}/^{206}\text{Pb}$ age.Stock names in the 'location' column are shown in Fig. 1b. Mean ε_{Nd} and ε_{Hf} values are weighted means of all analyses in a sample. Titanite ages are U–Pb isochron lower-intercept dates.

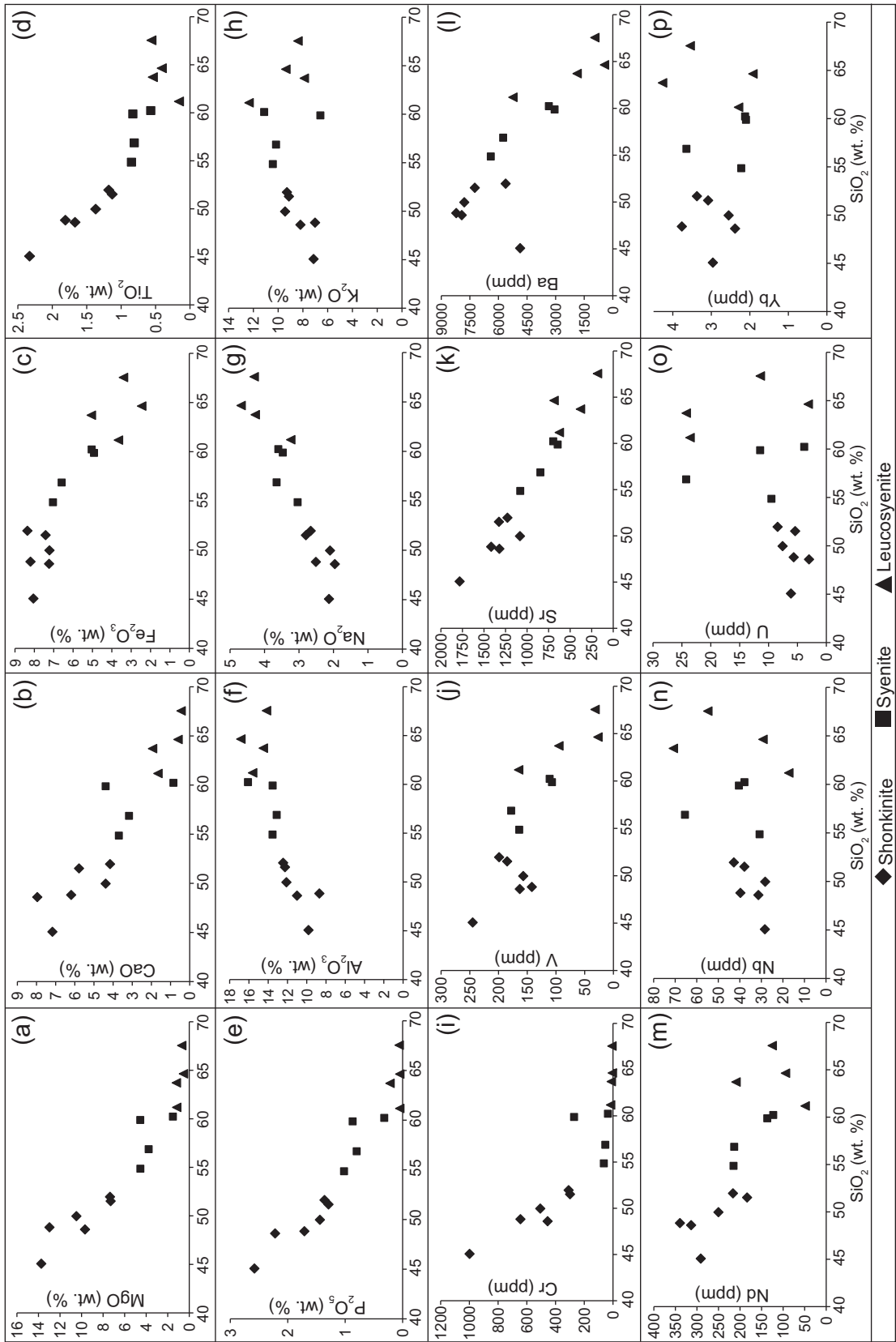


Fig. 3. Whole-rock major and trace element variations versus silica for MPIS ultrapotassic rocks. (a–h) Major elements; (i–p) trace elements.

Table 2: Whole-rock geochemical data

Sample:	MP- PO913-2	MP- PO913-5A	MP- PO913-6	MP- PO913-9B	MP- PO913-10A	MP- PO913-10B
<i>wt %</i>						
SiO ₂	60.01	63.69	59.99	64.54	51.87	56.76
TiO ₂	0.57	0.54	0.83	0.41	1.18	0.81
Al ₂ O ₃	16.04	14.50	13.56	16.81	12.43	13.10
Fe ₂ O ₃	5.02	5.06	4.93	2.46	8.35	6.58
MnO	0.07	0.02	0.07	0.01	0.11	0.06
MgO	1.51	1.20	4.56	0.54	7.35	3.76
CaO	0.85	1.94	4.40	0.61	4.15	3.16
Na ₂ O	3.59	4.27	3.48	4.67	2.66	3.64
K ₂ O	11.09	7.89	6.60	9.37	9.27	10.15
P ₂ O ₅	0.32	0.22	0.87	0.05	1.36	0.80
Total	99.07	99.32	99.29	99.47	98.73	98.83
<i>ppm</i>						
Rb	444	347	228	446	658	568
Sc	3	4	12	0	22	13
V	111	95	107	27	199	178
Ni	10	4	72	0	106	64
Ga	17	22	17	19	17	17
Cu	53	38	64	38	75	100
Zn	119	78	111	45	183	106
Cr	35.2	11.9	271.0	4.7	309.0	53.4
Sr	697	381	645	687	1228	846
Y	32.5	67.7	34.0	25.9	57.2	56.8
Zr	508	1176	496	530	845	946
Nb	37.9	70.9	40.4	29.3	42.8	65.5
Cs	3.2	2.7	3.0	2.4	15.8	7.0
Ba	3356	1874	3054	437	5622	5753
La	148.5	259.6	160.4	88.8	224.6	190.3
Ce	289.4	492.3	307.5	195.2	481.5	430.9
Pr	32.6	56.8	36.0	24.7	55.4	52.4
Nd	123.0	209.4	136.8	94.6	216.4	213.6
Sm	21.2	36.2	22.9	15.3	39.0	41.3
Eu	4.79	8.28	5.15	3.84	8.99	9.34
Gd	14.8	26.8	16.2	11.5	27.9	29.6
Tb	1.59	3.11	1.64	1.31	2.82	3.07
Dy	7.30	14.73	7.35	5.92	12.52	13.72
Ho	1.146	2.359	1.194	0.942	2.021	2.125
Er	2.82	5.65	2.82	2.38	4.59	4.95
Tm	0.341	0.707	0.338	0.301	0.541	0.589
Yb	2.12	4.27	2.10	1.92	3.37	3.65
Lu	0.279	0.569	0.296	0.226	0.464	0.514
Hf	11.2	26.5	12.8	11.9	19.8	24.2
Ta	27.6	22.3	22.9	11.3	12.5	16.1
Pb	154.0	60.8	87.1	36.1	91.1	57.0
Th	45.8	301.9	100.6	42.8	120.2	184.3
U	3.8	24.3	11.5	3.1	8.4	24.3

(continued)

composition or the ²⁰⁷Pb-corrected ²⁰⁶Pb/²³⁸U date of single LASS-ICP-MS spots. However, the two youngest samples in terms of cross-cutting relationships and titanite U–Pb dates (MP-P0913-10C and MP-P0714-17) have some of the highest (>800°C) and the most consistent apparent Zr-in-titanite temperatures.

In situ Nd isotopic measurements on titanite from three ultrapotassic samples from the Tors stock give single population weighted means of εNd_i: MP-P0913-10B = −4.7 ± 0.4 (MSWD = 1.3, *n* = 20); MP-P0913-10C = −4 ± 0.4 (MSWD = 0.5, *n* = 20); MP-P0913-10D = −4.1 ± 0.5 (MSWD = 1.5, *n* = 20), (Fig. 8). These three samples also yield the youngest U–Pb isochron dates in the MPIS, and contain some of the largest titanite crystals of the studied samples. In contrast, the other seven samples yield dispersed εNd_i values from approximately −2 to −13, with a range of up to ~9 epsilon units

within a single sample (−2 to −11 in MP-P0714-26; Fig. 8). For four of the seven samples, the majority of analyses (66 of 71 spots) fall between −3.5 and −7. The remaining three samples yield the most scattered, and negative, εNd_i values (as low as −13); one of these samples (MP-P0913-5A) also contains abundant xenoliths of host granite and gneiss as well as abundant inherited (~1700–1640 Ma) zircons. The other two samples (MP-P0714-16 and MP-P0714-26) also do not yield single-population U–Pb isochrons, indicating a possible relationship between the disturbance of the U–Pb and Nd isotopic systems. In general, more primitive and more consistent εNd_i is associated with larger crystals; however, there is no apparent relationship between εNd_i and position in crystals or location of samples in the field area. In the oldest (~1430–1420 Ma) and youngest (1380–1370 Ma) rocks, εNd_i is typically lower with

Table 2: Continued

Sample:	MP- PO913-10C	MP- PO913-10D	MP- P0714-16	MP- P0714-17	MP- P0714-19	MP- PO913-22A	MP- P0714-23	MP- P0714-26
<i>wt %</i>								
SiO ₂	51.44	54.66	49.90	60.96	48.56	48.92	67.47	45.30
TiO ₂	1.13	0.85	1.37	0.16	1.67	1.81	0.56	2.34
Al ₂ O ₃	12.24	13.50	12.09	15.56	11.00	8.71	14.16	9.87
Fe ₂ O ₃	7.41	7.01	7.21	3.65	7.23	8.22	3.40	8.09
MnO	0.10	0.07	0.07	0.04	0.07	0.17	0.00	0.06
MgO	7.29	4.52	10.47	1.17	9.67	13.01	0.70	13.81
CaO	5.77	3.69	4.38	1.65	7.95	6.20	0.45	7.21
Na ₂ O	2.80	3.03	2.10	3.23	1.96	2.51	4.29	2.14
K ₂ O	9.12	10.39	9.43	12.31	8.19	7.03	8.39	7.18
P ₂ O ₅	1.29	1.02	1.44	0.05	2.22	1.71	0.06	2.59
Total	98.57	98.74	98.46	98.78	98.52	98.29	99.48	98.60
<i>ppm</i>								
Rb	604	652	652	679	277	364	329	435
Sc	20	15	16	5	22	20	0	21
V	185	164	157	165	163	142	32	245
Ni	99	105	478	0	207	396	0	475
Ga	16	20	17	20	16	16	22	17
Cu	161	147	95	47	136	30	29	77
Zn	141	132	133	46	130	194	37	112
Cr	299.3	63.8	506.4	16.8	455.4	644.4	7.3	998.7
Sr	1326	1079	1082	626	1322	1417	183	1783
Y	50.9	44.4	50.7	22.8	47.7	63.1	39.1	58.4
Zr	644	420	516	1235	420	423	1124	492
Nb	37.9	30.8	28.2	17.3	31.4	39.7	54.9	28.4
Cs	13.6	10.7	11.9	6.0	7.6	6.9	2.6	7.8
Ba	7241	6402	7793	5243	7926	8214	943	4863
La	191.2	217.2	248.5	42.8	354.8	655.3	197.1	307.0
Ce	407.4	464.1	555.5	90.9	722.4	1056.5	356.0	661.4
Pr	46.8	54.4	63.4	11.9	82.6	100.0	37.2	74.5
Nd	183.6	215.1	250.1	48.9	313.5	339.5	125.4	291.2
Sm	32.7	38.5	42.6	10.0	47.9	49.3	19.4	48.3
Eu	7.67	8.32	9.56	2.87	11.43	10.10	4.17	10.89
Gd	23.6	26.2	30.4	8.1	31.1	33.6	13.4	33.9
Tb	2.42	2.49	2.90	0.92	2.80	3.14	1.54	3.05
Dy	11.12	10.58	11.81	4.36	11.47	13.51	7.48	13.27
Ho	1.754	1.560	1.727	0.756	1.720	2.048	1.296	1.963
Er	4.14	3.40	3.85	1.96	3.75	4.95	3.56	4.38
Tm	0.488	0.384	0.435	0.322	0.408	0.600	0.553	0.529
Yb	3.08	2.22	2.55	2.29	2.38	3.77	3.55	2.96
Lu	0.417	0.310	0.328	0.384	0.295	0.521	0.519	0.380
Hf	15.6	11.9	13.4	43.1	10.0	10.9	26.2	11.7
Ta	13.8	13.3	10.1	14.9	12.6	14.5	15.4	11.3
Pb	255.7	83.4	45.6	687.0	75.8	23.4	28.3	45.5
Th	74.0	64.3	100.3	407.6	39.6	81.3	104.9	58.8
U	5.4	9.5	7.6	23.6	3.0	5.7	11.4	6.1

Reported values for major element oxides and Rb to Zn were measured by XRF; reported values for Cr to U were measured by LA-Q-ICP-MS.

increasing whole-rock silica content (Fig. 8). In general, samples with older dates have lower ϵ_{Nd_i} values (Fig. 8). Representative examples of titanite Nd isotopic data are shown in Table 4, and the complete set of titanite Nd isotopic data is presented in Supplementary Data Electronic Appendix 6.

Zircon textures, U–Pb, trace elements, and Hf isotopes

Zircon in Mountain Pass rocks is diverse in morphology. Metamict, pseudo-octahedral, opaque grains are abundant in most samples, and do not luminesce in CL, but some grains show irregular, blotchy CL-bright domains (Fig. 9a and b). Translucent, pink to reddish-brown,

rounded or anhedral to euhedral grains that range from 30 μm to 3 mm in size are also present (Fig. 9c), but are less common. Some show typical oscillatory or sector zoning in CL (e.g. Fig. 9d), and others show irregular zoning (e.g. Fig. 9e). Zoning patterns do not appear to correlate with either whole-rock composition or age.

Representative zircon geochronology data are presented in Table 5, and the complete set of zircon LASS-ICP-MS data (including trace element data) is given in Supplementary Data Electronic Appendix 7. Zircon from 14 samples of Mountain Pass shonkinite and syenite are characterized by moderate to high U (~300–10 000 ppm), radiogenic Pb loss, high common Pb content, high or variable LREE, highly variable Ti contents (~10–450 ppm), and correspondingly variable apparent

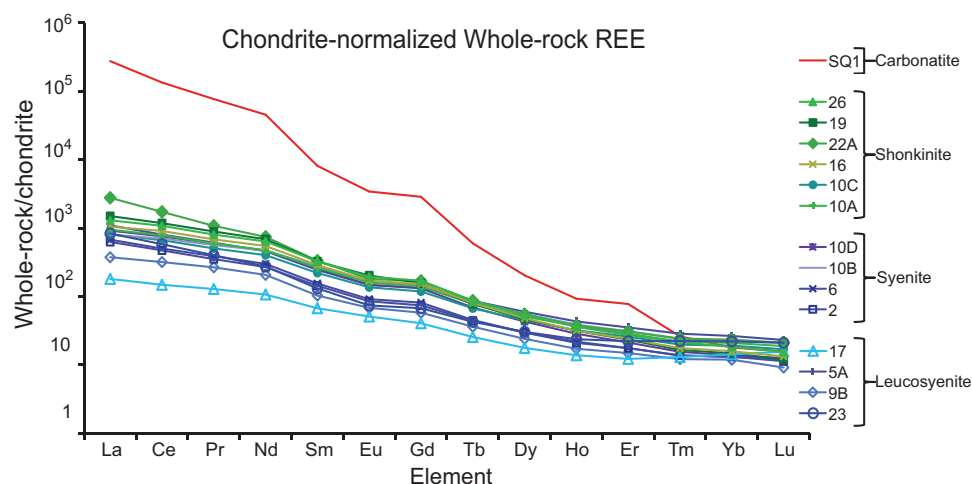


Fig. 4. Chondrite-normalized REE patterns for all whole-rock samples analyzed in this study.

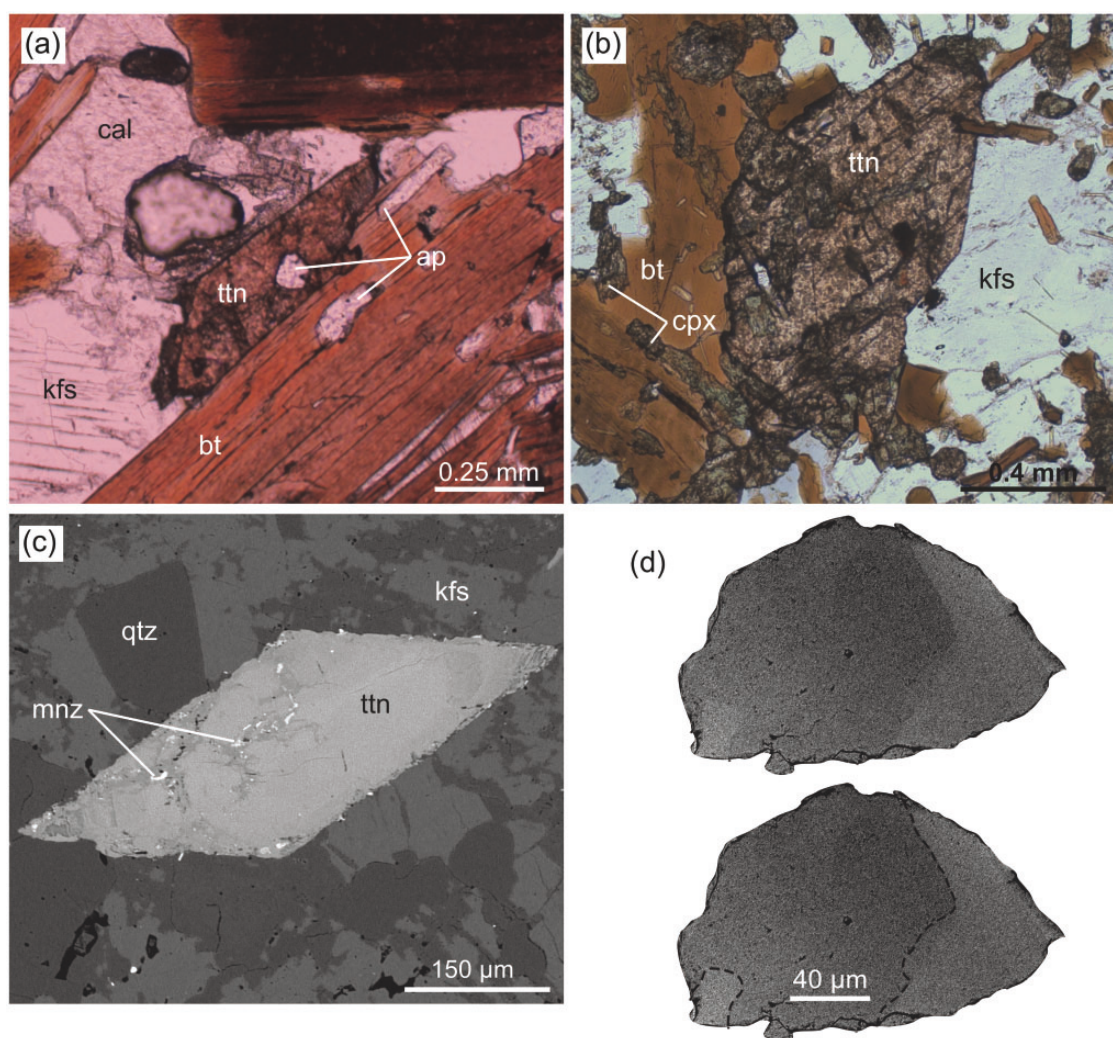


Fig. 5. Examples of typical titanite from MPIS ultrapotassic rocks. (a) Plane-polarized light (PPL) photomicrograph of euhedral titanite in shonkinite thin section (MP-P0714-19). (b) PPL photomicrograph of subhedral titanite in shonkinite thin section (MP-P0913-10C). (c) Back-scattered electron (BSE) image of titanite grain in leucosyenite thin section with veins containing monazite (MP-P0913-9B). (d) BSE image of zoned titanite in grain mount (MP-P0714-19). Zones are outlined by dashed lines in the lower image. ap, apatite; bt, biotite; cal, calcite; cpx, clinopyroxene; kfs, K-feldspar; mnz, monazite; qtz, quartz; ttn, titanite.

