# Dissolution-reprecipitation metasomatism and growth of zircon 

 within phosphatic garnet in metapelites from western
## Massachusetts

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#### Abstract

Highly restitic garnet-kyanite-phlogopite metapelitic schists from the Goshen Dome of western Massachusetts contain: a population of prograde monocrystalline, megacrystic garnet, some with significant P in substitution for Si ; precipitates of hydroxylapatite and rutile; and $<1 \mu \mathrm{~m}$ zircon crystals of undetermined origin and abundance on the order of $10^{5} / \mathrm{mm}^{3}$. The unusual P content and the abundant internal precipitate suite are similar to features reported in garnet from ultrahigh-pressure (UHP) and mantle settings, suggesting a potential (U)HP origin for the garnet megacrysts. Zircon included in megacrysts is surrounded by radial fractures, indicating in situ volumetric expansion or new growth. Cores display rare earth element (REE) profiles and cathodoluminescence (CL) zoning consistent with magmatic growth, and yield only Paleozoic dates (447-404 Ma). The embayed core-rim boundary is marked by a several $\mu \mathrm{m}$ wide band of CL-dark zircon enriched in $\mathrm{Y}, \mathrm{P}, \mathrm{U}$, and Th that is interpreted as the accumulation of redistributed xenotime component from the original zircon rim during metamorphism. Outside of this band, the rim has elevated $\mathrm{Hf}, \mathrm{Th} / \mathrm{U} \ll 1$, and steep heavy REE profiles. The metamorphic rims yield concordant dates from 400 to 381 Ma. Matrix zircon grains have magmatic cores (1726-415 Ma) with similar core-rim boundaries enriched in Y, P, U, and Th. Metamorphic rims on matrix zircon yield slightly younger dates (393-365 Ma) and are compositionally heterogeneous.


The difference between the youngest core and oldest rim indicates a short interval (c. 4 Ma ) between deposition of detrital zircon and the onset of metamorphism in the earliest Acadian.

The oldest zircon rim dates are found within phosphatic garnet megacrysts of possible very high-pressure origin. The compositional uniformity of these rims indicates equilibrium with a single source; the anomalous composition suggests a combination of dissolution-reprecipitation and new growth of zircon that is derived from garnet. The range in both composition and dates indicate that matrix zircon rims formed in response to local changes in mineralogy and fluid/melt composition and/or availability. New growth of zircon on these grains cannot be confirmed, suggesting that dissolution-reprecipitation reactions during continued metamorphism may be the dominant mechanism that formed these rims. The data collectively suggest that dissolution-reprecipitation may be a common mechanism for producing metamorphic rims on zircon that does not require additional Zr and Hf , which are limited within most metamorphic settings.

Keywords: zircon, garnet, LASS, dissolution-reprecipitation, metasomatism, metamorphism

## Introduction

Although the diffusion rate of Pb in geochronologic minerals, such as zircon and monazite, is slow under most geologic conditions (Cherniak and Watson 2001; Cherniak et al. 2004), the distribution of radiogenic Pb -crucial to $\mathrm{U}-\mathrm{Th}-\mathrm{Pb}$ geochronology - can be affected by several mechanisms during metamorphic or thermal events. Recent studies by secondary ionization mass spectrometry (SIMS—Kusiak et al. 2013) and atom probe tomography (APT) demonstrate that short-range diffusion on reheating can cause Pb atoms in zircon (Valley et al. 2015) and monazite (Snoeyenbos et al. 2013) to aggregate with various other ions in radiogenic damage spots in the crystal lattice. The bulk composition of a crystal-including the Pb distributionmay be modified along a reaction front propagating through a crystal via a dissolutionreprecipitation reaction. In zircon (Geisler et al. 2007; Rubatto et al. 2008; Hay and Dempster 2009; Harlov et al. 2012), xenotime (Harlov and Wirth 2012), and monazite (Harlov et al. 2011; Williams et al. 2011), dissolution-reprecipitation reactions are mediated by an alkali-bearing intergranular fluid that enables complete removal of radiogenic Pb , thus resetting the radiometric age along a reaction front that propagates into the crystal. Other compositional changes (e.g. accumulation of $\mathrm{Th}, \mathrm{U}$ or decreases in other minor and trace elements) may also occur along the reaction front (Tomaschek et al. 2003; Geisler et al. 2007; Rubatto et al. 2008), but detailed study is required to fully explain these reactions.

Dissolution-reprecipitation reactions commonly affect only a portion of the crystal, thereby leaving metasomatized, geochronologically-reset concordant domains adjacent to unreacted
concordant domains (Schwartz et al. 2010). In many cases, the texture, radiometric age, and chemical composition produced by the propagation of dissolution-reprecipitation reactions in zircon and monazite can appear similar to metamorphic or igneous overgrowths on an inherited core (Rubatto et al. 2008; Vonlanthen et al. 2012). Because conditions favoring metasomatism by dissolution-reprecipitation-e.g. changes in pressure-temperature (P-T) conditions, changes in fluid activity, and the availability and diffusivity of componentsoverlap with conditions of metamorphic overgrowth as conventionally understood, both processes may occur simultaneously and may be initiated under similar conditions. Identification of the relative contribution of each of these mechanisms to the formation of a metamorphic rim requires integration of compositional, textural, and geochronologic information.

We present a case study of two zircon populations that have been examined in detail via in situ electron probe microanalysis (EPMA), laser ablation split stream (LASS) inductively coupled plasma mass spectrometry (ICPMS), and cathodoluminescence (CL) imaging. The first population (herein referred to as zircon1) consists of zircon included in phosphatic garnet megacrysts within coarse garnet-kyanite-phlogopite schist. Elevated P and the precipitate suite included in garnet suggest preservation of potentially very high-pressure metamorphism. The second zircon population (herein referred to as zircon2) is included in the recrystallized phlogopite, kyanite, quartz, and non-phosphatic garnet matrix surrounding these megacrysts. Both zircon populations exhibit embayed core-rim boundaries marked by a thin CL-dark band that is enriched in $\mathrm{U}, \mathrm{Y}, \mathrm{P}$, and Th. These components are interpreted to have been derived from
the original zircon and were mobilized and localized along an inward-propagating dissolutionreprecipitation reaction front in response to metamorphism on a low-temperature/highpressure path, as suggested by experimental work by Tomaschek (2010). The compositional and dates of zircon1 rims indicates equilibration with and derivation from a single source-the host garnet. Precipitation of zircon from garnet may also explain the myriad c. $1 \mu \mathrm{~m}$ zircon crystals found only within the garnet megacrysts. Compositional heterogeneity among zircon2 rims indicates response to local changes in mineralogy and fluid/melt composition and/or availability during protracted Acadian metamorphism.

## Setting

Multiple phases of orogenesis within the northern Appalachians have been documented (e.g. Robinson et al. 1998; Macdonald et al. 2014), but only two main phases are classically recognized in the Paleozoic assembly of western Massachusetts: (1) the west-directed Taconian accretion of the Shelburne Falls (or Bronson Hill) Arc against the Laurentian margin that began ca. 475-470 Ma (Karabinos et al. 1998), and (2) west-directed thrusting of Devonian metasediments and regional high-temperature metamorphism associated with the Acadian orogeny (Armstrong et al. 1992) over the previously accreted Taconian arc rocks. Monazite from regional schists suggests that the high-temperature metamorphism associated with the Acadian orogeny occurred between $390-350 \mathrm{Ma}$, with peak pressures attained at c. 370 Ma (Pyle and Spear, 2003; Pyle et al., 2005; Cheney et al., 2006). Garnet geochronology from the Townshend Dam in southern Vermont is broadly consistent with this timeframe and indicates prograde garnet growth from $383.1 \pm 6.8 \mathrm{Ma}$ (oldest garnet core) to $374.9 \pm 1.8 \mathrm{Ma}$ (youngest garnet rim) (Gatewood et al., 2015).

The Goshen Dome, located in western Massachusetts (Fig. 1a), has been mapped as a tectonic window through the Devonian Goshen Formation (interpreted as an Acadian thrust sheet) into core gneisses and associated rocks (Fig. 1b) with unclear internal relations (Hatch and Warren, 1981). Central to the structure is the poorly exposed Collinsville Gneiss, which yielded a U-Pb zircon date of $473 \pm 2$ Ma that has been interpreted as the timing of igneous activity (Karabinos et al. 1998). The overlying Cobble Mountain Formation on the western side of the Dome contains a novel package of high-grade rocks originally described by O’Brien and Koziol (2008) as granulite facies assemblages. Subsequent study of garnet chemistry reinterpreted the garnet megacrysts within this unit as potentially ultrahigh-pressure (UHP) relics (Snoeyenbos et al., 2011). This heterogeneous package of rocks consists of numerous complexly folded and boudinaged migmatitic garnet amphibolites and kyanite schists, and restitic, coarse-grained, garnet-kyanite-phlogopite schists. The coarse-grained, schists contain multiple garnet populations that range from 0.5 to 8 cm in diameter. These coarse-grained schists crop out as sheets several meters thick associated with highly strained rocks of lower metamorphic grade.