Table 3: Representative titanite LASS-ICP-MS geochronology data

Spot	Pb (ppm)	Th (ppm)	U (ppm)	Th/U	Measured isotopic ratios				Apparent isotopic ages (Ma)								
					$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{235}\text{U}$	2 σ %	$^{206}\text{Pb}/^{238}\text{U}$	2 σ %	$^{207}\text{Pb}/^{206}\text{Pb}$ age	2 σ abs	$^{206}\text{Pb}/^{238}\text{U}$ age	^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ age	2 σ abs		
MP-P0913-6 titanite (spot size = 40 μm , shot frequency = 4 Hz, shot count = 100, laser energy = 3 mJ at 100%)																	
1	40.3	175	49.5	3.55	0.5027	1.55	31.99	2.66	0.4586	2.16	0.812	4249	65.9	2435	1390	52.6	39.4
2	45.3	247	59.2	4.16	0.45142	1.52	26.18	2.51	0.4207	2.00	0.797	4090	62.0	2265	1417	45.3	34.7
3	53.0	291	71.3	4.08	0.44319	1.51	25.39	2.53	0.415	2.03	0.803	4063	61.2	2240	1420	45.5	34.7
4	68.3	419	99.2	4.21	0.40812	1.51	22.02	2.53	0.3912	2.03	0.803	3939	59.3	2130	1429	43.2	33.2
5	43.4	211	53.5	3.93	0.4717	1.53	29.08	2.57	0.4491	2.07	0.804	4155	63.5	2393	1451	49.6	37.7
6	110.3	1219	177.0	6.90	0.17531	1.51	6.639	2.53	0.2748	2.02	0.801	2609	39.5	1566	1428	31.7	28.3
7	43.6	211	54.1	3.91	0.47983	1.51	30.03	2.54	0.454	2.04	0.804	4180	63.0	2415	1443	49.3	37.6
8	85.9	949	142.9	6.66	0.15106	1.51	5.609	2.55	0.2692	2.05	0.805	2358	35.7	1538	1441	31.6	28.8
9	83.9	947	160.8	5.90	0.15221	1.51	5.458	2.55	0.2607	2.05	0.804	2371	35.9	1495	1395	30.6	27.8
10	48.9	290	69.5	4.20	0.41797	1.51	22.98	2.56	0.3974	2.06	0.807	3975	60.0	2159	1426	44.5	33.9
11	59.4	492	44.2	11.20	0.45881	1.51	27.27	2.55	0.4312	2.05	0.804	4114	62.3	2313	1431	47.4	36.1
12	69.3	365	89.2	4.12	0.4522	1.57	27.09	2.76	0.4353	2.27	0.822	4092	64.3	2331	1462	52.9	39.3
13	94.1	1003	147.7	6.78	0.1904	1.61	7.459	2.66	0.2837	2.13	0.798	2746	44.1	1611	1445	34.2	30.2
14	87.5	989	146.0	6.77	0.153	1.51	5.624	2.53	0.2651	2.03	0.802	2380	36.0	1517	1417	30.8	28.0
15	34.3	94	26.7	3.53	0.6325	1.51	56.99	2.59	0.6534	2.10	0.811	4584	69.3	3244	1417	68.0	55.6
16	28.4	73	26.4	2.77	0.5954	1.51	49.12	2.57	0.5978	2.08	0.810	4497	67.9	3023	1442	63.0	50.1
17	37.7	159	45.9	3.47	0.4979	1.51	32.39	2.57	0.4724	2.08	0.809	4235	64.1	2496	1445	51.9	39.4
18	60.7	686	117.1	5.87	0.13786	1.52	4.967	2.55	0.2614	2.05	0.803	2201	33.5	1498	1423	30.7	28.3
19	63.7	721	123.2	5.88	0.13648	1.51	4.927	2.56	0.2632	2.06	0.806	2183	33.1	1507	1435	31.1	28.7
20	72.8	333	149.7	2.22	0.38206	1.51	19.54	2.55	0.3718	2.05	0.806	3840	57.9	2040	1423	41.9	32.3
21	66.1	395	72.2	5.49	0.48209	1.51	29.61	2.63	0.4443	2.15	0.818	4187	63.4	2372	1406	51.1	38.0
22	31.6	123	36.7	3.38	0.5182	1.51	34.98	2.65	0.4901	2.18	0.821	4294	65.0	2573	1433	56.0	41.8
23	41.6	188	53.4	3.54	0.48186	1.51	29.85	2.56	0.4509	2.06	0.806	4187	63.4	2401	1427	49.5	37.6
24	46.6	293	96.9	3.02	0.3327	1.54	15.78	2.66	0.3464	2.17	0.816	3630	55.8	1919	1438	41.6	32.7
25	52.8	281	61.5	4.58	0.47583	1.51	29.16	2.56	0.4451	2.06	0.808	4168	62.8	2375	1427	49.1	37.1
26	39.3	149	43.0	3.47	0.5386	1.53	37.61	2.61	0.5052	2.12	0.810	4350	66.5	2638	1410	55.8	42.5
27	103.1	1131	174.9	6.47	0.15656	1.57	5.778	2.60	0.2693	2.07	0.796	2419	38.0	1538	1432	31.8	28.9
28	86.3	922	99.4	9.31	0.21349	1.52	8.527	2.54	0.2897	2.03	0.802	2932	44.5	1641	1432	33.4	28.8
29	52.9	296	72.0	4.11	0.43585	1.51	24.85	2.54	0.4128	2.04	0.803	4038	61.1	2230	1432	45.5	34.8
30	52.6	257	67.7	3.80	0.47042	1.51	28.81	2.56	0.4427	2.07	0.807	4151	62.7	2365	1435	48.9	37.0
31	83.8	605	79.0	7.63	0.4611	1.56	27.39	2.66	0.4317	2.16	0.810	4121	64.4	2315	1426	49.9	37.5

(continued)

(continued)

Table 3: Continued

Spot	Pb (ppm)	Th (ppm)	U (ppm)	Th/U	Measured isotopic ratios					Apparent isotopic ages (Ma)							
					$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{235}\text{U}$	2 σ %	$^{206}\text{Pb}/^{238}\text{U}$	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ age	2 σ abs	$^{206}\text{Pb}/^{238}\text{U}$ age	^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ age	2 σ abs		
					MMP-P0913-10C titanite (spot size = 40 μm , shot frequency = 4 Hz, shot count = 100, laser energy = 3 mJ at 75%)												
1	30.1	166	61.9	2.64	0.4358	1.52	23.19	2.55	0.3824	2.04	4037	61.4	2089	1383	42.7	1383	33.9
2	32.5	197	66.2	2.92	0.3964	1.53	19.81	2.56	0.3587	2.06	3895	59.4	1978	1385	40.8	1385	32.3
3	23.7	104	39.0	2.65	0.5671	1.51	38.66	2.67	0.493	2.20	4426	67.0	2586	1380	56.8	1380	45.5
4	25.5	110	41.7	2.61	0.5623	1.55	39.06	2.76	0.4994	2.28	4413	68.4	2613	1412	59.6	1412	47.1
5	28.1	153	55.1	2.75	0.4463	1.52	24.02	2.64	0.3876	2.16	4073	61.9	2113	1376	45.6	1376	35.5
6	38.6	231	74.6	3.07	0.4073	1.52	20.74	2.61	0.3671	2.12	3936	60.0	2017	1392	42.7	1392	33.6
7	35.7	178	65.3	2.72	0.5012	1.52	30.06	2.59	0.4329	2.10	4245	64.3	2321	1389	48.8	1389	38.8
8	51.0	279	102.1	2.73	0.44484	1.51	23.86	2.59	0.387	2.10	4068	61.6	2111	1378	44.4	1378	34.8
9	24.7	114	40.3	2.83	0.5528	1.54	36.21	2.61	0.4745	2.11	4389	67.7	2505	1371	52.8	1371	43.2
10	23.6	107	39.6	2.68	0.5527	1.52	36.81	2.66	0.4825	2.19	4388	66.8	2540	1393	55.6	1393	44.4
11	58.2	348	182.8	1.90	0.3231	1.51	14.26	2.54	0.3191	2.05	3585	54.2	1787	1378	36.5	1378	29.6
12	41.2	161	57.0	2.81	0.6325	1.52	50.83	2.53	0.5815	2.03	4584	69.5	2957	1391	59.9	1391	53.8
13	25.3	123	47.5	2.61	0.4999	1.55	29.41	2.62	0.428	2.11	4241	65.6	2299	1377	48.5	1377	38.6
14	26.2	134	43.6	3.09	0.5112	1.53	30.71	2.63	0.4353	2.14	4274	65.3	2331	1370	49.8	1370	39.5
15	25.7	110	42.4	2.62	0.5547	1.52	37.16	2.60	0.485	2.12	4394	66.7	2551	1394	54.0	1394	44.0
16	47.0	269	122.2	2.23	0.3881	1.52	19.07	2.49	0.3554	1.98	3864	58.8	1962	1390	38.8	1390	31.2
17	28.1	126	50.8	2.51	0.5325	1.52	33.94	2.62	0.4603	2.14	4334	65.9	2443	1387	52.2	1387	41.8
18	33.3	196	61.9	3.21	0.41205	1.52	21.28	2.67	0.3742	2.19	3954	60.0	2051	1407	45.0	1407	35.0
19	39.0	252	76.9	3.31	0.3611	1.53	17.29	2.57	0.346	2.06	3754	57.5	1917	1411	39.6	1411	31.7
20	52.8	285	107.7	2.67	0.4378	1.53	23.56	2.43	0.3882	1.89	4044	61.8	2116	1398	39.9	1398	32.8
21	62.1	312	124.5	2.56	0.4809	1.52	27.5	2.41	0.4134	1.88	4184	63.5	2232	1379	41.9	1379	34.9
22	66.2	343	129.9	2.67	0.46914	1.51	26.55	2.41	0.4083	1.87	4147	62.7	2209	1391	41.4	1391	34.3
23	37.7	189	66.3	2.88	0.5079	1.53	31.39	2.44	0.4455	1.91	4264	65.2	2377	1410	45.3	1410	38.2
24	27.4	134	43.0	3.16	0.5392	1.52	34.73	2.44	0.4665	1.90	4352	66.1	2470	1387	47.0	1387	40.4
25	41.1	176	182.1	0.98	0.35225	1.51	16.345	2.42	0.3355	1.90	3717	56.1	1866	1387	35.4	1387	28.9
26	24.5	115	41.4	2.80	0.5378	1.52	34.88	2.47	0.4703	1.95	4348	66.1	2487	1401	48.4	1401	41.0
27	32.7	155	58.6	2.66	0.5212	1.52	32.69	2.44	0.4541	1.91	4302	65.3	2415	1400	46.1	1400	39.0
28	53.5	267	80.4	3.36	0.54294	1.51	35.2	2.46	0.4694	1.94	4362	65.9	2483	1384	48.2	1384	40.9
29	40.6	156	52.8	2.98	0.6534	1.53	55.24	2.47	0.613	1.94	4631	70.6	3084	1387	60.1	1387	57.1

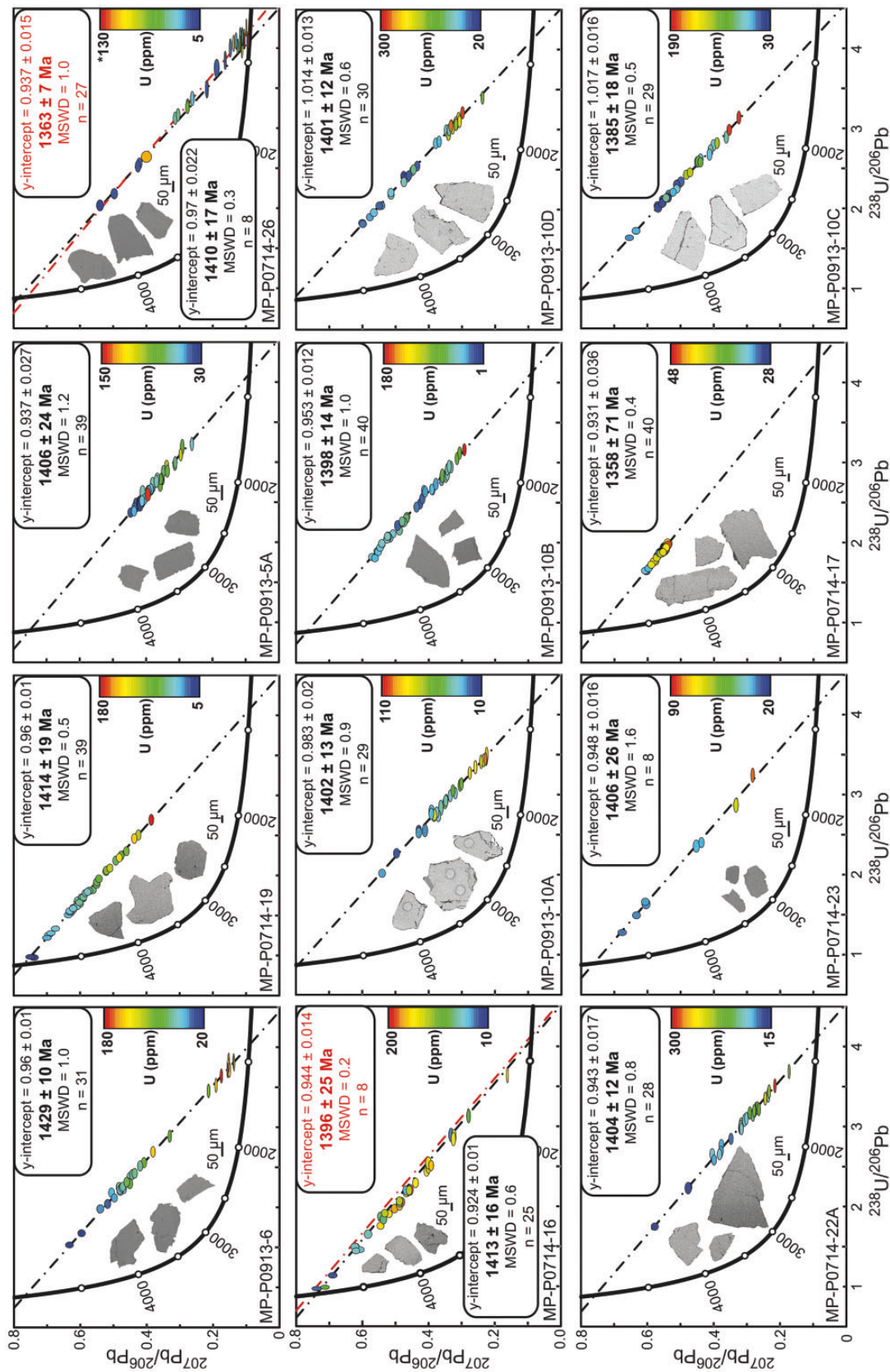


Fig. 6. Titanite U-Pb concordia plots for MPIS ultrapotassic rocks. Analyses are colored by U content; warmer colors represent higher concentrations. It should be noted that there are two age populations shown for MP-P0714-26 (top right corner) and MP-P0714-16 (left of middle row); the younger age populations are shown by red isochrons; also that for MP-P0714-26 the U-content scale does not include one analysis that has much higher U content (450 ppm vs <130 ppm). BSE images of representative grains are shown in each plot; it should be noted that scale is different for each plot.

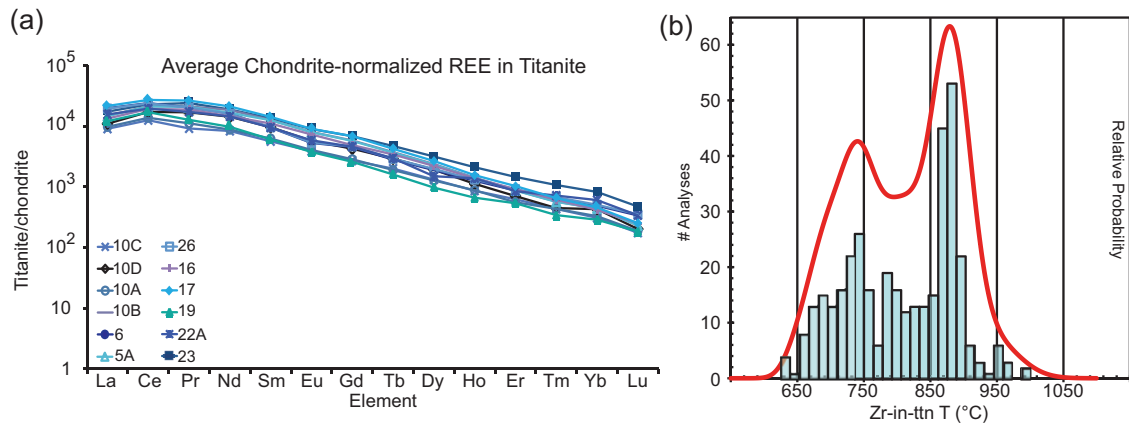


Fig. 7. Titanite trace element plots. (a) Average chondrite-normalized REE patterns for titanite from all analyzed samples. (b) Probability distribution plot of Zr-in-titanite temperatures for all titanite samples calculated using the calibration of [Hayden et al. \(2008\)](#) with adjustment of activities for Si and Ti according to the Appendix.

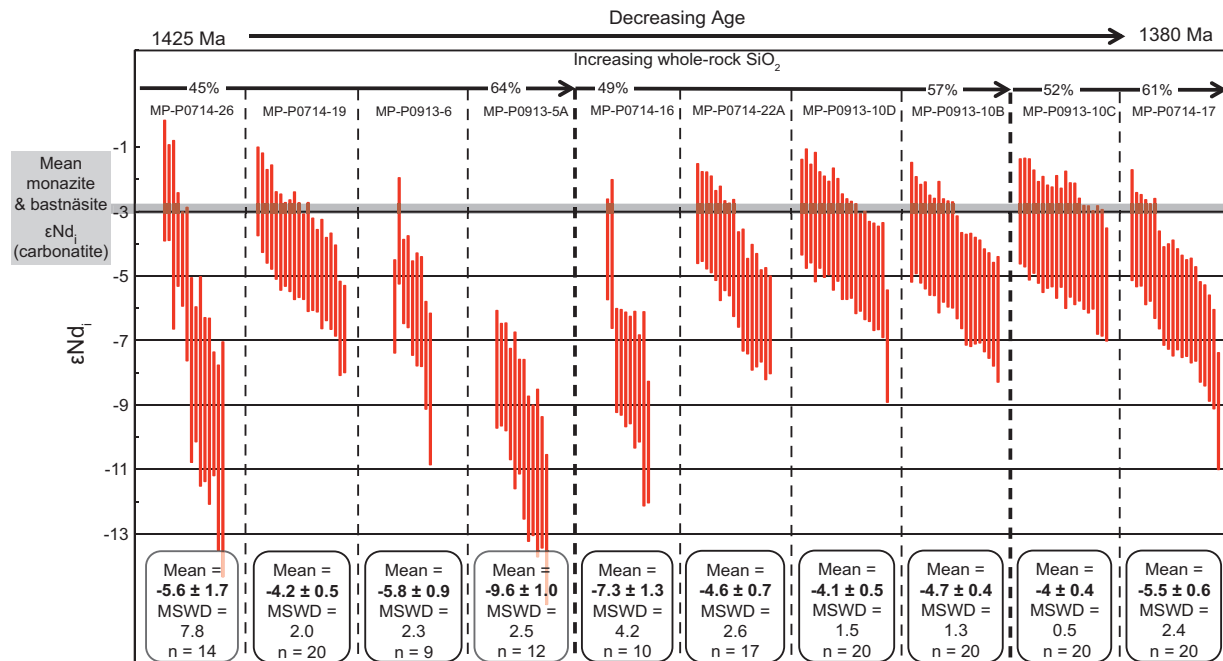


Fig. 8. Titanite Nd isotopic data for MPIS ultrapotassic rocks. Each set of analyses is from a single sample; weighted means are shown in boxes below each set of analyses. Samples are arranged by age, with age decreasing from left to right. Within each age group, samples increase in whole-rock silica content from left to right. Mean ϵ_{Nd} of monazite and bastnaesite from MPIS carbonatite is shown by the grey bar.

Ti-in-zircon temperatures (800–1500°C, Ti and Si activities assumed to be 0.8 and unity, respectively; see the Appendix for analytical details). Most of the U–Pb data are highly discordant on Tera–Wasserburg concordia diagrams, defining broad arrays that appear to be the result of a mixture of radiogenic Pb loss and high or variable common Pb content (Fig. 10a–f). In general, per cent discordance correlates positively with U content, LREE content, and mass-204 signal intensity (a proxy for common Pb content) (e.g. Fig. 10c and d). Zircon is present in only one carbonatite sample (MP-P0913-1B), and all crystals examined are metamict and do not yield meaningful U–Pb data. Of 15 samples, eight yielded

only discordant zircon U–Pb data (e.g. MP-P0913-10A, Fig. 10c and d).

A minority of zircons (134 of 436 analyses) from seven out of 15 MPIS rocks yielded small populations of concordant or near-concordant U–Pb dates, primarily from low- to moderate-U grains (~80–500 ppm). The dates primarily form two clusters; one at ~1460–1400 Ma, and another at 1800–1640 Ma (Fig. 10a and b), although one sample additionally yielded sparse analyses from 1600 to 1430 Ma (Fig. 10b). Elongate or rounded, colorless to brown zircons from two samples that contain gneissic or granitic xenoliths (MP-P0913-5A and MP-P0913-6; e.g. Fig. 2a) yield dates >1460 Ma and

Table 4: Representative LA-MC-ICP-MS Nd isotopic data

Spot	^{146}Nd (V)	Total Nd	% ^{144}Sm	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	$^{143}\text{Nd}/^{144}\text{Nd}$ std corr'd	2SE	$^{145}\text{Nd}/^{144}\text{Nd}$	2SE	$^{147}\text{Sm}/^{144}\text{Nd}$	2SE	$^{147}\text{Sm}/^{144}\text{Nd}$ std corr'd	2SE	2SE propagated	β (Sm)	β (Nd)	Age (Ma)	$\varepsilon_{\text{Nd}_i}$	2SE
<i>MP-P0913-SQ1 monazite</i>																			
1	1.537	6.59	1.0129	0.511105	37	0.511168	37	0.348420	20	0.049067	76	0.047754	76	2389	-1.406	-1.629	1380	-2.34	0.8
2	1.533	6.57	1.0132	0.511069	33	0.511132	33	0.348405	24	0.049064	66	0.047751	66	2388	-1.4	-1.6267	1380	-3.05	0.8
3	1.507	6.46	1.0042	0.511036	43	0.511099	43	0.348385	26	0.048656	65	0.047354	65	2369	-1.405	-1.6213	1380	-3.62	0.9
4	1.518	6.51	1.0042	0.511080	26	0.511143	26	0.348412	22	0.048656	95	0.047354	95	2370	-1.406	-1.6256	1380	-2.76	0.7
5	1.508	6.46	0.9964	0.511080	36	0.511143	36	0.348404	21	0.048255	63	0.046964	63	2349	-1.405	-1.6223	1380	-2.69	0.8
6	1.531	6.56	1.0049	0.511077	39	0.511140	39	0.348394	21	0.048680	140	0.047377	140	2373	-1.407	-1.6223	1380	-2.83	0.9
7	1.504	6.45	0.9962	0.511057	33	0.511120	33	0.348414	19	0.048250	140	0.046959	140	2352	-1.392	-1.6193	1380	-3.14	0.8
8	1.532	6.57	1.0073	0.511096	39	0.511159	39	0.348388	24	0.048826	80	0.047519	80	2377	-1.411	-1.6188	1380	-2.48	0.9
9	1.524	6.53	1.0016	0.511060	32	0.511123	32	0.348414	22	0.048531	90	0.047232	90	2363	-1.405	-1.6183	1380	-3.13	0.8
10	1.511	6.47	0.9999	0.511065	51	0.511128	51	0.348402	24	0.048441	98	0.047145	98	2359	-1.405	-1.6192	1380	-3.02	1.1
11	1.519	6.51	1.0189	0.511080	38	0.511143	38	0.348403	24	0.049362	95	0.048041	95	2404	-1.405	-1.617	1380	-2.88	0.9
12	1.506	6.46	1.0177	0.511084	4	0.511147	40	0.348408	17	0.049300	130	0.047981	130	2403	-1.401	-1.6166	1380	-2.8	0.9
13	1.521	6.52	1.0212	0.511068	35	0.511131	35	0.348397	20	0.049450	140	0.048127	140	2410	-1.383	-1.615	1380	-3.13	0.8
14	1.513	6.49	1.0086	0.511081	29	0.511144	29	0.348409	22	0.048878	98	0.047570	98	2381	-1.412	-1.6182	1380	-2.78	0.7
15	1.54	6.61	1.0247	0.511092	44	0.511155	44	0.348423	28	0.049666	74	0.048337	74	2418	-1.409	-1.6171	1380	-2.7	1
16	1.527	6.54	0.9839	0.511098	38	0.511161	38	0.348420	23	0.047649	94	0.046374	94	2321	-1.404	-1.6262	1380	-2.24	0.9
17	1.428	6.12	0.976	0.511036	34	0.511099	34	0.348418	25	0.047320	120	0.046054	120	2306	-1.419	-1.6271	1380	-3.39	0.8
18	1.497	6.41	0.9804	0.511075	42	0.511138	42	0.348406	23	0.047500	110	0.046229	110	2314	-1.419	-1.6264	1380	-2.66	0.9
19	1.495	6.4	0.9917	0.511083	37	0.511146	37	0.348391	22	0.048072	75	0.046786	75	2340	-1.417	-1.6257	1380	-2.6	0.8
20	1.499	6.42	0.9792	0.51106	33	0.511123	33	0.348398	18	0.047434	62	0.046165	62	2309	-1.416	-1.6214	1380	-2.94	0.8
21	1.456	6.24	0.9718	0.511076	38	0.511139	38	0.348413	25	0.047080	140	0.045820	140	2295	-1.397	-1.6217	1380	-2.57	0.8
22	1.452	6.22	0.9718	0.511048	38	0.511111	38	0.348411	26	0.047080	130	0.045820	130	2295	-1.403	-1.6178	1380	-3.12	0.8
23	1.454	6.23	0.9749	0.511061	36	0.511124	36	0.348396	22	0.047230	110	0.045966	110	2301	-1.408	-1.6169	1380	-2.89	0.8
24	1.452	6.22	0.9759	0.511070	41	0.511133	41	0.348393	21	0.047257	99	0.045992	99	2302	-1.412	-1.6154	1380	-2.72	0.9
25	1.416	6.06	0.9632	0.511045	37	0.511108	37	0.348409	21	0.046700	120	0.045450	120	2276	-1.43	-1.6136	1380	-3.11	0.8
26	1.552	6.65	0.9778	0.511050	37	0.511113	37	0.348404	25	0.047386	70	0.046118	70	2307	-1.403	-1.6144	1380	-3.13	0.8
27	1.575	6.75	0.9838	0.511091	46	0.511154	46	0.348395	30	0.047708	74	0.046431	74	2323	-1.431	-1.616	1380	-2.38	1
28	1.543	6.61	0.9874	0.511063	38	0.511126	38	0.348405	18	0.047850	150	0.046570	150	2333	-1.406	-1.6135	1380	-2.96	0.9
29	1.568	6.72	0.9818	0.511121	38	0.511184	38	0.348410	21	0.047570	100	0.046297	100	2317	-1.406	-1.6169	1380	-1.77	0.8
30	1.617	6.93	0.9843	0.511089	35	0.511152	35	0.348402	18	0.047696	71	0.046420	71	2322	-1.386	-1.6146	1380	-2.42	0.8

(continued)

Table 4: Continued

Spot	^{146}Nd (V)	Total Nd	% ^{144}Sm	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	$^{143}\text{Nd}/^{144}\text{Nd}$ std corr'd	2SE	$^{145}\text{Nd}/^{144}\text{Nd}$	2SE	$^{147}\text{Sm}/^{144}\text{Nd}$	2SE	$^{147}\text{Sm}/^{144}\text{Nd}$ std corr'd	2SE	propagated	β (Sm)	β (Nd)	Age (Ma)	ϵ_{Nd_i}	2SE
<i>MP-P0913-6 titanite</i>																			
1	1.047	4.62	2.464	0.511538	47	0.511583	47	0.348410	24	0.119500	1500	0.116473	1500	6014	-1.492	-1.6725	1420	-6	1.4
2	1.77	7.94	3.327	0.511842	39	0.511887	39	0.348401	23	0.161300	1700	0.157214	1700	8042	-1.4758	-1.6716	1420	-7.49	1.7
3	1.616	7.22	3.096	0.511809	52	0.511854	52	0.348409	23	0.150090	960	0.146288	960	7377	-1.4865	-1.6711	1420	-6.14	1.7
4	1.648	7.42	3.534	0.512005	39	0.512050	39	0.348415	22	0.171200	1800	0.166864	1800	8535	-1.4219	-1.6309	1420	-6.06	1.7
5	1.572	7.05	3.326	0.512038	39	0.512083	39	0.348395	22	0.161180	890	0.157097	890	7905	-1.4239	-1.6243	1420	-3.63	1.6
6	1.127	4.99	2.643	0.511612	44	0.511657	44	0.348418	23	0.127900	1400	0.124460	1400	6388	-1.486	-1.6651	1420	-6.05	1.5
7	1.189	5.26	2.634	0.511652	41	0.511697	41	0.348411	22	0.127900	1300	0.124465	1300	6358	-1.454	-1.6497	1420	-5.23	1.4
8	1.483	6.57	2.722	0.511691	26	0.511736	26	0.348404	18	0.131940	930	0.128598	930	6497	-1.48	-1.6668	1420	-5.22	1.3
9	2.137	9.68	3.83	0.512011	84	0.512056	84	0.348398	39	0.185660	830	0.180957	830	9086	-1.455	-1.6428	1420	-8.52	2.3
<i>MP-P0913-10C titanite</i>																			
1	0.428	1.905	2.892	0.511893	59	0.511938	59	0.348429	38	0.140110	540	0.136561	540	6849	-1.399	-1.618	1380	-3.03	1.7
2	0.438	1.952	2.923	0.511815	79	0.511860	79	0.348375	38	0.141600	1100	0.138013	1100	6988	-1.409	-1.6166	1380	-4.81	2
3	0.617	2.757	3.126	0.511919	51	0.511964	51	0.348428	31	0.151470	620	0.147633	620	7408	-1.423	-1.6263	1380	-4.49	1.7
4	0.576	2.572	3.0983	0.511967	47	0.512012	47	0.34839	32	0.150120	320	0.146318	320	7323	-1.408	-1.6237	1380	-3.31	1.6
5	0.787	3.5	2.9464	0.511867	72	0.511912	72	0.348437	35	0.142790	360	0.139173	360	6968	-1.425	-1.6246	1380	-4	1.9
6	0.63	2.79	3.025	0.511913	44	0.511958	44	0.348415	33	0.146740	730	0.143023	730	7188	-1.423	-1.617	1380	-3.79	1.5
7	0.383	1.704	2.875	0.511852	67	0.511897	67	0.348415	33	0.139400	100	0.135869	100	6867	-1.403	-1.6064	1380	-3.71	1.8
8	0.567	2.522	2.8853	0.511859	51	0.511904	51	0.348391	24	0.139820	160	0.136279	160	6816	-1.394	-1.6003	1380	-3.65	1.6
9	0.555	2.473	2.947	0.511858	50	0.511903	50	0.348411	33	0.142800	1000	0.139183	1000	7031	-1.418	-1.6206	1380	-4.18	1.6
10	0.527	2.344	2.87	0.511813	53	0.511858	53	0.348425	33	0.139100	1200	0.135577	1200	6884	-1.42	-1.616	1380	-4.42	1.6
11	0.377	1.681	2.933	0.511816	77	0.511861	77	0.348381	35	0.142200	1100	0.138598	1100	7017	-1.412	-1.601	1380	-4.9	2
12	0.418	1.853	2.751	0.511795	56	0.511840	56	0.348418	43	0.133350	170	0.129972	170	6501	-1.405	-1.5859	1380	-3.78	1.6
13	0.398	1.77	2.859	0.511836	89	0.511881	89	0.348389	46	0.138550	860	0.135041	860	6807	-1.386	-1.5959	1380	-3.88	2.1
14	0.483	2.151	2.978	0.511891	44	0.511936	44	0.348475	26	0.144400	1000	0.140742	1000	7108	-1.418	-1.591	1380	-3.81	1.5
15	0.833	3.71	2.941	0.511839	44	0.511884	44	0.348418	25	0.142500	1100	0.138891	1100	7031	-1.402	-1.6065	1380	-4.5	1.5
16	0.659	2.948	3.153	0.511891	54	0.511936	54	0.348418	25	0.152800	2400	0.148930	2400	7824	-1.406	-1.6136	1380	-5.26	1.7
17	0.462	2.056	2.8478	0.511876	56	0.511921	56	0.348384	32	0.137980	340	0.134485	340	6733	-1.393	-1.5868	1380	-2.99	1.6
18	0.475	2.116	2.919	0.511894	72	0.511939	72	0.348402	29	0.141460	740	0.137877	740	6933	-1.388	-1.5926	1380	-3.24	1.9
19	0.408	1.821	2.852	0.511833	66	0.511878	66	0.348419	39	0.138240	720	0.134739	720	6775	-1.392	-1.5869	1380	-3.88	1.8
20	0.367	1.63	2.7958	0.511813	76	0.511858	76	0.348382	44	0.135430	150	0.132000	150	6602	-1.371	-1.5746	1380	-3.79	1.9

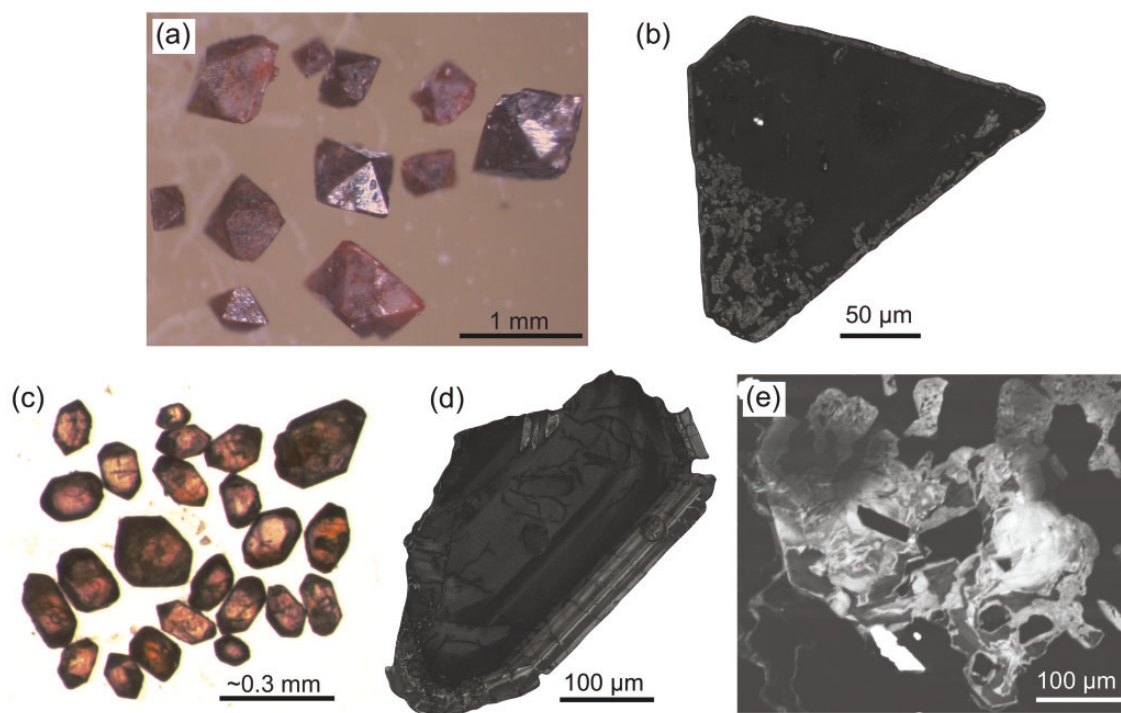


Fig. 9. Examples of typical zircon from MPIS ultrapotassic rocks. (a) Pseudo-octahedral, metamict zircons separated from shonkinite (MP-P0714-22A). (b) Cathodoluminescence (CL) image of metamict zircon grain (MP-P0714-17). (c) Euhedral, pink to reddish-brown zircons separated from melanosyenite (MP-P0913-6). (d) CL image of zircon in grain mount showing oscillatory zoning (MP-P0714-26). (e) CL image of anhedral zircon with irregular zoning pattern in shonkinite thin section (MP-P0913-10A).

have $\text{Th}/\text{U} < 1$; pink to reddish-brown, euhedral to anhedral zircon with low aspect ratios ($\leq 2:1$) yield dates < 1460 Ma and chiefly have $\text{Th}/\text{U} > 1$. Mean $^{207}\text{Pb}/^{206}\text{Pb}$ and concordia dates < 1460 Ma range from 1458 ± 7 to 1407 ± 11 Ma (e.g. Fig. 10e and f; Supplementary Data Electronic Appendix 8). Only one sample gave > 10 concordant, Mesoproterozoic dates out of 30–40 analyses (MP-L0613-BDAY), yielding a concordia age of 1425 ± 5 Ma ($n = 25$; Supplementary Data Electronic Appendix 8). Where titanite and zircon occur in the same sample, concordant, Mesoproterozoic zircon dates overlap titanite dates within uncertainty in all cases except one (MP-P0913-10C). Multiple dates within single crystals are consistently similar.

Zircons that yield concordant and slightly discordant data have similar REE concentrations to typical igneous zircon from a variety of igneous rocks (e.g. Belousova *et al.*, 2002), and yield Ti-in-zircon apparent temperatures from ~ 600 to 850°C (Fig. 11a and b).

Zircons from three Mountain Pass host-rock samples are primarily colorless to brown and elongate or moderately rounded, and yielded zircon dates of ~ 1820 – 1765 Ma (feldspar augen gneiss, sample MP-P0913-12), ~ 1820 – 1640 Ma (coarse-grained alkali granite, sample MP-P0914-5B) and 1800 – 1660 Ma (garnet–biotite–sillimanite gneiss, sample MP-P0913-4) (Supplementary Data Electronic Appendix 8). U–Pb discordance is common in the host-rock zircons, and generally correlates positively with U content and mass-204 signal intensity, but ~ 50 – 70% of the zircon analyses are concordant.

Th/U is consistently < 1 . Chondrite-normalized REE profiles are highly variable, and Ti-in-zircon apparent temperatures mostly range from 650 to 800°C (Supplementary Data Electronic Appendix 8).

The ϵ_{Hf_i} values from Mesoproterozoic zircons typically range from ~ 0.5 to 3 . Five of seven samples analyzed yield single populations ($\text{MSWD} \sim 1$; Fig. 12). Two samples with fewer analyses have higher MSWD owing to one or two outlying analyses (e.g. MP-P0913-10B, Fig. 12). Taken as a whole, data from all the samples give a weighted mean of 1.9 ± 0.2 ($\text{MSWD} = 0.9$; seven of 76 analyses rejected; Fig. 12). ϵ_{Hf_i} values > 3 occur only in one sample—a shonkinite dike (MP-P0913-10C) that cross-cuts syenite, which also yielded the oldest zircon age (1458 ± 7 Ma; mean $^{207}\text{Pb}/^{206}\text{Pb}$ age), the youngest titanite age (1385 ± 18 Ma), and the most primitive ϵ_{Nd_i} values (weighted mean $= -4 \pm 0.4$). Despite the higher ϵ_{Hf_i} of this sample, excluding it does not affect the mean ϵ_{Hf_i} for all samples (weighted mean ϵ_{Hf_i} without MP-P0913-10C $= 1.72 \pm 0.24$). Representative examples of zircon Hf isotopic data are shown in Table 6, and the complete set of zircon Hf isotopic data is provided in Supplementary Data Electronic Appendix 9.

Monazite textures, U–Th/Pb, trace elements, and Nd isotopes

Monazite in the ultrapotassic rocks primarily occurs in veins and as inclusions in other phases (e.g. titanite, Fig. 5c), and as fine, subhedral to anhedral grains in altered

Table 5: Representative zircon LASS-ICP-MS geochronology data

Spot	Used in age interp.?	%	discordance	Pb (ppm)	Th (ppm)	U (ppm)	Th/U	Measured isotopic ratios				Apparent isotopic ages (Ma)				
								$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{235}\text{U}$	2 σ %	$^{206}\text{Pb}/^{238}\text{U}$	2 σ %	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ age	2 σ abs
MP-L0613-BDAY zircon (spot size = 20 μm , shot frequency = 4 Hz, shot count = 80, laser energy = 4 mJ at 100%)																
1	Yes	1.52	196	306	90	3.45	0.09	1.83	3.045	2.50	0.2457	1.65	1439	26.3	1417	23.4
2	No	4.72	150	231	94	2.46	0.09248	1.79	3.146	2.34	0.2463	1.45	1491	26.7	1421	20.6
3	No	3.09	217	342	190	1.81	0.09065	1.63	3.046	2.21	0.2439	1.43	1453	23.7	1408	20.1
4	No	0.35	127	180	146	1.25	0.09114	1.67	3.191	2.22	0.2536	1.39	1463	24.4	1458	20.3
5	No	3.88	135	199	132	1.52	0.0926	2.21	3.187	2.76	0.2492	1.60	1493	33.0	1436	23.0
6	Yes	0.02	144	221	125	1.78	0.08937	1.82	3.07	2.36	0.2474	1.45	1426	25.9	1426	20.6
7	No	16.46	223	307	171	1.81	0.1075	1.82	3.873	2.27	0.2577	1.30	1771	32.2	1479	19.2
8	No	1.18	119	185	125	1.48	0.09058	1.66	3.148	2.20	0.249	1.38	1452	24.1	1434	19.8
9	Yes	1.63	160	248	103	2.43	0.08965	1.75	3.069	2.34	0.244	1.49	1432	25.1	1409	21.0
10	Yes	2.22	133	205	95	2.14	0.09041	1.67	3.106	2.32	0.2454	1.55	1448	24.2	1416	22.0
11	No	3.94	138	215	151	1.44	0.09142	1.76	3.155	2.37	0.2445	1.52	1469	25.8	1411	21.5
12	Yes	2.43	111	168	122	1.39	0.09094	1.74	3.157	2.32	0.2469	1.48	1459	25.4	1424	21.1
13	Yes	0.29	195	298	128	2.34	0.08943	1.63	3.106	2.16	0.2468	1.36	1427	23.3	1423	19.3
14	Yes	0.89	102	157	124	1.27	0.08957	1.67	3.083	2.11	0.2457	1.21	1430	23.9	1417	17.2
15	No	26.25	141	188	87	2.16	0.1196	1.85	4.203	2.40	0.2516	1.46	1963	36.4	1448	21.2
16	No	14.91	123	183	182	1.00	0.1015	1.85	3.493	2.45	0.2456	1.55	1665	30.8	1417	22.0
17	Yes	1.55	109	163	116	1.41	0.09039	1.84	3.089	2.32	0.2472	1.35	1448	26.6	1425	19.3
18	Yes	2.13	187	289	191	1.52	0.09027	1.64	3.066	2.15	0.2451	1.33	1445	23.6	1414	18.8
19	No	4.57	264	415	151	2.80	0.09265	1.66	3.148	2.13	0.2474	1.27	1494	24.8	1426	18.0
20	Yes	0.73	156	238	148	1.64	0.09017	1.66	3.067	2.15	0.2486	1.29	1443	23.9	1432	18.5
21	Yes	1.59	172	268	103	2.62	0.08995	1.73	3.047	2.24	0.2453	1.36	1438	24.8	1415	19.2
22	Yes	2.62	173	268	168	1.60	0.09052	1.65	3.031	2.21	0.2447	1.39	1450	24.0	1412	19.7
23	Yes	0.68	132	201	86	2.38	0.09021	1.77	3.085	2.32	0.2489	1.44	1444	25.5	1434	20.7
24	No	16.26	553	738	311	2.38	0.1105	1.96	3.982	3.12	0.2666	2.39	1821	35.8	1525	36.4
25	Yes	0.01	94	141	119	1.19	0.0898	1.73	3.09	2.17	0.2491	1.23	1435	24.9	1435	17.7
26	Yes	0.93	383	569	279	2.05	0.09041	1.58	3.13	2.25	0.249	1.54	1448	22.9	1434	22.0
27	No	6.65	100	148	100	1.48	0.09361	1.78	3.198	2.49	0.2449	1.69	1514	27.0	1413	23.9
28	No	24.90	117	152	102	1.51	0.1199	1.90	4.251	2.65	0.2574	1.80	1968	37.4	1478	26.5
29	No	6.05	209	299	125	2.40	0.0955	1.96	3.364	2.57	0.2535	1.62	1552	30.4	1458	23.5
30	No	6.72	117	169	186	0.91	0.09414	1.63	3.215	2.46	0.2466	1.78	1525	24.9	1422	25.4
31	No	0.92	54	74	101	0.73	0.09095	1.76	3.159	2.55	0.2512	1.79	1459	25.7	1446	25.9
32	Yes	1.13	154	228	75	3.05	0.09067	1.79	3.094	2.73	0.2495	2.02	1453	26.1	1437	29.0
33	No	9.45	224	341	129	2.65	0.0973	1.94	3.323	2.83	0.2494	2.02	1587	30.8	1437	29.0
34	Yes	0.34	254	379	162	2.33	0.08998	1.61	3.056	2.17	0.2489	1.38	1439	23.2	1434	19.8
35	Yes	0.29	168	244	101	2.43	0.09011	1.74	3.117	2.54	0.2512	1.79	1442	25.0	1446	25.9
36	Yes	2.47	72	110	110	1.01	0.09061	1.74	3.045	3.01	0.2455	2.41	1452	25.3	1416	34.2
37	Yes	0.99	263	378	149	2.56	0.08969	1.70	3.085	2.25	0.2514	1.40	1433	24.4	1447	20.3
38	Yes	1.11	166	167	100	1.00	0.08994	1.65	3.043	2.32	0.2469	1.58	1438	23.7	1424	22.5
39	No	3.08	150	225	137	1.64	0.09105	1.72	3.054	2.29	0.2455	1.45	1461	25.2	1416	20.6
40	No	26.33	165	146	286	0.52	0.1428	1.83	5.77	2.93	0.2965	2.25	2274	41.6	1675	37.6
41	Yes	1.82	318	486	244	1.99	0.09023	1.59	3.027	2.22	0.2458	1.48	1444	23.0	1418	21.0
42	No	39.30	176	183	114	1.62	0.1668	1.66	6.118	2.33	0.2697	1.58	2538	42.2	1541	24.3
43	Yes	0.41	98	152	82	1.85	0.0899	1.87	3.033	3.01	0.2484	2.32	1437	26.8	1431	33.1
44	Yes	0.64	262	408	147	2.79	0.08925	1.68	2.999	2.80	0.2451	2.19	1423	23.9	1414	31.0
45	Yes	0.09	142	221	132	1.68	0.0893	1.65	3.014	2.33	0.2473	1.58	1424	23.5	1426	22.5