## Sample Descriptions

Four garnet-kyanite-phlogopite schists were sampled from the anomalous package of rocks located within the Cobble Mountain Formation (Fig. 1b). Two of the samples (RBTS and

WMBTS) were collected from different exposures of coarse-grained schist. Three garnet megacrysts were analyzed for this study: two specimens from RBTS, herein referred to as RBTS (Figs. 2-3) and RBTS-B (Fig. 4), and one specimen from WMBTS (Fig. 5). Garnet megacrysts in RBTS are $>3 \mathrm{~cm}$ in diameter with rounded and partially resorbed margins. The megacryst from WMBTS is a 3 cm diameter, equant, euhedral garnet (Fig. 5a) with a light pink core and a dark purple rim. Zircon1 is found within these phosphatic garnet megacrysts. Two samples that lack garnet megacrysts, G12B and G12G, were collected from different schists composed mainly of non-phosphatic garnet, quartz, kyanite, cordierite, phlogopite, chlorite, and rutile. Zircon2 is found in G12B, G12G, and in the matrix surrounding the garnet megacryst in WMBTS.

## Garnet-megacryst-bearing samples (RBTS, WMBTS)

RBTS is located at the northern end of the exposure of the anomalous package of rocks (Fig. 1b). WMBTS is 10 m structurally below RBTS and 2 m above the lower bounding shear zone (Fig. 1b). These samples are principally composed of phosphatic garnet, kyanite, quartz, phlogopite, plagioclase, cordierite, rutile, and ilmenite, with minor chlorite associated with retrograde metamorphism. Zircon and apatite are found throughout the samples; monazite is found in all contexts except within the pristine garnet megacryst in WMBTS.

Doubly-polished, thick $(100 \mu \mathrm{~m})$ petrographic sections were prepared for studying the inclusion suites in the garnet megacrysts because they contain a larger volume of material than standard preparations and allow investigation of inclusions and precipitates in three dimensions. All three phosphatic garnet specimens-RBTS, RBTS-B, and WMBTS-have Mn- and Ca-rich cores,
and $\mathrm{Mg} \#$ increase systematically from core to rim, consistent with prograde growth. The notable smoothness of the Mn profiles indicates some diffusional relaxation. At the rim and along fractures, the elevated Mn distribution and external morphology record minor resorption. Another distinctive feature of the phosphatic garnet megacrysts is extremely low O-isotope ratios, at least in specimen RBTS. The $\delta^{18} \mathrm{O}$ of the core measured by secondary ion mass spectrometry (SIMS) is as low as 2.0 \%, with fractionation to $3.0 \%$ at the rim (Russell 2012; specimen RBTS is designated 'CH-2' in that work). Such values and profiles are similar to eclogitic and known UHP garnet (Russell 2012).

Garnet megacrysts contain abundant sub- $\mu \mathrm{m}$ hydroxylapatite inclusions, as identified by confocal Raman. These inclusions are anhedral blebs disposed along linear to slightly helical trails normal to the garnet crystal faces and sub-parallel within each sector of the megacryst. The arrangement of apatite inclusion trails by sector is especially apparent in WMBTS (Fig. 5a) but may also be discerned in RBTS (Fig. 2a). The density of apatite inclusions is greatest in the high-Ca cores of these specimens. Their disposition along curvilinear trails recalls that of precipitates in high-pressure garnet described by van Roermund et al. (1999), who interpreted such precipitate trails as having formed along un-annealed growth dislocations in the garnet lattice. The apatite trails are closely associated with fine (sub- $\mu \mathrm{m}$ ) rutile needles in the garnet in several parallel orientations.

The distribution of intrinsic P in specimen RBTS (Fig. 2d) is low (ca. $0.03 \mathrm{wt} \mathrm{w}_{\mathrm{P}} \mathrm{P}_{2} \mathrm{O}_{5}$ ) in the highCa , hydroxylapatite inclusion-rich core, but considerably higher (locally $>0.10 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ ) in the
low-Ca garnet zone surrounding the high-Ca core, where hydroxylapatite inclusions are distinctly less abundant. The relationship between Ca content and the distribution of hydroxylapatite inclusions is accentuated in specimen RBTS-B. Specimens RBTS and RBTS-B have nearly the same major element compositional profiles, but unusually among these garnet megacrysts, a portion of the low-Ca mantle region of RBTS-B is almost entirely free of fine inclusions (Fig. 4). This region of specimen RBTS-B has intrinsic P up to $0.22 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ and few fine hydroxylapatite inclusion trails. The corresponding part of specimen RBTS has only up to $0.14 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$, but the garnet is clouded by sub- $\mu \mathrm{m}$ hydroxylapatite trails and rutile inclusions.

Other apparent precipitates within garnet RBTS are rutile blades up to $200 \mu \mathrm{~m}$ long and only a few $\mu \mathrm{m}$ thick. Many of them are twinned, some of them 'butterfly' twins, whereas others are coplanar (Fig. 3c). Rutile twins range in color from pale brown to violet and blue. Locally, clusters of thin zircon blades up to $30 \mu \mathrm{~m}$ long are found. Micrometer to sub- $\mu \mathrm{m}$ subhedral to euhedral zircon crystals are observed throughout garnet specimen RBTS with a density of ca. $103 / \mathrm{mm}^{2}$ (white flecks in Fig. 3b), or ca. $10^{7}$ such zircons over the area of the RBTS garnet in thin section. The dimensions of the zircon blades and micro-crystals present a challenge for analysis by EPMA, and their minor element compositions and $\mathrm{Hf} / \mathrm{Zr}$ signatures are as yet unknown. Zircon inclusions of detrital origin ( 25 to $100 \mu \mathrm{~m}$ ) are distributed throughout the garnet megacryst in RBTS, nearly all of which are surrounded by shattered garnet (Fig. 3b). Epidote inclusions ( $\sim 20$ $\mu \mathrm{m})$ occur along late penetrative fractures. The dark pink rim domain contains mm-scale rutile and ilmenite grains that are oriented parallel to garnet growth faces. Millimeter-scale monazite
grains decorate the outer 1 cm of the megacryst, but monazite is not found within the core of the garnet. There are no primary quartz inclusions in the megacryst.

Specimen WMBTS contains a suite of inclusions and precipitates identical to that in specimen RBTS, with the exception of the zircon blades and monazite near the rim. This specimen lacks penetrative fractures with epidote and other alteration products. Specimen WMBTS retains little intrinsic P in the garnet, but the abundant hydroxylapatite precipitate trails are interpreted to reflect an elevated original P content. Among the three garnet megacrysts presented here, significant intrinsic P is found mainly where $\mathrm{X}_{\mathrm{Grs}}<0.03$. Elevated intrinsic P is not found in specimen WMBTS, but the Ca content is not below $X_{G r s}=0.06$, even in the low-Ca mantle.

The unusual P content of the garnet megacrysts in this study (up to at least $0.22 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ ), together with their abundant internal precipitates of apatite and rutile, invite close comparison with similar features reported in garnet from ultrahigh-pressure (UHP) and mantle settings (Haggerty et al. 1994; Ye et al. 2000; Mposkos and Kostopoulos 2001; Ruiz Cruz and Sanz de Galdeano 2013). However, in the present example, the phosphatic garnet does not contain free $\mathrm{SiO}_{2}$ inclusions, as might be expected for typical garnet in metapelites, nor has any free C yet been found either in the garnet or in matrix, so detection of conventional UHP minerals remains problematic at this locality.

The matrix surrounding these garnet megacrysts is composed of recrystallized quartz, phlogopite, kyanite, cordierite, plagioclase, and chlorite, with zircon, apatite, and monazite as
accessory phases. Smaller matrix garnet grains (mm- to cm -scale) lack the distinctive hydroxylapatite and rutile precipitates that are abundant in the megacrysts and have an inclusion suite that is principally composed of mm-scale rutile, ilmenite, quartz, and phlogopite. Kyanite and cordierite are poikiloblastic, and cordierite commonly surrounds decomposed kyanite. Matrix-hosted zircon and monazite measure $<100 \mu \mathrm{~m}$ and are typically aligned with the fabric. The fabric wraps around the megacryst, but cordierite and kyanite are typically aligned with the foliation.

## Matrix samples (G12B, G12G)

Sample G12B is located 3 m south from the sample location for RBTS (Fig. 1b). This sample contains garnet with three different morphologies and inclusion arrays. The largest garnet grains ( $>1 \mathrm{~cm}$ ) have curved inclusion trails of rutile and ilmenite. These grains do not typically have primary quartz or phlogopite inclusions. Although some smaller garnet grains ( $<1 \mathrm{~cm}$ ) are relatively pristine with a few 10-100 $\mu$ m-scale rutile + ilmenite + quartz $\pm$ phlogopite inclusions, many garnet grains are skeletal with mm-scale quartz and rutile inclusions. All garnet is rimmed by chlorite, phlogopite, quartz $\pm$ cordierite $\pm$ kyanite (Fig. 6). Kyanite exhibits three different textures: 1) subhedral cm-scale grains with embayed margins, 2) deformed cm-scale grains with undulatory extinction, and 3) skeletal fragments of cm-scale porphyroblasts rimmed by cordierite (Fig. 6). Rutile inclusions are abundant in all kyanite grains. The coarse-grained matrix is comprised of phlogopite, chlorite, and quartz with decomposed kyanite and minor plagioclase (Fig. 6d). Sillimanite and andalusite are absent, whether as replacement textures or pseudomorphs. Quartz is abundant in the matrix; vein quartz is commonly present as large (up
to 20 cm ) boudins of cm -scale crystals. Rutile and ilmenite are concentrated in the chlorite + phlogopite $\pm$ garnet domains and largely absent from the recrystallized quartz domains. The fabric wraps around both garnet and kyanite domains. Zircon, apatite, and monazite are abundant in both the matrix and the porphyroblasts.