(continued)

(continued)

Table 5: Continued

Spot	Used in age interp.?	%	discordance	Pb (ppm)	Th (ppm)	U (ppm)	Th/U	Measured isotopic ratios				Apparent isotopic ages (Ma)				
								$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{235}\text{U}$	2 σ %	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ age	2 σ abs	$^{206}\text{Pb}/^{238}\text{U}$ age	
MMP-P0714-21 zircon (spot size = 25 μm , shot frequency = 4 Hz, shot count = 100, laser energy = 5 mJ at 100%)																
1	No	70.36	970	4677	710	6.58	0.10339	1.56	1.169	2.52	0.0812	0.785	1699	28.8	504	12.0
2	No	38.47	1001	2419	611	3.99	0.09951	1.80	2.3	6.26	0.168	0.958	1628	33.5	1002	61.5
3	No	14.14	1215	2094	494	4.22	0.09527	1.63	3.015	2.55	0.2286	0.770	1547	30.7	1328	31.5
4	No	12.88	1188	2002	461	4.28	0.09505	1.66	3.039	2.38	0.2316	0.716	1543	31.3	1344	29.0
5	No	82.58	1434	9120	1121	8.14	0.13194	1.57	1.086	2.65	0.0594	0.806	2137	27.5	372	9.4
6	No	13.30	983	1578	328	4.78	0.09589	1.67	3.097	2.74	0.2331	0.793	1559	31.4	1352	34.4
7	No	75.21	1094	6160	804	7.69	0.10866	1.60	1.07	2.53	0.0712	0.773	1790	29.3	444	10.5
8	No	12.21	1020	1648	341	4.82	0.09473	1.65	3.06	2.73	0.2325	0.798	1536	31.0	1349	34.4
9	No	37.99	1094	2363	589	3.99	0.10075	1.60	2.37	6.07	0.172	0.965	1651	29.8	1024	61.5
10	No	14.65	998	1623	392	4.11	0.09608	1.71	3.024	2.69	0.2297	0.772	1563	32.1	1334	32.9
11	No	13.40	950	1502	387	3.84	0.09604	1.72	3.095	2.50	0.2333	0.725	1562	32.3	1353	30.4
12	No	62.38	971	3923	699	5.56	0.10161	1.58	1.432	2.40	0.1021	0.752	1667	29.3	627	14.1
13	No	12.28	853	1388	412	3.35	0.09473	1.62	3.032	2.59	0.2323	0.780	1536	30.5	1348	32.6
14	Yes	2.80	225	351	123	2.87	0.09044	1.58	3.034	2.56	0.2439	0.786	1449	30.2	1408	33.9
15	No	77.36	811	4512	871	5.24	0.11252	1.62	1.043	2.96	0.0672	0.838	1854	29.3	420	11.8
16	Yes	2.67	146	227	101	2.23	0.09015	1.58	3.013	2.47	0.2431	0.769	1442	30.2	1404	32.6
17	No	19.44	1340	2440	466	5.21	0.09645	1.62	2.858	2.43	0.2166	0.743	1570	30.5	1265	28.3
18	No	10.72	1032	1649	359	4.60	0.09444	1.63	3.039	2.58	0.2359	0.773	1531	30.8	1366	32.7
19	Yes	2.58	110	176	79	2.26	0.08961	1.55	2.959	2.38	0.2412	0.757	1431	29.7	1394	31.2
20	No	35.89	1076	2499	655	3.89	0.09719	1.69	2.258	3.02	0.1705	0.829	1584	31.7	1016	28.8
21	No	4.06	463	746	204	3.67	0.09109	1.56	3.029	2.24	0.2429	0.716	1462	29.7	1403	29.2
22	No	7.44	1129	1942	389	5.04	0.09234	1.56	3.023	2.29	0.238	0.729	1488	29.7	1377	29.3
23	No	81.08	972	4955	1045	4.78	0.14287	1.65	1.343	3.05	0.069	0.841	2275	28.5	430	12.4
24	No	40.10	1060	3450	710	4.81	0.09458	1.54	1.98	6.75	0.153	0.974	1533	29.1	918	61.6
25	No	79.21	955	6305	1008	6.39	0.10259	1.59	0.788	3.20	0.0558	0.868	1685	29.4	350	10.8
26	No	70.20	1168	5561	799	7.11	0.11327	1.74	1.397	3.26	0.09	0.846	1866	31.4	556	17.0
27	No	17.43	1437	2753	572	4.93	0.09643	1.56	2.949	2.13	0.2225	0.677	1570	29.4	1296	25.4
28	No	13.00	1118	1830	466	4.01	0.09543	1.63	3.04	2.60	0.2325	0.777	1550	30.8	1349	32.6
29	No	15.87	827	1510	355	4.37	0.09549	1.67	2.98	4.69	0.2242	0.934	1551	31.4	1305	59.8
30	No	8.58	602	956	254	3.84	0.09294	1.62	3.02	2.47	0.2369	0.754	1500	30.8	1372	31.4
31	No	30.38	933	2053	547	3.83	0.09512	1.58	2.378	2.47	0.1813	0.768	1544	29.8	1075	24.9
32	No	11.80	1214	2045	491	4.31	0.09467	1.60	3.055	2.39	0.2335	0.743	1535	30.1	1354	30.0

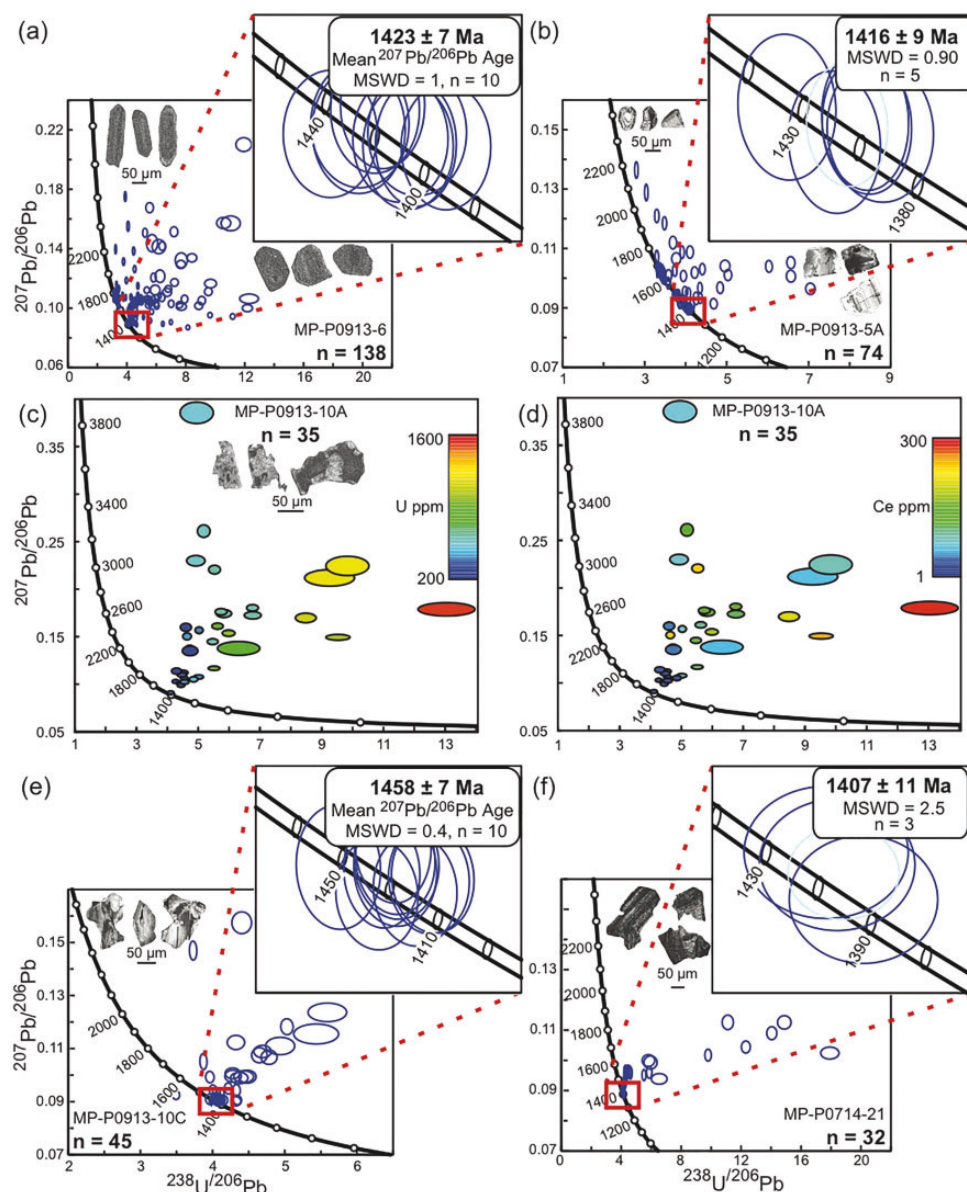


Fig. 10. Representative Tera–Wasserburg concordia plots for U–Pb analyses of zircon in MPIS ultrapotassic rocks. CL images of representative grains are shown in each plot except (d); it should be noted that scale is different for each plot. (a) Sample MP-P0913-6. (b) Sample MP-P0913-5A. (c) Sample with only discordant analyses, colored by U content (MP-P0913-10A). Greater discordance in high-U grains should be noted. (d) Sample with only discordant analyses, colored by Ce content (MP-P0913-10A). Greater discordance in high-Ce grains should be noted. (e) Sample MP-P0913-10C. (f) Sample MP-P0714-21.

samples (Fig. 13a; see description of alteration textures in syenite, above). Euhedral grains were found only in two samples that show abundant evidence for alteration (MP-P0913-2 and MP-P0913-7; [Supplementary Data Electronic Appendices 1 and 3](#)). In contrast, monazite is a common accessory mineral in carbonatite, occurring as euhedral to anhedral grains that vary from ~25 to 200 μm in size in carbonatite sample MP-L0613-BDAY2 (Fig. 13b), and as anhedral, porous, crumbly grains from ~50 μm to ~1 mm in carbonatite sample MP-P0913-SQ1 ([Supplementary Data Electronic Appendix 3](#)).

Representative monazite geochronology data are presented in [Table 7](#) and the complete monazite LASS-ICP-MS dataset (including trace element data) is given

in [Supplementary Data Electronic Appendix 10](#). Monazite from the ultrapotassic rocks and carbonatites typically contains 3–50 ppm U and has low (typically <5 ppm) radiogenic ^{206}Pb ; thus, U–Pb analyses have large uncertainties and do not yield meaningful dates. However, monazite contains significant Th (typically 2000–20 000 ppm) and has low common ^{208}Pb (i.e. >85% is radiogenic); it is therefore possible to calculate $^{208}\text{Pb}/^{232}\text{Th}$ dates. Weighted mean, common-Pb corrected $^{208}\text{Pb}/^{232}\text{Th}$ dates for monazite in ultrapotassic samples MP-P0913-2 and MP-P0913-7 are 1376 ± 36 Ma ($n = 13$, $\text{MSWD} = 4.5$) and 1401 ± 32 Ma ($n = 8$, $\text{MSWD} = 1.9$), respectively (Fig. 13c). The weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date from carbonatite sample MP-

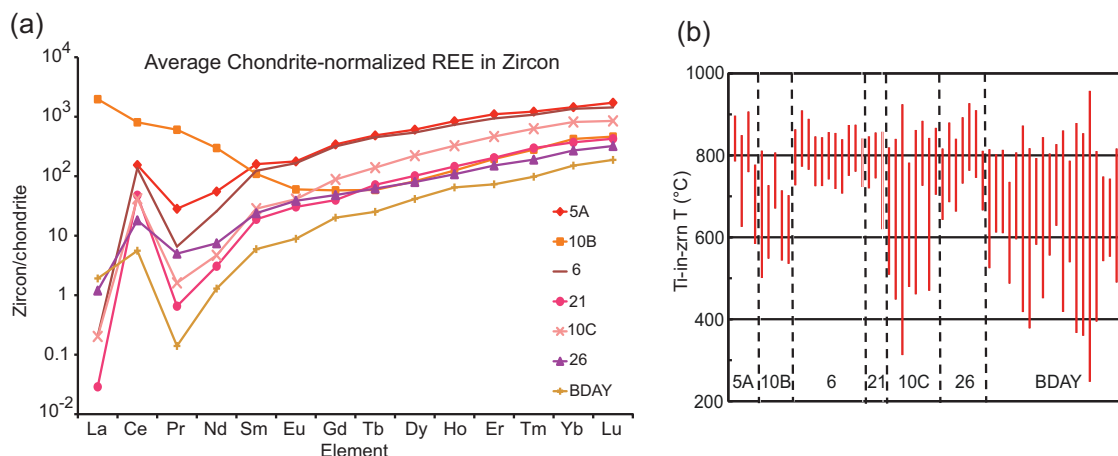


Fig. 11. Selected trace element plots for concordant zircon from MPIS ultrapotassic rocks. (a) Average chondrite-normalized REE patterns for all concordant zircons. (b) Ti-in-zircon apparent temperatures for all concordant zircons. High uncertainties are a product of poor precision as a result of low Ti content in zircon (<10 ppm).

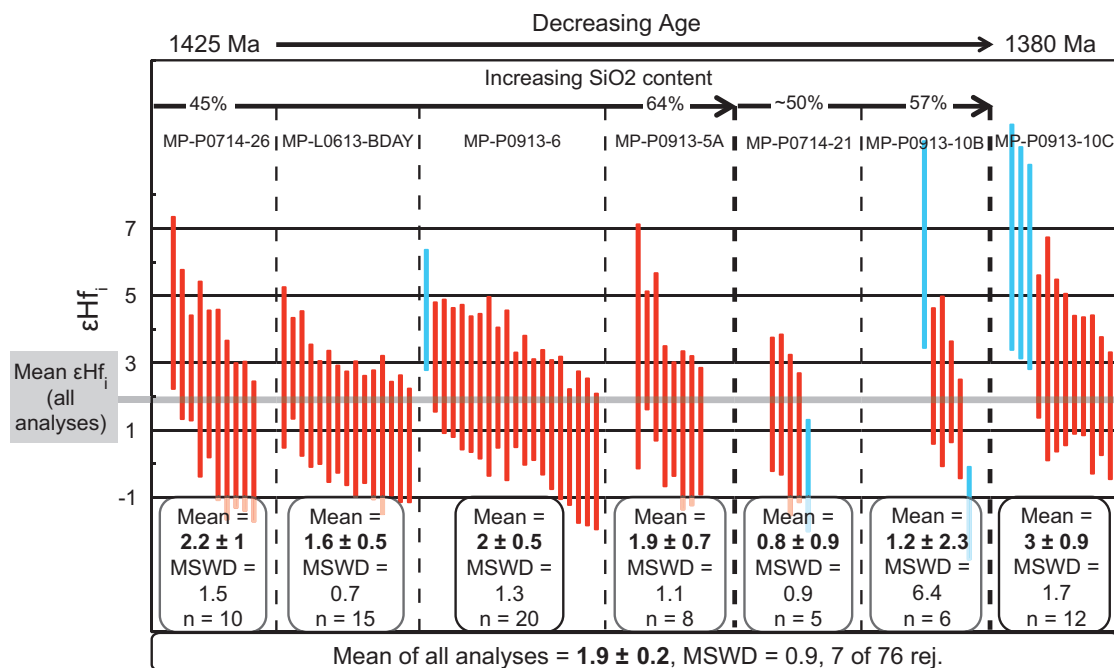


Fig. 12. Weighted mean plot of ϵHf_i for all measured MPIS zircons. Each set of analyses is from one sample. Analyses are only from zircon that yielded concordant U–Pb analyses. Samples are arranged by age, with age decreasing from left to right. Within each age group, samples increase in whole-rock silica content from left to right. Blue bars represent analyses that were rejected in the weighted mean calculation for all analyses. The mean of all analyses is shown by the gray bar.

L0613-BDAY2 is 1396 ± 16 Ma ($n=23$, MSWD = 4.2), whereas carbonatite sample MP-P0913-SQ1 defines a more narrow range, giving a weighted mean of 1371 ± 10 Ma ($n=46$, MSWD = 1.6) (Fig. 13c). Multiple analyses of single crystals indicate that some monazite grains are zoned with respect to Th, but Th content does not correlate with the common-lead corrected $^{208}\text{Pb}/^{232}\text{Th}$ dates.

Chondrite-normalized REE patterns in monazite from the ultrapotassic rocks and carbonatites show enrichment in LREE, with steep negative LREE to HREE slopes,

and minor negative Eu anomalies (Fig. 13d). Monazite from carbonatite sample MP-P0913-SQ1 shows greater depletion in HREE. Nd isotopic analysis of monazite from carbonatite sample MP-P0913-SQ1 yielded consistent ϵNd_i values, with a weighted mean of -2.8 ± 0.2 (MSWD = 0.8; Fig. 13e). Monazite Nd isotopic data are reported in Table 4.

U–Pb monazite dates from one host-rock sample, a garnet–biotite–sillimanite gneiss (MP-P0913-4), yield a mean $^{207}\text{Pb}/^{206}\text{Pb}$ date of 1693 ± 8 Ma (MSWD = 2.2; Supplementary Data Electronic Appendix 8).

Table 6: Representative zircon LA-MC-ICP-MS Hf isotopic data

Spot	Hf beam (V)	βHf	βYb	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2\sigma$	$^{176}\text{Yb}/^{177}\text{Hf}$	Analysis age (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}_i$	εHf_i	$\pm 2\sigma$	Propagated 2σ	T_{DM}	T_{DM}^{C} 2-stage
<i>MP-P0913-5A zircon</i>															
1	7.3	-1.46	-1.98	0.281927	0.000049	0.000562	0.000007	0.029	1420	0.281912	1.0	1.7	1.9	1835	2088
2	5.2	-1.46	-1.96	0.282021	0.000067	0.001744	0.000072	0.090	1420	0.281974	3.3	2.4	2.5	1751	1953
3	9.6	-1.49	-1.99	0.281958	0.000059	0.001699	0.000086	0.067	1420	0.281912	1.1	2.1	2.2	1834	2087
4	6.8	-1.46	-1.98	0.281939	0.000043	0.000631	0.000012	0.034	1420	0.281922	1.4	1.5	1.7	1821	2066
5	8.1	-1.46	-2.01	0.282020	0.000100	0.001380	0.000120	0.061	1420	0.281983	3.6	3.5	3.6	1739	1934
6	6.7	-1.46	-1.99	0.281956	0.000055	0.001173	0.000021	0.057	1420	0.281924	1.5	2.0	2.1	1818	2060
7	6.8	-1.46	-1.98	0.282003	0.000045	0.000872	0.000023	0.043	1420	0.281980	3.5	1.6	1.7	1743	1941
8	6.5	-1.44	-1.94	0.281928	0.000063	0.000572	0.000028	0.030	1420	0.281913	1.1	2.2	2.3	1834	2086
<i>MP-P0714-21 zircon</i>															
1	6.1	-1.45	-1.98	0.281888	0.000042	0.000250	0.000011	0.012	1405	0.281881	-0.4	1.5	1.7	1876	2163
2	5.4	-1.46	-1.95	0.281928	0.000064	0.000477	0.000004	0.023	1405	0.281915	0.8	2.3	2.4	1830	2089
3	5.3	-1.45	-1.98	0.281973	0.000055	0.001211	0.000024	0.059	1405	0.281941	1.7	2.0	2.1	1796	2034
4	6.1	-1.45	-2.02	0.281951	0.000052	0.000375	0.000005	0.019	1405	0.281941	1.7	1.8	2.0	1795	2034
5	5.5	-1.45	-1.98	0.281933	0.000050	0.000749	0.000027	0.038	1405	0.281913	0.7	1.8	1.9	1833	2094
<i>MP-L0613-BDAY zircon</i>															
1	4.7	-1.45	-2.03	0.281914	0.000063	0.000143	0.000016	0.007	1425	0.281910	1.1	2.2	2.3	1837	2088
2	5.9	-1.45	-1.76	0.281904	0.000043	0.000097	0.000003	0.005	1425	0.281901	0.8	1.5	1.7	1849	2107
3	6.1	-1.46	-1.96	0.281930	0.000051	0.000159	0.000002	0.008	1425	0.281926	1.7	1.8	1.9	1816	2055
4	7.2	-1.44	-1.62	0.281969	0.000064	0.000087	0.000002	0.004	1425	0.281967	3.1	2.3	2.4	1761	1966
5	7.2	-1.45	-2.07	0.281970	0.000037	0.000151	0.000005	0.008	1425	0.281966	3.1	1.3	1.5	1762	1967
6	6.1	-1.45	-1.96	0.281917	0.000040	0.000082	0.000002	0.004	1425	0.281915	1.3	1.4	1.6	1831	2078
7	6.0	-1.45	-1.84	0.281917	0.000053	0.000075	0.000000	0.004	1425	0.281915	1.3	1.9	2.0	1831	2078
8	6.2	-1.45	-1.88	0.281927	0.000040	0.000135	0.000002	0.007	1425	0.281923	1.6	1.4	1.6	1819	2060
9	5.7	-1.44	-2.05	0.281910	0.000049	0.000110	0.000002	0.005	1425	0.281907	1.0	1.7	1.9	1841	2095
10	5.7	-1.45	-1.93	0.281938	0.000047	0.000125	0.000001	0.006	1425	0.281935	2.0	1.7	1.8	1804	2035
11	6.8	-1.44	-1.96	0.281933	0.000038	0.000130	0.000003	0.008	1425	0.281929	1.8	1.3	1.5	1812	2048
12	6.7	-1.45	-1.90	0.281957	0.000057	0.000139	0.000001	0.007	1425	0.281953	2.6	2.0	2.1	1779	1995
13	7.1	-1.45	-1.88	0.281909	0.000043	0.000070	0.000001	0.003	1425	0.281907	1.0	1.5	1.7	1841	2095
14	5.5	-1.45	-2.15	0.281914	0.000050	0.000139	0.000002	0.007	1425	0.281910	1.1	1.8	1.9	1837	2088
15	7.1	-1.45	-1.98	0.281918	0.000043	0.000085	0.000002	0.004	1425	0.281916	1.3	1.5	1.7	1830	2076