Sample G12G is located 10 m structurally below RBTS and G12B (Fig. 1b). Thin sections from this sample are similar to G12B and typically contain a matrix of quartz + chlorite + plagioclase that wraps around cm-scale porphyroblasts of garnet, cordierite, and kyanite. Garnet contains mm-scale apatite inclusions and $\sim 10 \mu \mathrm{~m}$ rutile needles that are oriented parallel to garnet crystal growth faces. Garnet is commonly rimmed by quartz, cordierite, and chlorite; mm-scale rutile grains in chlorite are abundant throughout the matrix. Cordierite contains abundant inclusions of kyanite, quartz, phlogopite, and chlorite. Kyanite is rimmed by cordierite, chlorite, and phlogopite. Zircon, apatite, and monazite are abundant in both the matrix and the porphyroblasts.

## Methods

Zircon included in garnet megacrysts from WMBTS and RBTS and in the matrix for G12B, G12G and WMBTS were imaged by cathodoluminescence (CL) and mapped by electron microprobe analysis (EPMA). Quantitative EPMA and laser ablation split stream (LASS) inductively coupled plasma mass spectrometry (ICPMS) data were also collected from representative zircon and garnet in these samples.

## Scanning Electron Microscope (SEM) Analysis

Zircon grains were located in situ using backscattered electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDS) on the LEO 1450VP Scanning Electron Microscope (SEM) at Bowdoin College. Panchromatic CL images were collected using a Centaurus CL detector attached to an FEI Quanta 400F field emission SEM (UC Santa Barbara) and a TESCAN CL detector attached to a TESCAN Vega3 SEM that uses a LaB6 source (Boston College). Both instruments were operated at 10.0 kV and a beam current that was optimized for each instrument (between 77 and 100 pA ).

## Electron Probe MicroAnalysis (EPMA)

Quantitative compositional analysis and mapping of zircon and garnet were performed on the CAMECA SX-50 and SX-UltraChron instruments at the University of Massachusetts. Mapping and major and minor element analysis of garnet were done on the $\mathrm{SX}-50$ at 15 kV and beam current of 200nA (mapping) and 40 nA (analysis). Zircon mapping and analysis, and trace element analysis of garnet were done on the Cameca SX-UltraChron EPMA at 300nA (mapping) and 200 nA (analysis). Minor and trace element quantitative analysis was performed using Probe for EPMA software (Probe Software, Inc.) and included the use of multi-point backgrounds, multiple spectrometer count integration, extended count times ( 100 to 600 sec ), and matrix-iterated interference corrections. Large and very large PET (LPET and VLPET) monochromators were utilized as appropriate.

## Laser Ablation Split Stream (LASS) Analysis

Largely following the methods of Kylander-Clark et al. (2013), polished sections and reference material mounts were loaded in a Photon Machines HelEx cell connected to a Photon Machines 193 nm excimer laser at the LASS Facility at UC Santa Barbara. The HelEx cell was purged with He gas; a combination of He and Ar carrier gases swept the ablated material through Teflon tubing to a T-junction where the analyte was split into two streams that were measured simultaneously - one stream was measured on the Nu Plasma multi-collector ICPMS for U-Pb isotopes; the other stream was measured on the Nu AttoM single-collector ICPMS for $\mathrm{Ti}, \mathrm{Y}, \mathrm{Hf}$, and rare earth elements (REE). Prior to analysis, each spot was cleaned with two laser pulses to remove surface contaminants and/or residual material from an adjacent analysis. Zircon was analyzed at 15, 20 and $24 \mu \mathrm{~m}$ spot sizes. Operating conditions (e.g. gas flows, laser energy) were optimized for each spot size and produced laser pit depths $<8 \mu \mathrm{~m}$. Analyses were conducted following traditional sample-RM bracketing protocols to correct for bias and drift of the instrument (e.g. Kylander-Clark et al. 2013).

91500 (1062.4 $\pm 0.4 \mathrm{Ma}$; Wiedenbeck et al. 1995) and GJ1 (Jackson et al. 2004) were used as primary RMs for age and composition, respectively. The specific piece of GJ1 used in these is $601.7 \pm 1.3 \mathrm{Ma}\left({ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}\right.$ date; Kylander-Clark et al. 2013). Plešovice ( $337.13 \pm 0.37 \mathrm{Ma}$; Slama et al. 2008) was also analyzed as a secondary RM. Over a two-day analytical session, Plešovice
 of $605.6 \pm 1.2 \mathrm{Ma}(\mathrm{MSWD}=0.86, \mathrm{n}=61)$. These uncertainties represent internal uncertainties only and are not propagated for systematic biases. Each analytical run began with a block of 8
analyses on the RMs. The RM block was followed by blocks of 5 to 8 measurements on unknowns and 2 RM measurements. At the end of the run, a second block of 8 analyses on the RMs was measured. Ratios were bias, drift, and age corrected using Iolite (Paton et al. 2010) following procedures detailed in Kylander-Clark et al. (2013). Although the uncertainty on an individual ratio was typically $<1 \%(2 \sigma)$, the long-term reproducibility of secondary RMs is c . $1.5 \%(2 \sigma)$ and is attributed to variation in laser energy and gas flow within the cell (KylanderClark et al. 2013). Therefore, to account for measurement uncertainty, the assumed uncertainty in the age of the RM, and the long-term reproducibility of the RMs analyzed, we conservatively assign $2 \%$ uncertainty $(2 \sigma)$ to unknown analyses to enable comparison among analytical sessions.

## Results

Zircon grains imaged via CL reveal zoning patterns and guide locations for wave dispersive spectrometry (WDS) and LASS analysis. The cores of zircon1 exhibit oscillatory zoning in CL (Fig. 7a). Approximately half of the zircon1 cores are broken by fractures that displace zircon fragments by ca. 5-10 $\mu \mathrm{m}$ (Fig. 7b). Many zircon1 cores have distinctly scalloped or embayed margins that crosscut the oscillatory zoning; other cores preserve a subhedral to euhedral outline.

Regardless of position within the garnet megacryst, all zircon1 cores (including their isolated or displaced fragments) are surrounded by a distinctive and complex rim ca. $2-10 \mu \mathrm{~m}$ in width.

Within this rim, a band of CL-dark zircon up to several $\mu \mathrm{m}$ thick is located immediately adjacent to the core, often with lobate boundaries. Surrounding this CL-dark band, the rims of nearly all zircon1 are characterized by complex zoning patterns that are dominantly CL-bright (Fig. 7a-b). The external margins of these metamorphic rims are typically curved to lobate. All zircon1 grains are surrounded by radial fractures that extend up to $100 \mu \mathrm{~m}$ into the garnet (Fig. 3d-e) and mainly originate from lobes and protrusions in the periphery of the zircon1 grains.

Most zircon2 grains are subhedral; a few grains are octahedral (see Data Supplement Figure 1). The cores of zircon 2 typically exhibit oscillatory zoning in CL. All cores are mantled by a CLdark band (Fig. 8) and most rims have complex CL-bright domains that vary greatly in CL brightness, zoning and width ( 1 to $20 \mu \mathrm{~m}$ ). Beyond the CL-bright domain, many rims are CLdark to the edge of the grain (Fig. 8c). Although a few zircon2 grains are fractured, no metamorphic rims formed post-fracturing. None of the grains exhibit radial fractures extending into the host mineral.

Mapping by EPMA reveals that the cores of nearly all zircon grains in both populations have minor Hf variation (Figs. 7, 8), which is consistent with primary igneous zonation (e.g. Corfu et al. 2003). Some zircon2 apparently lack this core (see Data Supplement Figure 1), but these may represent low-angle cuts through the rim that did not intersect the core. The thin CL-dark band is strongly enriched in Th, U, P, and $Y$ (Fig. 7a-b, 8). Within this band, Th is enriched immediately adjacent to the unreacted core, mainly in an envelope less than 100 nm thick, as determined by APT; the width of U-enrichment is broader than that of Th (Snoeyenbos et al.
2012). The elevated $P$ and $Y$ in the CL-dark domains are spatially covariant, reflecting enrichment in the xenotime component. WDS mapping also reveals a monotonic intensity of Hf $\mathrm{M} \alpha$ from the inner margin of the rim to the outer margin of the grain (Fig. 7), despite CL and/or minor element zonation measured in the complex rim.

Within zircon1, quantitative analysis reveals that core compositions vary widely in $\mathrm{HfO}_{2}$ and $\mathrm{ThO}_{2}$ (color-filled symbols, Fig. 9a-b; Table 1; full analytical results in Data Supplement Table 1) whereas the rims are nearly uniform (white-filled symbols, Fig. 9a-b; Table 1). Outside of the Th-rich inner band, the rims are enriched in $\mathrm{HfO}_{2}$ and devoid of $\mathrm{ThO}_{2}$. The rim compositions show remarkable large-scale grain-to-grain uniformity within each garnet and do not correlate with the composition of the zircon core or the location within the garnet (Fig. 9a-b). The core compositions in zircon2 also vary widely in $\mathrm{HfO}_{2}$, but the mean compositions of the core and rim overlap (Table 1) and the rim compositions vary considerably among grains (Fig. 9c).

The cores of zircon1 analyzed via LASS ICPMS analysis yielded ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates that range from c. 447 to $404 \mathrm{Ma}( \pm 2 \%, 2 \sigma)$ (Table 2). Chondrite-normalized REE patterns measured from the cores (green lines, Fig. 10a) show a positive Ce anomaly, a negative Eu anomaly, and high heavy rare earth element (HREE) concentrations with a positive slope, consistent with magmatic growth (gray field, Fig. 10a; adapted from Hoskin and Ireland 2000; Hoskin and Schaltegger 2003). The Th/U of these analyses varies from 0.3 to 1.2 (Fig. 10b).