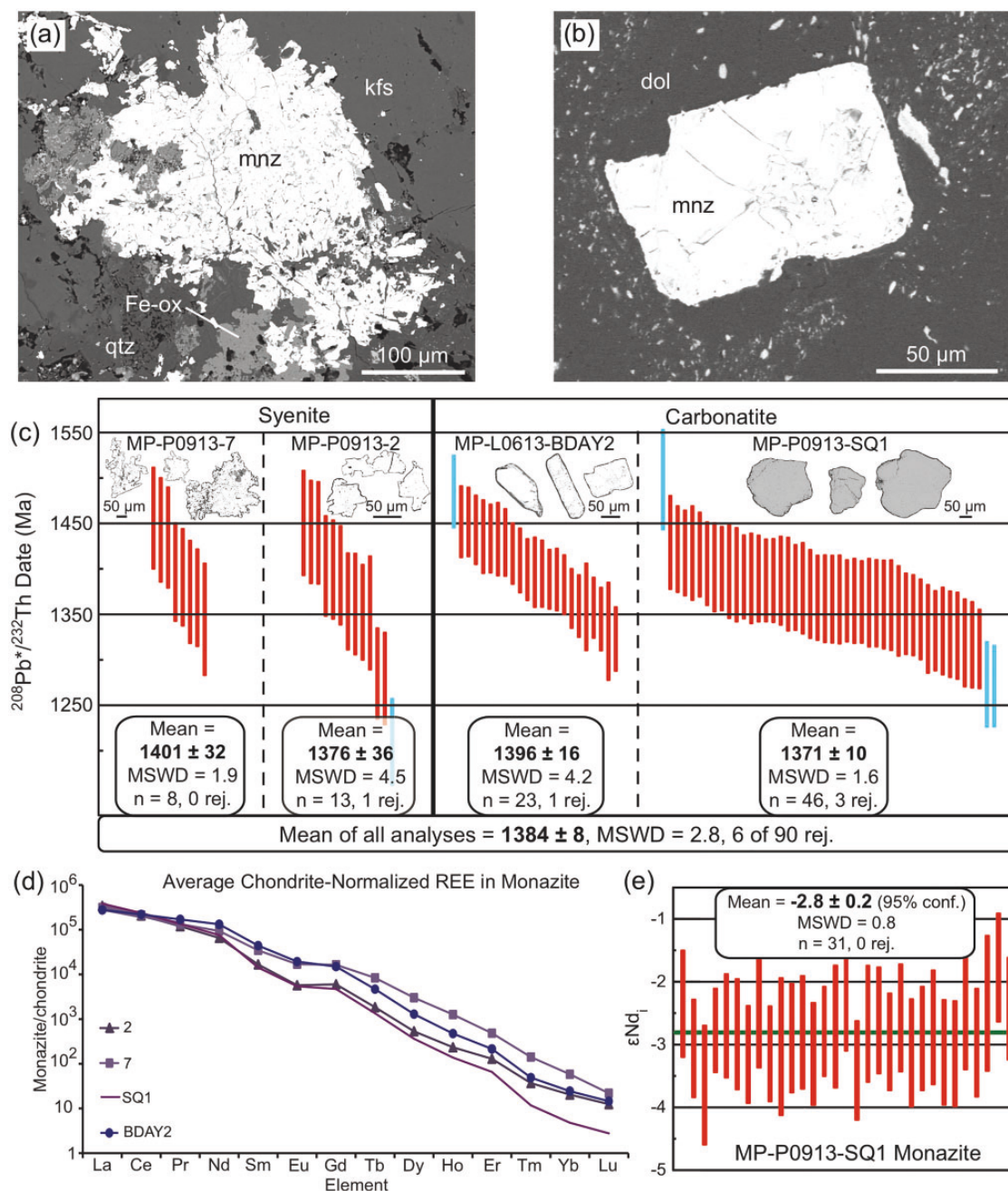


Fig. 13. Examples of monazite grains and monazite data from MPIS rocks. (a) BSE image of anhedral monazite in altered syenite (MP-P0913-7). (b) BSE image of euhedral monazite in carbonatite (MP-L0613-BDAY2). (c) Weighted mean plot of all common-Pb corrected Th–Pb dates from monazite in MPIS rocks. Blue bars represent analyses rejected from the weighted mean calculation. BSE images of representative grains are shown for each sample. It should be noted that scale is different for each sample. (d) Average chondrite-normalized REE patterns for monazite from MPIS ultrapotassic rocks and carbonatite. (e) Weighted mean plot of ϵ_{Nd} for monazite in carbonatite (MP-P0913-SQ1). dol, dolomite; Fe-ox, Fe-oxide; kfs, K-feldspar; mnz, monazite; qtz, quartz.

Chondrite-normalized REE profiles are flat among the LREE, have pronounced negative Eu anomalies, and show a range of HREE contents (10–100 times chondritic values; [Supplementary Data Electronic Appendix 8](#)).

Bastnäsité textures, U–Pb and Nd isotopes

Bastnäsité, the primary REE ore-bearing mineral at Mountain Pass, was observed only in carbonatite

samples. It occurs as tabular or elongate to acicular, subhedral to euhedral, honey-yellow to light brown crystals up to $\sim 1\text{mm}$ in sample MP-P0913-SQ1 (Fig. 14a), and as anhedral intergrowths with barite in samples MP-P0913-1B and MP-L0613-BDAY2 (Fig. 14b). It is occasionally intergrown with synchysite or parisite (Fig. 14c). The grains are compositionally heterogeneous and contain abundant inclusions of calcite, dolomite, and barite.

Table 7: Representative monazite LASS-ICP-MS geochronology data

Spot	U (ppm)	Th (ppm)	Pb (ppm)	Th/U	% ²⁰⁸ Pb common	Measured isotopic ratios					Apparent isotopic ages (Ma)									
						²⁰⁸ Pb/ ²⁰⁴ Pb	2SE %	²⁰⁷ Pb/ ²⁰⁶ Pb	2SE %	²⁰⁶ Pb/ ²³⁸ U	2SE %	Rho	²⁰⁸ Pb/ ²³² Th	2SE %	²⁰⁸ Pb/ ²³² Th age	2SE abs.	²⁰⁸ Pb*/ ²³² Th age	2SE abs.		
MP-P0913-SQ1 monazite (spot size = 9 μm, shot frequency = 3 Hz, shot count = 80, laser energy = 4 mJ at 100%)																				
1	5.8	2660	262.9	402	12.47	17.71	4.18	0.8188	1.92	0.54	172	1.000	0.07895	3.10	1536	48	0.06910	3.26	1350	44
2	3.5	2962	282.9	787	10.59	19.5	5.64	0.7726	1.95	0.33	239	1.000	0.07628	3.11	1486	46	0.06820	3.27	1333	44
3	4.1	2678	264.4	599	12.23	18.73	3.68	0.8085	1.88	1.4	85.7	1.000	0.07882	3.11	1533	48	0.06918	3.27	1352	44
4	7.1	4920	460	654	2.51	25.3	11.5	0.599	2.54	0.64	61.0	0.999	0.07458	3.13	1454	45	0.07271	3.28	1419	47
5	8.3	4287	414.7	503	8.43	19.98	4.55	0.727	3.04	1.3	76.9	0.999	0.07722	3.22	1503	48	0.07071	3.28	1381	47
6	11.1	5210	484	465	5.69	21.7	4.61	0.6705	1.94	1.32	23.5	0.997	0.07408	3.13	1444	45	0.06987	3.28	1365	45
7	8.4	3820	383.5	472	8.91	19.18	3.96	0.7392	1.76	0.72	72.2	1.000	0.08007	3.15	1557	49	0.07294	3.31	1423	47
8	3.8	3462	342.5	952	9.89	19.85	4.13	0.7511	2.03	1.1	155	1.000	0.07892	3.08	1535	47	0.07111	3.24	1389	45
9	7.4	2913	280.8	442	7.46	22	5.45	0.6667	1.98	0.55	81.8	1.000	0.07684	3.13	1496	47	0.07111	3.28	1388	46
10	3.4	2395	242.8	855	10.16	17.84	5.33	0.7772	1.97	0.16	475	1.000	0.08083	3.10	1571	49	0.07262	3.25	1417	46
11	4.1	4624	443.2	1087	8.46	21.85	2.88	0.6812	1.73	2.1	71.4	1.000	0.07640	3.11	1488	46	0.06993	3.27	1366	45
12	3.5	3155	309.9	909	12.10	17.86	3.53	0.8062	1.96	1	100	1.000	0.07833	3.10	1524	47	0.06885	3.26	1346	44
13	6.4	2726	254.4	446	9.70	26.5	5.28	0.5913	2.29	2.9	65.5	0.999	0.07435	3.13	1450	45	0.06714	3.28	1314	43
14	7	2556	267.2	417	13.40	19.58	4.03	0.7444	1.86	2.4	83.3	1.000	0.08324	3.07	1616	50	0.07209	3.23	1407	45
15	3.4	3468	329	1031	4.98	21.4	6.07	0.6843	2.07	1.2	150	1.000	0.07556	3.11	1472	46	0.07180	3.26	1401	46
16	3.6	4280	411	1370	6.67	18.17	4.57	0.7697	1.85	-0.25	252	1.000	0.07642	3.12	1488	46	0.07132	3.27	1392	46
17	4.7	3020	299.7	641	9.27	20	4.20	0.683	2.46	0.2	500	1.000	0.07895	3.52	1536	54	0.07164	3.66	1398	51
18	2.3	2565	255.8	1176	11.32	16.8	4.40	0.8047	1.85	-0.46	185	1.000	0.07931	3.37	1543	52	0.07033	3.52	1374	48
19	7.5	2964	289.3	410	9.82	19.42	3.60	0.7396	1.92	0.65	86.2	1.000	0.07763	3.39	1511	51	0.07001	3.53	1368	48
20	16	2805	285.4	182	9.44	22.41	3.93	0.6615	2.00	0.785	12.6	0.988	0.08096	3.43	1574	54	0.07332	3.57	1430	51
21	4.6	2378	245.3	588	12.91	19.38	3.51	0.7612	1.90	0.5	460	1.000	0.08204	3.54	1594	56	0.07144	3.68	1395	51
22	11	2789	268.3	262	7.30	24.5	5.31	0.6041	2.01	0.71	64.8	1.000	0.07648	3.55	1490	53	0.07090	3.68	1384	51
23	6.3	2761	262.7	476	6.03	18.3	7.10	0.713	2.19	-0.06	1217	1.000	0.07566	3.34	1474	49	0.07110	3.48	1388	48
24	8.9	3330	318.5	431	8.14	22	5.45	0.636	2.33	0.31	181	1.000	0.07590	3.40	1479	50	0.06972	3.54	1362	48
25	9.8	2472	233.9	269	7.16	20.8	6.73	0.6725	1.96	0.61	90.2	1.000	0.07506	3.48	1463	51	0.06968	3.62	1362	49
26	8.7	2671	255.9	324	10.10	19.4	4.23	0.7468	2.00	0.83	74.7	1.000	0.07598	3.47	1480	51	0.06831	3.61	1336	48
27	6.8	2908	267.8	463	6.69	20.3	5.91	0.731	2.17	0.55	105	1.000	0.07307	3.43	1425	49	0.06818	3.57	1333	48
28	10.4	2702	261.2	270	7.90	19.68	4.93	0.7128	2.04	0.71	52.1	0.999	0.07672	3.46	1494	52	0.07066	3.60	1380	50
29	10.3	3009	268	319	8.01	19.3	5.70	0.7442	1.94	0.08	1188	1.000	0.07066	3.33	1380	46	0.06500	3.48	1273	44
30	5.1	3530	328.9	752	5.31	22.3	6.28	0.694	2.33	0.27	226	1.000	0.07385	3.23	1440	47	0.06993	3.38	1366	46
31	15.6	3850	365	274	6.75	24.6	4.47	0.62	2.24	0.97	20.7	0.994	0.07510	3.34	1464	49	0.07003	3.49	1368	48
32	8.8	3214	301.9	397	6.78	19.9	5.53	0.716	2.19	0.19	321	1.000	0.07439	3.49	1450	51	0.06935	3.63	1355	49
33	4.6	3523	335.1	833	6.92	19.5	5.64	0.7666	1.94	0.33	188	1.000	0.07532	3.23	1468	47	0.07011	3.38	1370	46
34	5.4	3098	294.2	625	10.29	18.84	4.25	0.77	2.12	0.6	183	1.000	0.07524	3.48	1466	51	0.06750	3.62	1320	48
35	10.3	3803	354	394	7.91	21.3	4.69	0.7104	1.83	1.13	35.4	0.999	0.07374	3.42	1438	49	0.06791	3.56	1328	47
36	3.1	3004	288.1	1515	10.51	18.11	3.92	0.8117	1.85	0.23	430	1.000	0.07598	3.39	1480	50	0.06800	3.54	1330	47
37	4.4	3560	333.4	719	5.95	19.73	4.97	0.744	2.06	0.3	250	1.000	0.07420	3.33	1447	48	0.06979	3.48	1364	47
38	6.8	3477	327.7	568	9.63	18.77	4.79	0.782	2.02	1.12	72.3	1.000	0.07457	3.42	1454	50	0.06739	3.56	1318	47
39	25.5	5670	574	198	2.84	35.9	8.36	0.434	2.78	0.423	11.19	0.970	0.07923	3.50	1541	54	0.07698	3.64	1499	55
40	8.1	3356	322	372	6.73	20.6	4.85	0.721	2.18	0.5	220	1.000	0.07511	3.34	1464	49	0.07005	3.48	1369	48
41	3	3414	339.3	1053	8.43	19.53	3.84	0.7509	1.97	1.1	136	1.000	0.07778	3.24	1514	49	0.07122	3.39	1391	47
42	2.7	4053	402.5	1299	10.10	19.74	3.50	0.7739	1.79	2.2	59.1	1.000	0.07767	3.38	1512	51	0.06982	3.53	1364	48
43	3	3461	356.9	1190	10.93	17.77	4.22	0.8131	1.85	-0.3	833	1.000	0.08069	3.29	1568	52	0.07187	3.44	1403	48
44	8.3	2955	270.4	312	9.06	23.1	5.63	0.6728	1.88	1.3	100	1.000	0.07158	3.51	1397	49	0.06510	3.65	1275	47
45	4.1	3334	345.8	629	10.41	21.03	4.09	0.6866	1.95	—	—	—	0.08115	3.49	1577	55	0.07270	3.63	1419	51
46	9.7	3562	346.3	337	6.34	25.4	5.91	0.6383	2.08	0.42	110	1.000	0.07605	3.39	1482	50	0.07123	3.54	1391	49

(continued)

(continued)

Table 7: Continued

Spot	U (ppm)	Th (ppm)	Pb (ppm)	Th/U	% ²⁰⁸ Pb common	Measured isotopic ratios					Apparent isotopic ages (Ma)						
						²⁰⁸ Pb/ ²⁰⁴ Pb	2SE %	²⁰⁷ Pb/ ²⁰⁶ Pb	2SE %	²⁰⁶ Pb/ ²³⁸ U	2SE %	Rho	²⁰⁸ Pb/ ²³² Th	2SE %	²⁰⁸ Pb/ ²³² Th age abs.	2SE %	²⁰⁸ Pb* / ²³² Th age abs.
MMP-L0613-BDAY2 monazite (spot size = 9 μm, shot frequency = 3 Hz, shot count = 80, laser energy = 4 mJ at 100%)																	
1	2.7	7570	758	3030	0.57	13	92.3	0.457	3.41	-0.14	143	1.000	0.07129	2.11	2.34	1384	32
2	3.2	6790	690	2174	1.19	11.3	17.7	0.586	2.54	0.14	78.6	0.999	0.07205	2.11	2.34	1390	32
3	10.1	7730	803	781	1.13	18	66.7	0.604	2.49	0.08	238	1.000	0.07352	2.13	2.35	1418	33
4	6.5	16290	1670	2364	0.54	18.5	28.6	0.3733	2.91	0.51	106	1.000	0.07215	2.18	2.40	1401	34
5	7.7	17210	1717	2128	0.85	13.3	12.8	0.533	2.55	0.37	40.6	0.998	0.07023	2.29	2.50	1361	34
6	12.3	24100	2448	1880	0.51	27	37	0.392	3.18	0.36	38.9	0.997	0.07154	2.23	2.44	1390	34
7	1.9	12940	1263	6536	0.31	14.8	18.2	0.444	3.29	0.05	520	1.000	0.07029	2.15	2.37	1369	32
8	7.5	15700	1516	2198	0.57	14.5	8.97	0.616	2.21	0.54	61.1	0.999	0.06994	2.22	2.44	1359	33
9	5.2	2161	227	420	2.70	14.7	15	0.64	2.40	0.35	88.6	1.000	0.07661	2.40	2.60	1453	38
10	4.9	3490	370	719	1.52	16.3	17.2	0.598	2.51	0.14	393	1.000	0.07749	2.47	2.66	1486	40
11	3.1	9310	939	3333	0.20	9.5	65.3	0.361	4.42	0.04	275	1.000	0.07383	2.60	2.79	1437	40
12	5.7	19560	1830	3448	0.39	22.4	38.4	0.467	3.54	0.24	313	1.000	0.06844	3.89	4.01	1333	54
13	5.6	12840	1305	2252	0.45	19.7	15.2	0.515	2.45	0.34	221	1.000	0.07441	2.41	2.61	1444	38
14	4.3	11270	1136	2500	0.39	18.8	17.6	0.4625	2.58	-0.14	429	1.000	0.07382	2.60	2.78	1434	40
15	26.2	8870	889	355	1.54	11.95	5.69	0.694	2.08	0.19	8.48	0.971	0.07342	2.28	2.49	1411	35
16	8	8080	815	1087	1.02	13.4	18.7	0.582	2.98	0.26	50	0.998	0.07409	2.37	2.57	1445	37
17	23.6	10560	1012	448	1.05	14.5	15.9	0.686	2.53	0.203	13.3	0.982	0.07033	3.37	3.51	1360	48
18	37.2	16540	1538	441	0.69	15.2	11.2	0.587	4.36	0.135	13.4	0.951	0.06820	2.45	2.64	1325	35
19	10	20530	2006	1949	0.22	22	72.7	0.381	3.02	0.29	29.7	0.995	0.07176	2.55	2.74	1398	38
20	52.6	16050	1526	309	1.29	13.22	4.99	0.678	2.32	0.158	8.29	0.963	0.06978	2.36	2.56	1346	35
21	12.7	4590	466	373	1.32	23.6	6.36	0.3244	2.06	0.393	13.8	0.989	0.07455	2.41	2.61	1435	37
22	27.9	5720	573.4	195	0.35	20	240	0.3513	2.43	0.1176	8.06	0.958	0.07177	2.41	2.61	1396	36
23	105	3644	288	31	5.05	17.04	3.93	0.5643	1.95	0.1233	5.29	0.938	0.05588	3.11	3.27	1045	34
24	234	2673	191.1	11	8.09	16.43	3.65	0.602	1.92	0.089	16.9	0.994	0.05048	6.64	6.72	917	62
25	215	4550	350	20	1.99	25.1	14.7	0.4443	2.58	0.0359	8.14	0.953	0.05433	3.77	3.90	1049	41
26	11	3745	398.9	327	1.15	32	37.5	0.4651	2.47	0.57	57.9	0.999	0.07541	2.49	2.69	1453	39

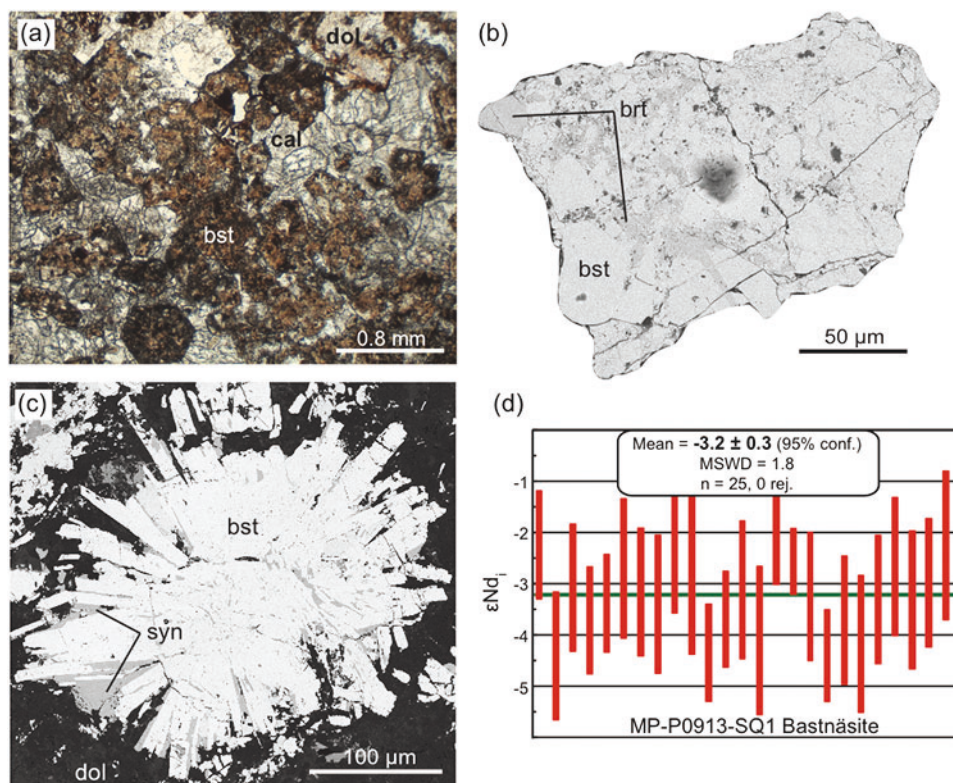


Fig. 14. Examples of bastnäsite in MPIS carbonatite. (a) Plane-polarized light photomicrograph of bastnäsite in a matrix of calcite and minor dolomite in carbonatite thin section (MP-P0913-SQ1). (b) BSE image of bastnäsite–barite intergrowth in grain mount (carbonatite sample MP-P0913-1B). (c) BSE image of intergrowth between bastnäsite and synchysite–parisite in carbonatite thin section. (d) Weighted mean plot of ϵNd_i for bastnäsite in carbonatite (MP-P0913-SQ1). brt, barite; bst, bastnäsite; cal, calcite; dol, dolomite; syn, synchysite/parisite.

Bastnäsite from two carbonatite samples was analyzed for U–Pb and Nd isotopes. Both samples are very low in U (<10 ppm), and have high and variable common Pb contents. The low U combined with the large scatter in Pb and U/Pb isotopic ratios suggest that bastnäsite has behaved as an open system with respect to Pb; thus reliable dates could not be calculated and bastnäsite U–Pb data are not considered further. The open-system behavior described here for bastnäsite was also reported by DeWitt *et al.* (1987, 2000). In contrast, Nd isotopic analysis of bastnäsite from sample MP-P0913-SQ1 yielded relatively consistent ϵNd_i values with a weighted mean ϵNd_i of -3.2 ± 0.3 (MSWD = 1.8), consistent with ϵNd_i from monazite in the same sample (Figs 13e and 14d). A date of 1380 Ma was used for bastnäsite ϵNd_i age correction, based on the sample's mean monazite Th–Pb date of 1371 ± 10 Ma (see above). Bastnäsite Nd isotopic data are reported in Supplementary Data Electronic Appendix 6.

DISCUSSION

Trace element sinks in an ultrapotassic silicate-carbonatite suite

Trends observed between whole-rock major element oxides in Mountain Pass shonkinite and syenite may be

attributed to differences in the modal abundance of major and accessory phases. The trends observed between major elements and silica in MPIS rocks, such as increasing Al_2O_3 with increasing silica and lack of trend between K_2O and silica, are common in other ultrapotassic suites (Foley *et al.*, 1987; Castor, 2008). Decreasing Mg and Ca contents with increasing silica content are controlled by the greater modal abundance of clinopyroxene (Mg, Ca) and apatite (Ca) in low-silica samples. Decreasing Fe content with increasing silica is probably a product of decreased abundance of clinopyroxene and biotite. Lower P_2O_5 is probably due to decreased abundance of apatite in more felsic samples. TiO_2 also decreases with increasing silica, probably owing to the high abundance of Ti-bearing biotite in mafic samples, which has been reported in previous studies (Haxel, 2005; Castor, 2008). Higher Ti in mafic samples may also be due in part to the presence of clinopyroxene (Haxel, 2007). Increased levels of Al and Na in high-silica samples are probably due to greater abundances of K-feldspar and plagioclase, the latter of which is mostly absent in mafic samples. Potassium does not show a marked trend, presumably because of the high abundance of biotite in mafic samples and K-feldspar in felsic samples.

The higher abundance of compatible trace elements (i.e. Cr, V) in mafic samples is characteristic of most

igneous suites, and is probably controlled primarily by clinopyroxene and biotite. The high abundance of incompatible trace elements in mafic MPIS samples (i.e. Ba, Sr, and LREE) is atypical of most igneous suites, but is common in ultrapotassic suites (Foley *et al.*, 1987; Castor, 2008) and reflects high modal percentages of incompatible element-rich phases in the mafic samples. Apatite analyzed in this study typically has Sr contents in the tens of thousands of ppm range (Supplementary Data Electronic Appendix 11), and is probably the predominant sink for Sr in the less evolved rocks, as it is most abundant in these samples. High Ba content is probably due to high-Ba biotite, which was noted by Haxel (2005) and Castor (2008). The absence of plagioclase in mafic MPIS rocks indicates that it is unlikely to account for high Sr and Ba in mafic samples, and is therefore not an important host to these elements.

Chondrite-normalized REE patterns of the whole-rock samples analyzed in this study are typical of ultrapotassic rocks, most notably the high LREE to HREE slope and lack of an Eu anomaly (e.g. Foley *et al.*, 1987; Castor, 2008), the latter indicating that plagioclase fractionation was not a significant factor in the magmatic history of the MPIS—consistent with the paucity of plagioclase in these rocks.

The higher abundance of LREE in low-silica samples is most probably due to the abundance of apatite. Apatite has been noted as an important REE host in alkaline rocks (e.g. Zhou & Wang, 1989; Krenn *et al.*, 2012), and forms up to ~3% of the mafic MPIS samples in this study. Previous studies have reported up to 5% apatite in mafic MPIS samples (Woyski, 1980; Haxel, 2005). For MPIS samples in which apatite was analyzed, its modal abundance accounts for ~30–40% and ~40–70% of the whole-rock Ce content for felsic and mafic samples, respectively (Supplementary Data Electronic Appendix 12). Titanite is also an important REE host—it is known to incorporate up to ~4 wt % REE in alkaline igneous rocks (e.g. Vuorinen & Hålenius, 2005), and is commonly considered an important REE sink in silicate magmas (e.g. Gromet & Silver, 1983; Sawka *et al.*, 1984). Although the modal abundance of titanite is poorly constrained in most samples, for samples in which its approximate modal abundance is known, the modal abundance of titanite accounts for ~5–20% of whole-rock Ce (Supplementary Data Electronic Appendix 12). Titanite in apatite-poor samples contains higher LREE—for example, titanite accounts for up to ~90% of whole-rock Ce in one apatite-poor leucosyenite sample (MP-P0714-17). However, titanite modal abundance is similar in both mafic and felsic samples, and therefore the observed trends in REE cannot be explained by differences in its relative abundance between rock types. Monazite is present in some felsic MPIS samples, and must account for some of the whole-rock LREE in these samples. Sodic amphibole may also contain a significant amount of the whole-rock LREE (e.g. Bea, 1996); however, amphibole composition was not determined.

The HREE, Th, and U contents of the samples do not show a trend with major element composition. Metamict, high-Th, high-U, and HREE-rich zircon (e.g. Fig. 9a and b, Supplementary Data Electronic Appendix 7) is ubiquitous in MPIS rocks of all compositions. Zircon has been shown to be a significant host to HREE in granitoids (Bea, 1996) and actinides in alkaline rocks (e.g. Žáček *et al.*, 2009), suggesting that zircon may be an important host to HREE, Th, and U in the MPIS. Concordant zircon grains utilized for geochronology data are less abundant and contain much lower Th, U, and HREE than metamict grains (e.g. Table 5), and are thus not considered. An approximate modal abundance of ~0.125–0.25% metamict zircon accounts for ~30–70% of whole-rock Yb content in felsic samples (Supplementary Data Electronic Appendix 12). In mafic samples, however, zircon only contains ~5–15% of the whole-rock Yb. Apatite and titanite each account for ~8–20% of the whole-rock Yb in all samples, regardless of composition. Sodic amphibole may account for the bulk of the remaining HREE—it is common in mafic to intermediate MPIS rocks, and is known to contain appreciable HREE (e.g. Bea, 1996). Approximately 5–30% of whole-rock Th can be attributed to zircon, whereas apatite accounts for ~4–10% (but as much as 20%) and titanite for <1–3% (Supplementary Data Electronic Appendix 12). Thorite was also observed in some samples, and probably contains the bulk of whole-rock Th—less than 0.02% modal thorite would be required to account for the whole-rock Th in most samples. For two samples with the highest whole-rock Th content (MP-P0913-5A and MP-P0714-17), ~0.03% and 0.05% modal thorite would be required, respectively. Where present, monazite also accounts for some of the whole-rock Th, but occurs primarily in felsic samples and is not present in significant abundance. Most of the whole-rock U (65–90% or more) can be attributed to zircon, whereas apatite and titanite each account for ~1–15% (Supplementary Data Electronic Appendix 12).

Together, these data indicate that apatite is probably the most important host of LREE in these rocks, followed by titanite. Apatite, titanite, and zircon are probably important HREE hosts, but amphibole may also host significant amounts of HREE in mafic samples. Thorite and zircon are the most important hosts to Th and U, respectively. Monazite contains abundant REE and Th, but is not present in significant amounts in most samples and appears to occur only as a secondary phase. The presence of monazite in veins may indicate that monazite grew from a late-stage fluid, as suggested by Stoeser (2013)—in this case, monazite may be an additional primary REE host in some samples. Alternatively, the presence of monazite and rutile in rocks with titanite that appears to be breaking down (Fig. 5c), and the lack of titanite in rocks that contain significant monazite and rutile (e.g. MP-P0913-2), may indicate that the latter two phases grew at the expense of titanite, and thus host REE, Th, and HFSE that were formerly hosted by titanite.

Based on these data, apatite, titanite, zircon, thorite, and sodic amphibole are likely to have played the most important roles in controlling the REE, HFSE, and actinide budget of the ultrapotassic magmas as they crystallized.

Geochronology of the MPIS

Ultrapotassic silicate rocks

With the exception of two samples that have undergone minor disturbance of the U–Pb system and therefore record two discrete age populations (samples MP-P0714-16 and MP-P0714-26), titanite in the ultrapotassic rocks of the MPIS consistently yields single-population U–Pb dates that range from 1429 ± 10 to 1385 ± 18 Ma (Fig. 6). In contrast, zircon yields complex and chiefly discordant U–Pb data (Fig. 10), providing minimal age information for most samples. Based on textural observations, monazite in the ultrapotassic rocks appears to be secondary, and yields scattered and imprecise Th–Pb and U–Pb dates (Fig. 13).

Several lines of evidence indicate that titanite is most probably a primary phase and that the titanite dates are best interpreted as the igneous crystallization ages of the ultrapotassic rock samples: (1) detailed petrographic observation indicates that titanite is generally euhedral to subhedral and shows interlocking textures with primary igneous mineral assemblages (Fig. 5a and b), suggesting that it crystallized directly from a melt; (2) where present, titanite alteration textures suggest that it is primary and has partially reacted to form secondary minerals (Fig. 5c), rather than grown in response to alteration; (3) chondrite-normalized REE patterns in Mountain Pass titanite are similar to chondrite-normalized REE patterns from Mountain Pass ultrapotassic rocks in terms of LREE enrichment and lack of an Eu anomaly (Figs 4 and 7a), suggesting that both crystallized from the same melt; (4) Zr-in-titanite thermometry predominantly yields temperatures of 700°C and higher, consistent with an igneous origin (Fig. 7b); (5) dates obtained from oscillatory-zoned, concordant zircon overlap the titanite dates within uncertainty in four of five samples. Taken together, and as stated above, these data suggest that titanite is most probably a primary igneous phase in the Mountain Pass ultrapotassic rocks, and has recorded the same igneous crystallization event that is sparsely recorded by zircon. We attribute titanite U–Pb age sub-populations in MP-P0714-16 and MP-P0714-26 to subtle loss of radiogenic Pb, and the ages of the samples are interpreted to be represented by their older age components (Fig. 6). The variability in apparent Zr-in-titanite temperatures in all but the youngest samples (MP-P0913-10C and MP-P0714-17) suggests that some titanite grains may have recorded lower apparent Zr-in-titanite temperatures in response to thermal disturbance during emplacement of later phases of magma, which may provide an explanation for the subtle loss of radiogenic Pb in MP-P0714-16 and MP-P0714-26.

Despite their scarcity, concordant zircon dates are present in six samples, ranging from 1458 ± 7 to

1407 ± 11 Ma, and, based on crystal morphology and oscillatory zonation, are regarded as reflecting igneous crystallization ages in five of these samples. Concordant dates from ~ 1635 to 1800 Ma are derived from multiple, discrete grains in MP-P0913-5A and MP-P0913-6; these are interpreted as xenocrystic zircon inherited from the host-rocks based on their similarity to zircon from the host-rock in terms of age, morphology, and $\text{Th/U} < 1$ (see description of zircon above). MP-P0913-5A also yielded zircon dates from 1600 to 1430 Ma from three large, rounded grains that do not overlap with either host-rock zircon dates, or zircon dates from other MPIS rocks (Fig. 10b, [Supplementary Data Electronic Appendix 8](#)). These are interpreted as ‘mixed’ dates resulting from sampling of both Mesoproterozoic overgrowths and inherited, Paleoproterozoic cores of grains. Additionally, these zircon grains have Th/U ratios < 1 ([Supplementary Data Electronic Appendix 8](#)), the same as for zircon older than 1640 Ma in the sample and zircon from the host-rocks. In contrast, all zircon grains younger than 1430 Ma in this sample (as well as most zircon grains from all other MPIS samples except MP-P0913-10B) have $\text{Th/U} > 1$ ([Supplementary Data Electronic Appendix 8](#)); therefore, zircon grains with $\text{Th/U} < 1$ are excluded from the age interpretation of MP-P0913-5A.

MP-P0913-10C is the only sample in which zircon yields only Mesoproterozoic dates, but titanite and zircon dates do not coincide (Figs 6 and 10e). This rock crosscuts another rock (MP-P0913-10B) that yields younger overlapping dates from titanite and oscillatory-zoned zircon (e.g. Figs 2c and 6, [Supplementary Data Electronic Appendix 8](#)). We therefore infer that the U–Pb zircon age does not reflect the crystallization age of this rock; instead, we prefer the interpretation that these zircon grains are inherited, and a result of recycling of older zircon within the MPIS.

Carbonatite

The Th–Pb monazite crystallization ages of carbonatite samples MP-L0613-BDAY2 and MP-P0913-SQ1 are inferred to be ~ 1405 – 1395 Ma and ~ 1380 – 1370 Ma, respectively. We attribute the excess scatter ($\text{MSWD} = 4.2$ and 1.6 , respectively) observed in the samples to be a result of variable but minor radiogenic Pb loss, which probably skews their mean dates toward younger ages. Regardless, monazite Th–Pb dates from carbonatite overlap titanite and zircon U–Pb dates < 1415 Ma from the ultrapotassic rocks within uncertainty—indicating that carbonatite magmatism and the latter stages of ultrapotassic magmatism at Mountain Pass were broadly coeval.

Timescales of ultrapotassic silicate–carbonatite magmatism at Mountain Pass

U–Pb zircon dates from ultrapotassic rocks in the Birthday and Corral stocks (Fig. 1b) constrain ultrapotassic magmatism in these locations to ~ 1430 – 1420 Ma

(Fig. 15). Although less precise, titanite dates corroborate these ages. Zircon and titanite dates from ultrapotassic rocks in the Tors, Mexican Well, and Wheaton stocks indicate a second stage of magmatism c. 1410–1400 Ma (Figs 1b and 15). The mean Th–Pb date of 1396 ± 16 Ma from monazite in carbonatite dike sample MP-L0613-BDAY2 suggests that this stage was accompanied by emplacement of carbonatite dikes (Figs 2d and 15). We interpret titanite dates of 1385 ± 18 Ma and 1358 ± 71 Ma from shonkinite and syenite dikes (MP-P0913-10C and MP-P0714-17), respectively, to record the latest stage of ultrapotassic magmatism at c. 1380–1370 Ma, on the following basis: (1) the dikes cross-cut 1410–1400 Ma syenite; (2) the dikes are continuous and do not appear to be deformed, suggesting that they were not comagmatic with the rock they cross-cut (Fig. 2c); (3) previous work suggests that a shonkinite vein cross-cuts carbonatite (Olson & Pray, 1954), indicating relatively late emplacement of shonkinite dikes and veins. The mean monazite Th–Pb date of carbonatite sample MP-P0913-SQ1 indicates that this stage was accompanied by emplacement of the Sulphide Queen stock (Figs 1b and 15).

The geochronology results reveal that ultrapotassic silicate–carbonatite magmatism at Mountain Pass occurred episodically over ~45–50 Myr, a relatively long period of time considering the small volume of

these rocks that is now exposed. However, alkaline and carbonatite magmatism in other locations around the world is commonly long-lived within a restricted area (Jones *et al.*, 2013). For example, alkaline igneous rocks in the Southern Granulite Terrain of India (Santosh *et al.*, 2014), the Paraná–Etendeka large igneous province in Paraguay (Gibson *et al.*, 2006), and the Monteregian Hills of Quebec, Canada (Eby, 1984) were all shown to have been emplaced in two distinct episodes ~20 Myr apart. Additionally, alkaline igneous rocks in the Chilwa Alkaline Province of Malawi were emplaced in three phases ~10 Myr apart (Eby *et al.*, 1995). The ~45 Myr age range of MPIS rocks is longer than these other occurrences, but regardless, the temporal range of ultrapotassic and carbonatitic magmatism at Mountain Pass is consistent with temporal relationships observed in other alkaline rock occurrences, and indicates repeated partial melting of the source(s) of the MPIS during the Mesoproterozoic.

Petrogenetic processes recorded by mineral-scale Nd and Hf isotopes

Titanite ε_{Nd} values from the ultrapotassic rocks at Mountain Pass predominantly range between –3.5 and –6, with the highest values in all but one sample overlapping the ε_{Nd} (–2.5 to –3.5) values obtained from

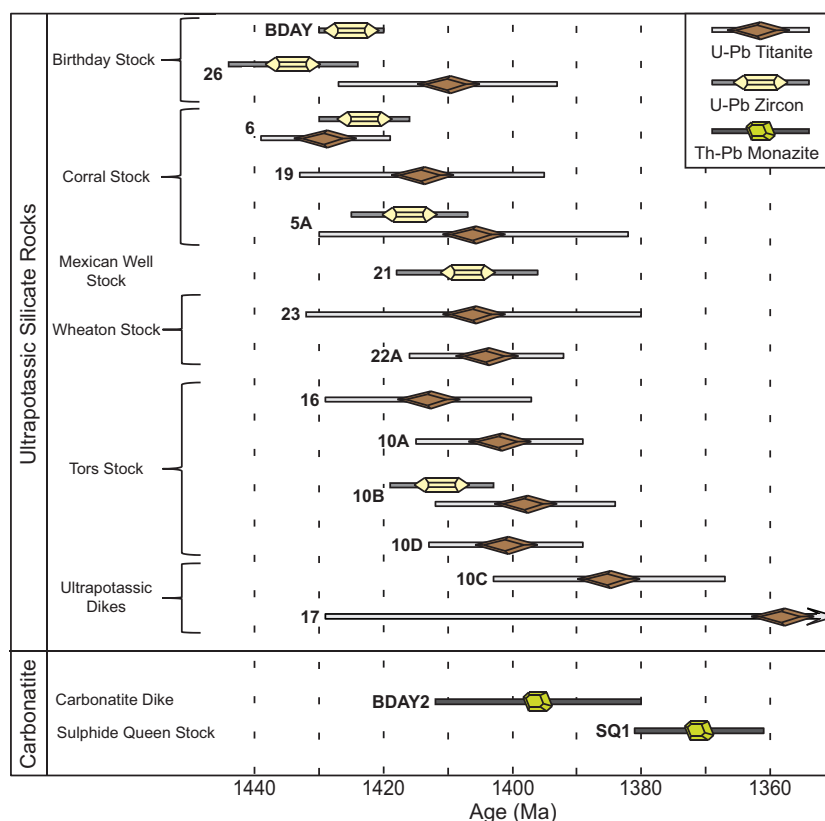


Fig. 15. Summary of titanite, zircon, and monazite dates from all samples analyzed in this study. Each date and associated uncertainty is from all analyses of a specific mineral interpreted as an age. It should be noted that the uncertainty of one sample extends to the right beyond the width of the plot ('17' = MP-P0714-17, titanite date = 1358 ± 71 Ma). Locations of samples in the field area are indicated.

monazite and bastnäsite in MPIS carbonatite (Fig. 8). The overlap of ϵNd_i of the carbonatite and the most primitive ϵNd_i of the ultrapotassic rocks supports the idea that they are related and probably derived from a common source.

In contrast to titanite Nd isotopic data, zircon ϵHf_i from Mesoproterozoic zircon in the same rocks does not systematically differ within or between samples, with all data from all samples giving a weighted mean of 1.9 ± 0.2 (MSWD = 0.9, Fig. 12). These data support the hypothesis that MPIS ultrapotassic rocks are all derived from the same source and, more regionally, coincide with previously reported zircon ϵHf_i for ~1.4 Ga granitoids throughout the Mojave Desert (Wooden *et al.*, 2012, Fig. 1a).

Variable titanite ϵNd_i and consistent zircon ϵHf_i indicate that the Nd isotopic signature of some titanite has been influenced by a process that did not have a noticeable effect on zircon ϵHf_i . Possible explanations include (1) magma mixing, (2) contamination of the magma by wall-rock, and/or (3) post-crystallization disturbance of the Nd isotopic system in titanite.

Pankhurst *et al.* (2011) attributed variable titanite ϵNd_i values in an A-type granite to mixing of parental magmas. DeWitt *et al.* (2000) interpreted Pb and Nd isotope data to record mixing of melts derived from mantle and lower crustal sources of variable age to produce the MPIS carbonatite magma. Thus, some variability in titanite ϵNd_i from MPIS ultrapotassic rocks may be attributable to mixing between magmas from different source regions with different Nd isotopic signatures. However, the same variability is not observed in carbonatite or the youngest ultrapotassic rocks, suggesting

that this may be the case only for the earliest MPIS rocks (Fig. 8).