Ma ( $\pm 2 \%, 2 \sigma$ ) (black lines, Fig. 10a; Table 2). Most rim analyses lack a positive Ce anomaly and have a shallow Eu anomaly. The slope of the HREE is significantly steeper than the analyzed cores; the slope is primarily attributed to middle rare earth element (MREE) depletion, rather than HREE enrichment. The Th/U ratio of these spots is less than 0.05 (Fig. 10b). Older rim analyses (c. 530 to 450 Ma ; Table 2) are analytically concordant, but have high common- Pb (dashed lines in Fig. 10a) and yield low $\mathrm{Th} / \mathrm{U}(<0.02$; Table 2). Two rim analyses from zircon1 yield younger dates ( 373 and 377 Ma ), $\mathrm{Th} / \mathrm{U}>0.2$ (blue circles, Fig. 10b), and REE patterns consistent with magmatic growth (blue lines, Fig. 10a; Table 2).

Because LASS analysis yields pits up to $8 \mu \mathrm{~m}$ in depth, some analysis volumes represent mixtures between core and rim compositions. Although highly discordant $\mathrm{U}-\mathrm{Pb}$ analyses often indicate mixtures, a mixture of core and rim domains that are similar in age may appear concordant. In these cases, post-analysis imaging by EPMA can provide useful information for data interpretation, as shown in Fig. 7 and 8. Variations in specimen height on the order of the laser pit depth $(<8 \mu \mathrm{~m})$ do not prevent acquisition of useful qualitative EPMA intensity data, and the $40^{\circ}$ takeoff angle of the spectrometers provides imaging of portions of the pit walls. For example, the Hf and U maps of the zircon grain in Fig. 7a show that the discordant analysis marked in red $(454 \mathrm{Ma})$ sampled through the zircon and into the garnet. The concordant spot marked in orange ( 393 Ma ) was placed to sample only the core observed in CL, but the analysis penetrated down through the core and into the high-Hf rim, as seen on the Hf map (Fig. 7a). Further, as implied by the Hf map and confirmed by the U map, this LASS analysis sampled the CL-dark U-rich dissolution-reprecipitation reaction front between core and rim and yet yielded
a concordant date. The rims for this grain yield older dates than the cores (black; Fig. 7a), but the analyses have high common Pb .

Zircon2 grains yield ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates that range broadly from 1726 to 365 Ma (Fig. 11), most of which are analytically concordant (Table 2; See Data Supplement Table 2). The uncertainty ranges from 8 to 30 Ma , which is largely dependent on the date and the reproducibility of the RM. All analyses $<400$ Ma yield low Th/U (Fig. 11b).

The youngest concordant date from the core of a zircon2 grain is 415 Ma . The REE patterns of core analyses from zircon2 (green lines, Fig. 11a) are consistent with magmatic growth. They have steep HREE patterns, a positive Ce anomaly and a negative Eu anomaly. The Th/U ratios vary broadly (Fig. 11; Table 2), but most analyses of cores yield Th/U greater than 0.1.

The dates of zircon2 rims vary, but the concordant analyses are all $<400 \mathrm{Ma}$. Half of the rim analyses yield flat to convex-up HREE patterns (black lines, Fig. 11a), which are consistent with growth during garnet stability (e.g. Rubatto 2002; Hoskin and Schaltegger 2003) and are compatible with the HREE composition of garnet measured in these samples (see Data Supplement Table 3). The other analyses yield HREE patterns similar to zircon2 cores (Fig. 11a). Nearly all analyses yield positive Ce and negative Eu anomalies and $\mathrm{Th} / \mathrm{U}$ less than 0.1 (Fig. 11b). There are no correlations between the host phase (e.g. cordierite, chlorite, kyanite) and the zircon REE composition; the zircon date and its REE composition; or the host phase and the zircon date.

Although two zircon2 rims yield concordant dates (434 and 405 Ma ), post-analysis imaging indicates that these LASS analyses partially sampled the older core. In samples where the difference in age between core and rim domains is small, results from mixed domains such as these can be analytically concordant, but they mix isotopic ratios from the two domains, so they should not be used to constrain the timing of metamorphism.

## InTERPRETATIONS

## Garnet megacrysts

One of the most distinctive features of the phosphatic garnet megacrysts is their abundant sub$\mu \mathrm{m}$ inclusions of hydroxylapatite and rutile. In thin section, these inclusions are arranged by sector in the host crystal, with the hydroxylapatite blebs in curvilinear trails normal to the sector face, and the coexisting rutile needles in several crystallographic orientations. Anti-correlation between the sub- $\mu \mathrm{m}$ hydroxylapatite inclusions and locally high intrinsic P in the garnet megacryst specimens presented here supports the interpretation that the sub- $\mu \mathrm{m}$ hydroxylapatite are precipitates from garnet compositions that were originally as high as 0.22 $\mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$.