The low ϵNd_i in titanite from ultrapotassic rock samples may be explained by assimilation of crustal material, either the host-rocks exposed at Mountain Pass or unexposed basement rocks of the Mojave Crustal Province. This hypothesis is supported by the general decrease in ϵNd_i with increasing SiO_2 content in the oldest (~1430–1420 Ma) and youngest (~1380–1370 Ma) MPIS samples (Fig. 8) — assimilation of felsic country rock and accompanying fractional crystallization would have increased the SiO_2 content of the magmas. A binary mixing model demonstrates that the variability in Nd isotopic signatures of MPIS titanite can be explained by assimilation (Fig. 16). In this model, mean titanite ϵNd_i values are used to approximate whole-rock ϵNd_i for each sample, parameters for the primary magma are estimated based on the most primitive MPIS samples (~45 wt % SiO_2 , ~325 ppm Nd, $\epsilon\text{Nd} \sim -3$), and parameters for the contaminant are estimated using 70 wt % SiO_2 to approximate a granitic (*sensu lato*) composition. Using these parameters, ~70% contaminant and ~30% primary magma would be required to produce the MPIS sample with the highest silica content (MP-P0913-5A, ~65 wt % SiO_2) through binary mixing. Assuming that MP-P0913-5A is 70% contaminant, a curve fit to the MPIS samples in ϵNd vs $1/\text{Nd}$ space defines a contaminant end-member with $\epsilon\text{Nd} \sim -15$ and a Nd concentration of ~150 ppm (Fig. 16). Nd abundance and isotopic data have not been reported for Mountain Pass host-rocks, making the definition of this end-member difficult. Additionally, a binary mixing model is perhaps an oversimplification, as fractional

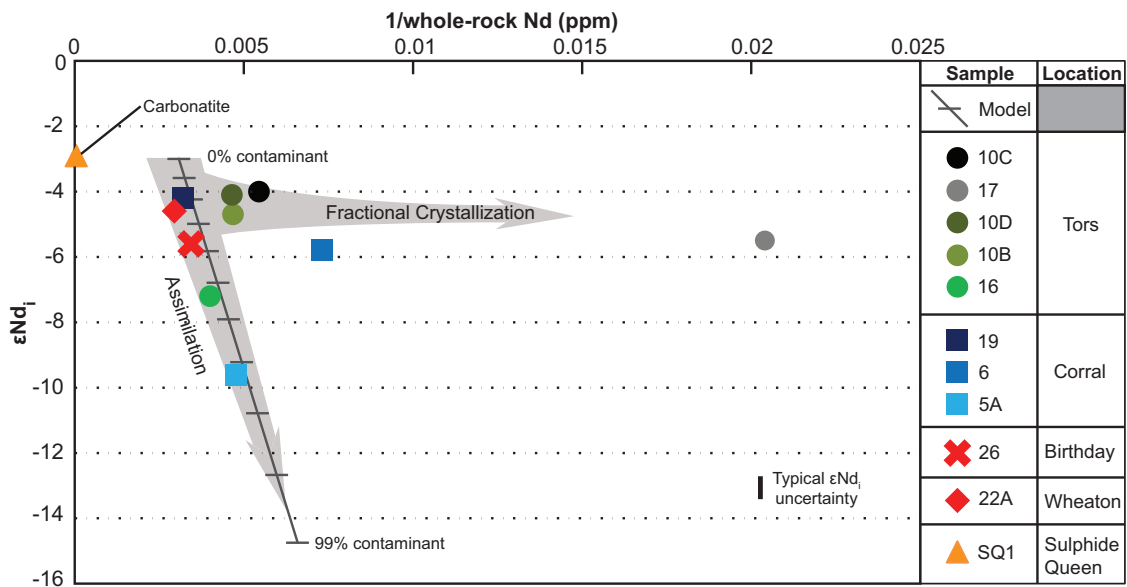


Fig. 16. Nd isotope binary mixing model for MPIS rocks. Each data point is a mean titanite ϵNd_i value from all analyses in one sample, used here to approximate whole-rock ϵNd_i . Typical uncertainty on the mean ϵNd_i is shown by the vertical bar at the lower right (± 0.7 ϵ -units). Each bar on the mixing model line represents 10% increments (i.e. addition of 10% contaminant to the original magma).

crystallization must have accompanied assimilation and would also have increased the SiO_2 content of the evolving magma. However, an assimilation–fractional crystallization model (DePaolo, 1981) with a ratio of assimilation rate to fractional crystallization rate (r) = 1 and relatively high bulk partition coefficient (D) = 0.8–1.2 for Nd (estimated based on the high proportion of apatite and titanite in the most primitive samples) yields a very similar result. In summary, a binary mixture of ~30% primary magma with 325 ppm Nd, $\epsilon_{\text{Nd}} = -3$, and 45 wt % SiO_2 and ~70% contaminant with ~150 ppm Nd, $\epsilon_{\text{Nd}} = -15$, and ~70% SiO_2 would be required to produce MP-P0913-5A (mean $\epsilon_{\text{Nd}_i} \sim -9.6$ and ~65 wt % SiO_2 , Figs 8 and 16). MP-P0913-5A contains abundant inherited zircon grains (Fig. 10b) and xenoliths of host gneiss and granite, providing direct evidence of crustal assimilation. Samples MP-P0913-6 and MP-P0714-17 fall off of the mixing curve and can be explained by a combination of fractional crystallization and assimilation ($\leq 40\%$ assimilation; Fig. 16).

The uniformity of the zircon ϵ_{Hf_i} in MPIS rocks indicates that the Hf isotope compositions of the magmas were unaffected by contamination. This could be explained by a contaminant with a very low Hf concentration relative to the primary magmas. Primitive MPIS samples contain ~12 ppm Hf (Table 2), requiring the Hf content of the contaminant to be $< \sim 2$ ppm based on the mixing parameters above. It is more likely that zircon was the dominant Hf reservoir in the contaminant and was not dissolved when incorporated into the ultrapotassic magma, resulting in contamination of the magma without a noticeable effect on the Hf isotopic composition of the melt. This is feasible, given the high distribution coefficient (K_d) for Hf between zircon and common silicate melts (e.g. Mahood & Hildreth, 1983; Fujimaki, 1986), and because of the abundance of euhedral (apparently undissolved), inherited zircon in some MPIS samples. An alternative explanation is that the MPIS and its host-rocks have a similar Hf isotopic composition. However, this would suggest that the host-rocks plot far above the ϵ_{Hf_i} – ϵ_{Nd_i} terrestrial array of Vervoort *et al.* (1999); that is, they have ϵ_{Hf_i} between ~2 and 0, and $\epsilon_{\text{Nd}_i} \approx -15$ (from the model presented above); this is therefore an unlikely explanation.

Post-crystallization disturbance of the Nd isotopic system in titanite could also explain the source of Nd isotopic variation in at least two samples (MP-P0714-16 and MP-P0714-26). These samples yielded two sub-populations of U–Pb data (Fig. 6), and also have some of the lowest and most variable ϵ_{Nd_i} values (as low as -10.7 ; Fig. 8). Titanite from these samples may record the ϵ_{Nd_i} of an altering fluid that post-dated crystallization (e.g. Shawe, 1952), in addition to potential mixing of magma from different sources and/or magma contamination by wall-rock. The variable ϵ_{Nd_i} and relatively low silica content in these two samples alone suggests that magma contamination may be a less likely scenario to account for their Nd isotopic composition. Furthermore, post-crystallization disturbance of titanite

provides a potential explanation for the subtle loss of radiogenic Pb observed in these two samples. We favor this interpretation over disturbance to the U–Pb system in these samples by later intrusion of magma, because the latter scenario does not explain the variability in ϵ_{Nd_i} in these samples.

In summary, mineral-scale Nd and Hf isotopic data reported here are interpreted to indicate derivation of Mountain Pass ultrapotassic rocks and carbonatite from the same source, potential mixing of magma from two or more sources to produce these magmas, and crustal contamination of some of the ultrapotassic magmas. Post-crystallization disturbance of the Nd isotopic signature in titanite by a secondary fluid can convincingly be demonstrated in only two of the analyzed samples.

Petrogenetic model for the Mountain Pass Intrusive Suite

Despite the temporal overlap between ultrapotassic and carbonatite magmatism at Mountain Pass, available data suggest that the two are unlikely to have differentiated from a common parental melt. Derivation of the carbonatite from a silicate melt by fractional crystallization implies either that the carbonatite is a cumulate that crystallized from a silicate melt (e.g. Gittins & Harmer, 2003; Downes *et al.*, 2005) or that it is the most evolved member of the suite and represents a late-stage, residual liquid. It seems unlikely that the carbonatite is a cumulate because it does not fall along an evolutionary trend with the ultrapotassic rocks (Fig. 17a and b). Furthermore, a cumulate should be composed primarily of crystals and is therefore unlikely to intrude subsequently as cross-cutting dikes or to differentiate into different types of carbonatite (i.e. sövite and befor-site); additionally, it should contain trapped intercumulus material that represents the silicate melt from which it crystallized, which is not observed.

Alternatively, if the carbonatite represents a late-stage, residual liquid, incompatible elements that are abundant in the carbonatite (i.e. Ba, Sr, LREE) should be least abundant in primitive (i.e. low-silica) members of the MPIS ultrapotassic suite and most abundant in evolved (i.e. high-silica) members. However, the most primitive members of the MPIS ultrapotassic suite have the highest Ba, Sr, and LREE, whereas the most evolved members have the lowest contents of these elements (Fig. 3). Furthermore, the carbonatite and ultrapotassic rocks do not occur in a concentrically zoned, plug-like intrusion with a relatively small core of carbonatite surrounded by alkaline silicate rocks, as has been documented in other locations and cited as evidence for carbonatite representing a volumetrically small, late-stage residual liquid (e.g. Juquiá complex in Brazil, Beccaluva *et al.*, 1992; Salmagorskii complex in Russia, Korobeinikov *et al.*, 1998). On the contrary, field evidence shows that the carbonatite and ultrapotassic magmas were emplaced separately (e.g. Fig. 2d),

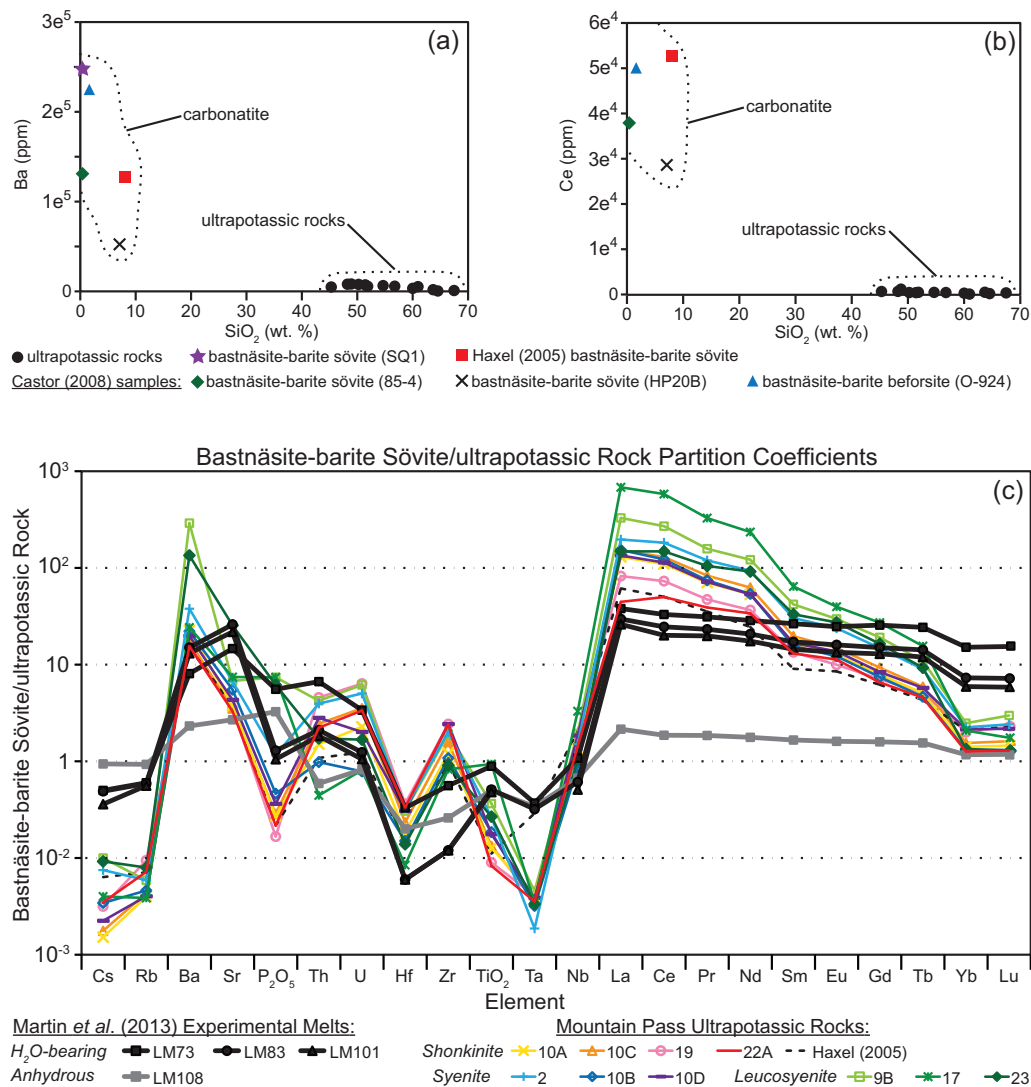


Fig. 17. Whole-rock variation diagrams and carbonatite/ultrapotassic rock trace element ratio plot for MPIS rocks. (a) Ba vs silica plot for MPIS carbonatite and ultrapotassic rocks. (b) Ce vs silica plot for MPIS carbonatite and ultrapotassic rocks. Sample SQ1 is not shown, but contains ~138 000 ppm Ce and <1 wt % SiO₂ and thus plots above the carbonatite samples shown. (c) Bastnäsite-barite sövite/ultrapotassic rock trace element patterns for MPIS rocks. Experimental data shown for comparison are from [Martin et al. \(2013\)](#). Bastnäsite-barite sövite data are from [Haxel \(2005\)](#); the plotted elements are all of those that are available from this dataset. Samples MP-P0913-5A, MP-P0913-6, MP-P0714-16, and MP-P0714-26 are interpreted as being contaminated based on Nd isotopes, and are not shown, but plot similarly to samples shown here.

requiring that a parental magma would have had to undergo protracted fractional crystallization prior to mobilization and emplacement of its products. Taken together, these data indicate that if the carbonatite and ultrapotassic rocks were derived from a common parental melt, liquid immiscibility and physical separation of carbonatite and ultrapotassic melts would have to have occurred at some point along its evolutionary path.

Partition coefficients between immiscible carbonatite and silicate liquids have been determined for a number of elements by experimental studies (e.g. [Veksler et al., 1998, 2012; Martin et al., 2012, 2013](#)), providing a quantitative method for evaluating whether or not carbonatite and alkaline silicate rocks at a given locality are potentially related by liquid immiscibility. We compared the experimental data of [Martin et al. \(2013\)](#) from H₂O-

bearing, potassic systems with MPIS data from [Haxel \(2005\)](#), [Castor \(2008\)](#), and this study to test the liquid immiscibility hypothesis for MPIS ultrapotassic rocks and carbonatite. Although the experiments of [Martin et al. \(2013\)](#) were performed at higher pressures (1–3 GPa) than that of the MPIS emplacement (~0.1 GPa), the experiments of [Veksler et al. \(1998\)](#) were carried out at lower pressures (<1 GPa) and yielded similar results for melts of comparable composition.

The ratios of trace elements between MPIS carbonatites [bastnäsite-barite sövite from [Haxel \(2005\)](#)] and ultrapotassic rocks (from this study) are significantly different from the experimentally derived carbonatite-silicate partition coefficients of [Martin et al. \(2013\)](#). The MPIS carbonatite/ultrapotassic rock ratios are lower for P₂O₅, TiO₂, Cs, Rb, and HREE, and higher for Zr than the

experimental melts (Fig. 17). Additionally, ratios are lower for Ta in all but one sample, and higher for LREE in all but one sample. Carbonatite/ultrapotassic rock trace element ratios for bastnäsite–barite sövite analyzed in this study show similar differences from the experimental data, and are also lower for K₂O, Na₂O, Al₂O₃, and Zr, and higher for Pb and LREE (see [Supplementary Data Electronic Appendix 13](#) for partition coefficient plots). Carbonatite/ultrapotassic rock trace element ratios calculated with MPIS carbonatite samples from [Castor \(2008\)](#) (sövite, dolomitic sövite, and beforite) show similar discrepancies.

A key difference between the MPIS carbonatite and experiments is that experimental immiscible carbonatite liquids are invariably alkali-rich (e.g. [Veksler et al., 1998, 2012; Martin et al., 2012, 2013](#)), whereas MPIS carbonatite is distinctly alkali-poor (Na₂O + K₂O < 2). However, this may be due in part to late-stage alkali loss, which some researchers have argued is common in carbonatites ([Bell et al., 1999; Martin et al., 2013](#)), and may also have resulted in depletion of large ion lithophile elements (LILE) such as Cs and Rb. Regardless of alkali content, carbonatite/ultrapotassic rock ratios for a multitude of elements differ from those of experimental immiscible carbonatite–potassic silicate melts, and suggest that the MPIS rocks are unlikely to be related by liquid immiscibility. This suggests, then, that MPIS carbonatite was generated as a primary carbonatitic melt.

A number of studies have contended that some, if not most, carbonatites are primary, mantle-derived melts (e.g. [Harmer & Gittins, 1998; Harmer, 1999; Gittins & Harmer, 2003; Ying et al., 2004](#)). In cases where primary carbonatites are associated with alkaline silicate rocks, the two may still be closely related despite being generated from separate melts. A number of studies have shown that carbonatite melts may metasomatize mantle rocks (e.g. [Green & Wallace, 1988; Yaxley et al., 1991; Hauri et al., 1993; Rudnick et al., 1993](#)), and [Harmer \(1999\)](#) presented a model in which these rocks may later partially melt and produce alkaline silicate melts. In this model, the alkaline silicate melts ascend with the assistance of volatiles, and subsequent carbonatite melt ascends by exploiting the conduit formed by earlier silicate melts and without significant interaction with country-rock. This model is consistent with the age and isotopic relationships of the MPIS in that (1) the earliest and most voluminous stages of magmatism resulted in the emplacement of alkaline silicate rocks, (2) alkaline silicate magmatism progressively decreased in volume and carbonatite magmatism progressively increased in volume, and (3) the carbonatite and silicate rocks have similar isotopic characteristics owing to their derivation from the same source, although the silicate rocks have more variable isotopic signatures as a result of crustal contamination. Although the composition of the MPIS ultrapotassic rocks and carbonatite are somewhat different from those in the model of [Harmer \(1999\)](#), this model provides an appropriate analog for the petrogenesis of the MPIS.

Tectonic setting of the MPIS

The spatial relationship and temporal overlap between the MPIS and ~1.4 Ga granitoids of similar age throughout the southwestern USA suggests that both were emplaced in response to the same thermal event ([Haxel, 2005](#)) and in a similar tectonic regime ([Gleason et al., 1994](#)). Although some studies have postulated an anorogenic origin for the ~1.4 Ga granitoids (e.g. [Anderson & Bender, 1989; Hoffman, 1989](#)), more recent studies have concluded that they were associated with a contractional orogenic event (e.g. [Nyman et al., 1994; Daniel & Pyle, 2006; Whitmeyer & Karlstrom, 2007; Daniel et al., 2013](#)). Alkaline and carbonatitic magmatism has been documented in contractional settings in other locations (e.g. [Tilton et al., 1998; Wang et al., 2001; Ying et al., 2004](#)), and commonly occurs peripherally to orogens (e.g. [Veizer et al., 1992; Jones et al., 2013](#)) or larger subalkaline igneous provinces (e.g. [Gibson et al., 2006; Ernst & Bell, 2010](#)). The occurrence of a belt of ultrapotassic rocks (including the MPIS) along the westernmost edge of a large, ~1.4 Ga granitoid suite ([Castor, 2008](#)) that may have been emplaced in an orogenic environment is consistent with this scenario. The ultrapotassic and carbonatite magmas and granitoid magmas were probably derived from distinct sources ([Gleason et al., 1994; Haxel, 2005](#)), which may have been juxtaposed to the east of the ultrapotassic belt, and both partially melted during a widespread and long-lived thermal event.

Implications for carbonatite–alkaline magmatism

The MPIS does not have a direct analog because of its unique features ([Haxel, 2005; Castor, 2008](#)), including the wide range of silica contents in the ultrapotassic rocks, the association between ultrapotassic (rather than potassic) rocks and significant amounts of carbonatite, and the geochemistry of the shonkinite and carbonatite, preventing direct comparison with other carbonatite–alkaline rock occurrences worldwide. However, the MPIS is most akin to the group of carbonatite–alkaline rock occurrences in which the two rock types are spatially and temporally associated but were generated as separate melts—for example, the Spitskof, Shawa, Dorowa, Kerimasi, and Napak complexes in Africa ([Harmer & Gittins, 1998; Harmer, 1999](#)), and the Jacupiranga complex in southern Brazil ([Huang et al., 1995](#)).

CONCLUSIONS

Whole-rock and mineral geochemistry data from the MPIS indicate that titanite, zircon, apatite, thorite, and sodic amphibole are the most important hosts of REE and actinides in the ultrapotassic rocks. Titanite and zircon from ultrapotassic rocks yield U–Pb ages of ~1425–1385 Ma and ~1425–1407 Ma, respectively, and record three discrete phases of magmatism (~1425, ~1405, and ~1380 Ma; Fig. 15). Trace element and textural data

indicate that titanite grew as an igneous phase in Mountain Pass rocks. Titanite yields identical dates to demonstrably igneous zircon, and is therefore interpreted to accurately record the igneous crystallization ages of the MPIS. Monazite Th–Pb ages from carbonatite are 1400–1380 Ma (Fig. 15) and overlap titanite and zircon dates from ultrapotassic rocks within uncertainty. Hf isotopic data from zircon in the ultrapotassic rocks are uniform, yielding a mean ϵHf_i of 1.9 ± 0.2 across all samples (Fig. 12), indicating derivation from a common source. The most primitive Nd isotopic values measured in titanite overlap ϵNd_i from monazite and bastnäsite in the carbonatite (Fig. 8), further supporting a genetic relationship between the carbonatite and ultrapotassic rocks of the MPIS. Whole-rock major and trace element data suggest that the carbonatite and ultrapotassic rocks are unlikely to have differentiated from a common parental magma. Combined, data from this study effectively demonstrate and resolve—contrary to previous studies—that carbonatite and ultrapotassic rocks younger than ~ 1410 Ma were contemporaneous, but were derived from separate melts from the same source region. In this way, the MPIS is most similar to carbonatite–alkaline rock suites in which the two rock types were generated as separate melts. We speculate that REE deposits of similar grade to the Mountain Pass may be more likely to occur in primary carbonatites than in carbonatites that separated from parental silicate melts.

APPENDIX: ANALYTICAL METHODS

Accessory minerals

Sample preparation

Accessory minerals were analyzed either in epoxy grain mounts or in thin section. Sample thin sections were prepared by Spectrum Petrographics of Vancouver, Washington. To prepare mineral separates, $\sim 2\text{--}3$ kg of each sample was crushed in a jaw crusher and disc mill, sieved, separated by density using a gold pan or Rodgers Table and then in methylene iodide ($\rho = 3.32\text{ g cm}^{-3}$), and separated by magnetic susceptibility using a Frantz isodynamic separator. Thirty to 50 grains of each mineral were picked from samples by hand under a binocular microscope, mounted in epoxy pucks, and polished to a $0.25\text{ }\mu\text{m}$ (titanite, monazite, apatite, bastnäsite) or $1\text{ }\mu\text{m}$ (zircon, rutile) finish. Backscattered-electron (BSE) and cathodoluminescence (CL) images of the samples were collected using scanning electron microscopy (SEM) to provide textural context for LASS-ICP-MS spot analysis placement. Representative example SEM images of sample grains with spot analyses shown are provided in [Supplementary Data Electronic Appendix 3](#).

U–Th–Pb

Mineral analyses were carried out using LASS-ICP-MS at the University of California, Santa Barbara (UCSB). The LASS-ICP-MS system combines a Photon Machines 193 nm ArF Excimer laser and Hel-Ex ablation cell with a Nu Instruments HR Plasma high-resolution MC-ICP-

MS system for collecting U–Th/Pb data and an Agilent 7700S quadrupole (Q)-ICP-MS system for collecting major and trace element data. Methods used in this study follow those outlined by [Cottle *et al.* \(2012, 2013\)](#) and [Kylander-Clark *et al.* \(2013\)](#), except that trace elements were measured via Q-ICP-MS (method outlined below). Different laser run conditions were used for each mineral depending on expected U, Th, and Pb content, varying in the range of $9\text{--}40\text{ }\mu\text{m}$ spot size, $3\text{--}7\text{ mJ}$ laser power at $75\text{--}100\%$, laser pulse frequency $3\text{--}4\text{ Hz}$, and $80\text{--}120$ shots per analysis (see [Supplementary Data Electronic Appendices 5, 7, 10 and 11](#)). Bastnäsite was ablated using line scans $25\text{ }\mu\text{m}$ wide and $100\text{ }\mu\text{m}$ long with a travel rate of $4\text{ }\mu\text{m s}^{-1}$. Before each ablation period, the laser was fired twice to remove contamination from the surface of the analyte, followed by an 8 s delay to permit sample washout. Masses $^{204}\text{Pb} + \text{Hg}$, ^{206}Pb , ^{207}Pb , and ^{208}Pb were measured on ion counters, and ^{232}Th and ^{238}U were measured on Faraday detectors. Typically, $20\text{--}40$ analyses were performed per sample, according to the abundance of the mineral of interest per sample. Every set of eight sample analyses was bracketed by analyses of a primary and a secondary natural reference material of the same mineral type as the sample. Information about the primary and secondary reference materials used is provided in [Supplementary Data Electronic Appendix 14](#). Bastnäsite is the only exception, owing to the lack of a widely distributed and/or well-characterized bastnäsite reference material; therefore, zircon and monazite were used as reference materials for bastnäsite and all three minerals were ablated using line scans to avoid addition of systematic uncertainty owing to differences in downhole fractionation of U and Pb. Zircon data were acquired during seven separate analytical sessions, monazite data over four, rutile data over one, and titanite, bastnäsite, and apatite over two sessions each.

Raw U–Th–Pb and trace element data were reduced using *Iolite v2.5* ([Paton *et al.*, 2011](#)) to correct for instrument drift, laser-ablation-induced down-hole elemental fractionation, plasma-induced elemental fractionation, and instrumental mass bias. Secondary reference materials were used to monitor accuracy and internal reproducibility from run to run, and between analytical sessions. External uncertainty was added to sample isotopic ratios in quadrature, and was assigned based on the additional uncertainty needed to produce an MSWD ~ 1 in a population ($n > 9$) of secondary reference material analyses from the same analytical session. $^{206}\text{Pb}/^{238}\text{U}$ typically required the addition of $\sim 1\text{--}1.5\%$ external uncertainty. $^{207}\text{Pb}/^{206}\text{Pb}$ measurements usually required addition of $< 1\%$ uncertainty. However, long-term $^{207}\text{Pb}/^{206}\text{Pb}$ reproducibility for this laboratory and setup is reported to be $1.5\text{--}2\%$ (e.g. [Kylander-Clark *et al.*, 2013](#); [Spencer *et al.*, 2013](#)); thus, 1.5% external uncertainty has been added to all $^{207}\text{Pb}/^{206}\text{Pb}$ ratios to account for long-term accuracy. U–Th/Pb data collected

from the secondary reference materials are shown in [Supplementary Data Electronic Appendix 15](#).

Isoplot 4.1 (Ludwig, 2012) was used to plot U–Pb data on Tera–Wasserburg diagrams, to calculate lower-intercept and concordia dates, and to calculate weighted means. Reported titanite ages are U–Pb isochron dates derived from Tera–Wasserburg plots. Zircon ages are U–Pb concordia dates derived from Tera–Wasserburg plots for samples that yield $MSWD < 1 + 2(2/f)^{1/2}$, where $f = n - 2$ (Wendt & Carl, 1991). For samples that do not yield a concordia age that meets this criterion, reported ages are weighted means of $^{207}\text{Pb}/^{206}\text{Pb}$ dates calculated from measured $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Zircon dates were calculated using data that are $< 3\%$ discordant; per cent discordance was calculated as the per cent difference between the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ dates from the corresponding isotopic ratios measured in the sample.

All reported monazite ages are common-Pb corrected $^{208}\text{Pb}/^{232}\text{Th}$ dates. Correction was applied according to the following steps. (1) Raw ^{232}Th , ^{208}Pb , and $^{204}\text{Pb} + \text{Hg}$ signals were corrected for instrumental drift and mass bias in Lolite v2.5 (Paton *et al.*, 2011). (2) Per cent common ^{208}Pb in the ^{208}Pb signal was calculated based on the mass-204 signal and the $^{208}\text{Pb}/^{204}\text{Pb}$ at a reference age of 1400 Ma from the Stacey & Kramers (1975) model of Pb evolution. Changes in the reference age of ≤ 100 Myr did not significantly change the final $^{208}\text{Pb}/^{232}\text{Th}$ date (< 1 Myr). The mass-204 signal was not corrected for isobaric interference of ^{204}Hg on ^{204}Pb ; however, the possible presence of Hg in the Ar gas supply should be accounted for in the background mass-204 signal, and we therefore consider the effect of neglecting this correction insignificant. (3) Radiogenic ^{208}Pb ($^{208}\text{Pb}^*$) was calculated by subtracting the common ^{208}Pb from the total measured ^{208}Pb . (4) Corrected $^{208}\text{Pb}^*/^{232}\text{Th}$ ratios were used to calculate $^{208}\text{Pb}/^{232}\text{Th}$ dates. Uncertainties were calculated by the same method as was used to calculate uncertainty for $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios as described above, with an additional 1% added in quadrature for uncertainty on the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio from the Stacey & Kramers (1975) model. Measured $^{208}\text{Pb}/^{232}\text{Th}$ ratios of the reference materials typically required addition of $\sim 3\%$ uncertainty.

Trace elements

Trace elements of interest were measured in titanite, zircon, monazite, and apatite by LASS-ICP-MS simultaneously with U–Th–Pb isotopes using an Agilent 7700 S Q-ICP-MS system; laser settings, ablation periods, and washout times used for trace element measurement were therefore identical to those described above. Zircon grains that appear to be metamict (see below) were also measured using LA-Q-ICP-MS for U–Th–Pb isotopes and trace elements of interest; analytical methods were otherwise identical to those used for titanite, zircon, monazite, and apatite. The Q-ICP-MS system is equipped with a second Edwards E2M 18 rotary interface pump, increasing sensitivity by about two-fold for

elements heavier than Mg. The Q-ICP-MS system was tuned such that ThO^+ and CeO^+ were less than $\sim 0.5\%$, and doubly charged ions less than 2%. Dwell time for elements of stoichiometric abundance (e.g. Ca, Ti, and Si for titanite; Zr and Si for zircon) was 5 ms. A dwell time of 10 ms was used for trace elements with expected abundances of 10 000–1000 ppm (e.g. REE in titanite; Hf in zircon). For trace elements with expected abundances of ~ 1000 ppm or less, or those that were used for geothermometry (e.g. Zr in titanite, Ti in zircon), dwell time was set to 20 ms. Sweep time was ~ 0.8 s. Analog detection mode was used for elements of stoichiometric abundance; pulse-counting mode was used for most elements and allowed to switch to analog mode automatically. Masses monitored during analysis are listed in [Supplementary Data Electronic Appendix 16](#).

'GJ1' zircon was used as the primary reference material for most trace elements in zircon samples [see Liu *et al.* (2010) for trace element reference values]. '91500' zircon was used as the primary reference material for Si, P, and Ta, because of the lack of 'accepted' values for these elements in 'GJ1' zircon. Trace element reference values used for '91500' are from the GeoReM database, application version 18 (October 2009; <http://georem.mpch-mainz.gwdg.de/>) (Jochum *et al.*, 2005). 'Stern' monazite was used as the primary reference material for monazite trace elements (reference values based on data compiled from UCSB LASS-ICP-MS and electron probe micro-analyzer laboratories). NIST SRM610 reference glass (Jochum *et al.*, 2011) was measured in conjunction with titanite, apatite, and metamict zircon and used as the primary trace element reference material for these phases. Secondary trace element reference materials used are the same as the primary U–Pb reference materials ([Supplementary Data Electronic Appendix 14](#)). Trace element data were reduced using the 'trace elements' data reduction scheme in Lolite v2.5 (Paton *et al.*, 2011). Zircon and monazite trace element data were reduced using the 'semi-quantitative' standardization method of Lolite. Ca was used as an internal standard for titanite and apatite, and Si was used as an internal standard for metamict zircon; Ca and Si values were assumed stoichiometric. These standardization schemes reproduced values in the secondary reference materials to within 10% or less for most trace elements. REE plots are normalized to the chondrite concentrations of McDonough & Sun (1995).

Zr-in-titanite apparent temperatures were calculated using the calibration of Hayden *et al.* (2008). Pressure was assumed to be 0.1 ± 0.1 GPa based on the presence of K-feldspar pseudomorphs after primary leucite in some samples (Castor, 2008), which has been experimentally shown to be unstable above ~ 0.1 GPa (Barton & Hamilton, 1978). Ti-in-zircon apparent temperatures were calculated using the calibration of Ferry & Watson (2007). For both geothermometers, TiO_2 activity was assumed to be 0.8 ± 0.2 , based on the apparent lack of

primary rutile, and SiO_2 activity to be unity, based on the presence of minor quartz. For samples where quartz was not observed in thin section, SiO_2 activity was assumed to be 0.9 ± 0.1 . Uncertainty in elemental concentration (2SE), TiO_2 activity, and SiO_2 activity are propagated into the reported temperature uncertainties. Additionally, uncertainty in pressure is propagated in the reported Zr-in-titanite apparent temperatures. Temperatures quoted here are weighted means calculated by Isoplot 4.1 (Ludwig, 2012), or are a range of values from non-single population groups of analyses.

Nd isotopes

Nd isotopes in titanite, monazite, and bastnäsite were measured *in situ* by LA-MC-ICP-MS at UCSB. The methods presented by Fisher *et al.* (2011b) were followed for this study, and are summarized here. For titanite and monazite, only grains that were analyzed for U–Pb geochronology were analyzed for Nd isotopes, with the exception of one sample (MP-P0913-10B). All minerals were ablated with 5 mJ laser energy at 100% and pulse rate of 6 Hz for each analysis. Laser spot sizes were 65 μm for titanite, 20 μm for monazite, and 15 μm for bastnäsite. Reference glasses were ablated with a spot size of 40 μm to obtain an optimal signal during monazite and bastnäsite analysis, and 65 μm during titanite analysis. Samples were ablated for 50 s, with a 30 s delay between analyses to allow washout. Masses 141–150 were measured on 10 Faraday cups with 1 a.m.u. spacing. Data were reduced using Lolite v2.5 (Paton *et al.*, 2011). The data were carefully screened to detect the presence of inclusions; portions of analyses that appeared to record measurement of inclusions were rejected during data processing.

During *in situ* measurement of Nd isotopes, the isobaric interference on ^{144}Nd by ^{144}Sm has been noted to constitute between 1.5 and 4.6% of the mass-144 signal in LREE-rich minerals (Fisher *et al.*, 2011b); thus, correcting this interference is vital to obtaining an accurate $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. In addition, determination of $^{147}\text{Sm}/^{144}\text{Nd}$ in the sample is necessary to accurately calculate the initial $^{143}\text{Nd}/^{144}\text{Nd}$ of the sample. To make these corrections, instrumental mass bias factors for Sm and Nd must first be determined. ‘JNdi-1’ glass was employed to evaluate Nd isotopic measurements without complication by isobaric interference ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512115 \pm 7$; Tanaka *et al.*, 2000). ‘JNdi-1’ doped with Ce, Pr, Sm, Eu, and Gd (‘LREE’ glass; Fisher *et al.*, 2011b) was employed to provide a homogeneous $^{147}\text{Sm}/^{144}\text{Nd}$ reference material, and to evaluate Nd isotope measurements where Sm is included. $^{147}\text{Sm}/^{149}\text{Sm}$ was used to calculate a Sm mass bias factor, using a natural $^{147}\text{Sm}/^{149}\text{Sm}$ ratio of 0.22332 (Isnard *et al.*, 2005). ^{144}Sm interference was then calculated using the measured ^{149}Sm and a natural $^{144}\text{Sm}/^{149}\text{Sm}$ ratio of 1.08680 (Dubois *et al.*, 1992). For Nd mass bias determination, a natural $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219 was used. A canonical $^{145}\text{Nd}/^{144}\text{Nd}$ value of 0.348415

(Wasserburg *et al.*, 1981) was used to monitor the accuracy of the Nd mass bias correction. $^{147}\text{Sm}/^{144}\text{Nd}$ was calculated using the mass bias corrected ^{147}Sm and the interference corrected ^{144}Nd . Natural reference materials ‘Trebilcock’ monazite ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512616 \pm 11$; Fisher *et al.*, 2011b) and ‘Hondo Canyon’ titanite ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512211 \pm 9$; Fisher *et al.*, 2011b) were analyzed between every 10–20 unknowns and used to monitor the accuracy of the corrected $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. The weighted mean corrected $^{143}\text{Nd}/^{144}\text{Nd}$ values ($\pm 2\text{SD}$) obtained for the reference materials are as follows: 0.512612 ± 18 ($n = 34$) for Trebilcock monazite; 0.512218 ± 59 ($n = 24$) for Hondo Canyon titanite.

The ϵ_{Nd_i} values were calculated relative to the chondritic uniform reservoir (CHUR) parameters of Jacobsen & Wasserburg (1980) (present-day $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$) with $^{143}\text{Nd}/^{144}\text{Nd}$ re-normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (Hamilton *et al.*, 1983; Bouvier *et al.*, 2008). Age corrections on the measured $^{143}\text{Nd}/^{144}\text{Nd}$ were applied using the sample age interpreted from titanite and/or zircon dates; changes of ~ 20 Myr in the correction age did not have a drastic effect on the epsilon values (~ 0.2 epsilon units). Uncertainties on the measured $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios were propagated into the ϵ_{Nd_i} values.

Hf isotopes

Hf isotopes in zircon were measured *in situ* by LA-MC-ICP-MS at UCSB. Methods used in this study are similar to those used by Hagen-Peter *et al.* (2015), and are summarized here. Only zircon grains that were analyzed for U–Pb geochronology and yielded concordant dates younger than ~ 1460 Ma were analyzed for Hf isotopes. Ablation spots were placed over the original U–Pb analysis spots to obtain Hf compositions that correspond to the measured U–Pb date of the zircon. A laser spot size of 50 μm , 4 mJ laser energy at 100%, and a pulse rate of 8 Hz were used to ablate samples for 50 s, with a 30 s delay between analyses to allow washout. Masses 171–180 were measured on 10 Faraday cups with 1 a.m.u. spacing.

Data were reduced using Lolite v2.31 (Paton *et al.*, 2011). Natural ratios of $^{176}\text{Yb}/^{173}\text{Yb} = 0.786847$ (Thirlwall & Anczkiewicz, 2004) and $^{176}\text{Lu}/^{175}\text{Lu} = 0.02656$ (Chu *et al.*, 2002) were used to subtract isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf . The Yb mass bias factor was calculated using a natural $^{173}\text{Yb}/^{171}\text{Yb}$ ratio of 1.123575 (Thirlwall & Anczkiewicz, 2004) and was used to correct for both Yb and Lu mass bias. A natural $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325 (Patchett & Tatsumoto, 1980, 1981) was used to calculate the Hf mass bias factor.

To assess accuracy and precision, synthetic reference material zircons ‘MUNZirc1’ and ‘MUNZirc3’ ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282135 \pm 7$; Fisher *et al.*, 2011a), as well as natural reference material zircons ‘91500’ ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282308 \pm 6$; Blichert-Toft, 2008), ‘GJ-1’ ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282000 \pm 5$; Morel *et al.*, 2008), ‘Plešovice’ ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282482 \pm 13$; Sláma *et al.*,

2008), and 'Mud Tank' ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282507 \pm 6$; Woodhead & Hergt, 2005) were analyzed between every 5–10 sample analyses. The weighted mean corrected $^{176}\text{Hf}/^{177}\text{Hf}$ values ($\pm 2\text{SD}$) obtained for the secondary reference materials were 0.282142 ± 38 ($n=8$) for MUNZirc1 and MUNZirc3, 0.282305 ± 42 ($n=5$) for 91500, 0.282000 ± 56 ($n=4$) for GJ-1, 0.282517 ± 24 ($n=5$) for Plešovice, and 0.282527 ± 42 ($n=5$) for Mud Tank.

The εHf_i values were calculated relative to CHUR (present-day $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$; $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$; Bouvier *et al.*, 2008) at the U–Pb age of each sample (concordia age if $\text{MSWD} < 2$ and mean $^{207}\text{Pb}/^{206}\text{Pb}$ age if $\text{MSWD} > 2$) using λ $^{176}\text{Lu} = 1.867 \times 10^{-11} \text{ a}^{-1}$ (Scherer *et al.*, 2001, 2003; Söderlund *et al.*, 2004). Age corrections on the measured $^{176}\text{Hf}/^{177}\text{Hf}$ were applied using the sample age interpreted from titanite and/or zircon dates; changing the correction age by ~ 20 Myr did not have a drastic effect on the epsilon values (~ 0.5 epsilon units). Uncertainties on the corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were propagated into the εHf_i values; uncertainties on the $^{176}\text{Lu}/^{177}\text{Hf}$ have negligible effect. Depleted-mantle model ages (T_{DM}) were calculated relative to a depleted-mantle model reservoir with present-day $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ (Nowell *et al.*, 1998; Griffin *et al.*, 2000, 2002) and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ (Griffin *et al.*, 2000). Two-stage depleted-mantle model ages (T_{DM}^{C}) were calculated using the same depleted mantle parameters and a crustal average $^{176}\text{Lu}/^{177}\text{Hf}$ of 0.015 for the evolution of the crustal magma source after it separated from the depleted mantle (Griffin *et al.*, 2002).

Whole-rock geochemistry

Samples representative of the range of rock types in the MPIS were selected for whole-rock geochemical analysis, with emphasis on those that contained accessory minerals that produced useful U–Pb age data. Between 0.5 and 0.75 kg of the least weathered or altered portions of each sample was first gently hammered into 1–2 cm fragments and powdered in a tungsten carbide (WC) ring mill and thoroughly mixed. More material was powdered for coarse-grained samples to ensure accurate representation of sample mineralogical composition. Sample powder ($3.5 \pm 0.0001 \text{ g}$) was combined with $7 \pm 0.0001 \text{ g}$ of di-lithium tetraborate flux for a low-dilution sample to flux ratio of 2:1, and thoroughly mixed by vortexer. The mixtures were then transferred to graphite crucibles and heated at 1000°C in a furnace for 30–40 min to ensure complete fusion. The resulting glass beads were then re-powdered in a WC ring mill to achieve optimal homogenization, and re-fused at 1000°C for an additional 30–40 min. The final glass bead was polished to an $\sim 15 \mu\text{m}$ finish, and 2–3 mm chips were then cut from the beads for trace element analysis. The chips were mounted in an epoxy puck and polished to a $1 \mu\text{m}$ finish. Whole-rock major elements were measured by XRF at Pomona College in Claremont, California using a PanAnalytical Axios wavelength-

dispersive system equipped with a standard set of crystals, a duplex detector, and calibrations constructed using 61 certified reference standards. Interference corrections are adapted from Johnson *et al.* (1999) and detection limits were described by Lackey *et al.* (2012).

Whole-rock trace elements were measured by LA-Q-ICP-MS at UCSB. The analytical setup was the same as that used for accessory phase trace elements, except that laser energy was set to 5 mJ and 30 s of washout was allowed between each analysis. Samples were ablated using line scans $50 \mu\text{m}$ wide and $250 \mu\text{m}$ long at a travel rate of $2 \mu\text{m s}^{-1}$ for ~ 2 min of data each. Prior to each ablation period, surface contamination was removed from the sample surface by performing a line scan $50 \mu\text{m}$ wide by $250 \mu\text{m}$ long at a travel rate of $70 \mu\text{m s}^{-1}$. Three line scans were performed on each sample. Whole-rock reference materials BCR-2, BHVO-2, AGV-2, Atho-G, ML3B-G, StHs6/80-G, GOR132-G, and T1-G were measured at the beginning and end of the analytical session, with Atho-G and AGV-2 measured between every nine unknowns. Reference values used for these reference materials are from the GeoReM database, application version 18 (January 2015; <http://georem.mpch-mainz.gwdg.de/>) (Jochum *et al.*, 2005). Atho-G was used as the primary reference material and AGV-2 as the secondary reference material to assess accuracy of the measurements of each element individually. Three analyses were performed on each sample to assist in the recognition of outliers; the reported values are the arithmetic mean of the three values. LA-Q-ICP-MS data were reduced using the 'Trace Elements IS' data reduction scheme in *lolyte* v2.5 (Paton *et al.*, 2011). Ca content was measured by XRF, and was used as the internal elemental standard. Elements reported here were reproduced within less than 10% of the accepted values for AGV-2, except for Cs, Tb, Pb, and U (13.5%, 10.5%, 14.4%, and 10.9% difference from accepted values, respectively).

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SUPPLEMENTARY DATA

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

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