Elevated P in garnet is well known from several HP/UHP crustal examples such as the Erzgebirge in the Bohemian Massif, $0.4 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ (Axler and Ague, 2015); the Kimi Complex of
the Rhodope Massif, 0.33 wt \% $\mathrm{P}_{2} \mathrm{O}_{5}$ (Mposkos and Kostopoulos 2001); the northern Rif, 0.12 $\mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ (Ruiz Cruz and Sanz de Galdeano 2013); and from mantle eclogites, $0.13 \mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ (Haggerty et al. 1994). In the crustal examples, hydroxylapatite and rutile $\pm$ ilmenite precipitates are also reported. The apparent exclusive analogy between the $P$ content and hydroxylapatite precipitates in garnet from the Goshen Dome locality and several diamond-bearing crustal UHP occurrences, suggests that these phosphatic garnet megacrysts are of unusually high-pressure origin. However, in the absence of free C or other conventional indicators, this hypothesis remains untested. Although P substitution in silicate garnet has a considerable pressure dependence (Konzett and Frost 2009), experimental characterization of P in garnet in compositions more directly relevant to typical crustal garnet compositions has been limited.

This raises a larger problem regarding the identification of crustal UHP metamorphism, which remains largely dependent on the formation and preservation of coesite and/or diamond, especially in higher temperature settings. Although pseudosection modeling can predict peak assemblages-even for rocks low in $\mathrm{SiO}_{2}$ or C -accurate results require knowledge of the bulk rock geochemistry during prograde to peak conditions, which is commonly unknown, particularly for rocks that fully recrystallized during exhumation. Garnet is certainly a common and relatively refractory phase in most settings and is known to accept substituents such as P , Ti, and Zr under HP/UHP conditions (Haggerty et al. 1994; Brunet et al. 2006; Dwarzski et al. 2006). A record of such substituents may be preserved either in compositional zonation or by the presence of precipitates representing these substituents originally in the garnet structure. Further experimental calibration of these substitutions in relevant compositions may allow for a
more quantitative interpretation of the P-T histories of garnet of unusual minor-element composition and/or containing multiphase precipitate suites, thus expanding the indicators by which we might identify (U)HP metamorphism.

## Metamorphic rims on zircon

Dissolution-reprecipitation involves dynamic, synchronous dissolution of zircon coupled with a simultaneous reprecipitation of zircon along a reaction front that propagates from the rim towards the core. The reaction front can produce compositional changes in minor and trace elements (Tomaschek et al. 2003; Geisler et al. 2007; Rubatto et al. 2008) and enable complete removal of radiogenic Pb , thereby resetting the age of the geochronometer. Previous studies also cite the presence of nm - to $\mu \mathrm{m}$-scale pores in zircon as evidence of dissolutionreprecipitation (Geisler et al. 2007; Vonlanthen et al. 2012), but these pores may not be preserved due to metamorphism (Tomaschek et al. 2003).

Based on these criteria, we interpret that the metamorphic rims on zircon in both populations were formed primarily from inward propagation of dissolution-reprecipitation reaction fronts. Components from the original zircon-i.e. U, Y, P, and, notably, Th—are now concentrated at the leading edge of the reaction front in the CL-dark band, adjacent to the unreacted core. Much of the original U, Y, P, and all the original Th have been concentrated in this band of anomalous xenotime-rich zircon solid solution. These components are interpreted to represent mainly redistribution of xenotime component from zircon in response to metamorphism along a low-temperature/high-pressure path, as suggested by experimental work on zircon-xenotime solid
solution by Tomaschek (2010). Alternative explanations for this distribution must call on a phase of deposition/growth (on the resorbed core) of a thin shell of new zircon with extremely elevated U, Th, Y, and P, followed by further growth of new zircon, which in zircon1 is entirely without Th (Fig. 9).

Although we do not know where the Pb from the dissolution-reprecipitation metasomatized rims collects, dissolution-reprecipitation can be effective at removing radiogenic Pb , effectively resetting the chronometer for the metasomatized rims. In some cases, dissolutionreprecipitation does not remove all the radiogenic Pb during (re)crystallization of the rims, as evident in Fig. 7a. Because of low concentrations of U in the convolute rims (ca. 20-50 ppm), minor trapped radiogenic Pb (and common -Pb ) can significantly affect the analysis, making it apparently older than the inner rim. The inner rim, however, has much higher $U$ concentrations ( $\sim 900 \mathrm{ppm}$ ) making any small amount of inherited Pb much less significant.

Zircon1 has several unique geochemical signatures. First, the Th-rich band around unreacted zircon cores is a strong marker of the maximum extent of the inward propagation of the metasomatic front. The lack of measurable Th in zircon1 rims (Fig. 9a-b; Table 1) indicates: 1) complete exclusion of Th during the metasomatic process, and 2) an absence of Th from the source material for any new zircon growth that might have occurred. Second, zircon1 rims have a monotonic $\mathrm{HfO}_{2}$ content that is unique to each garnet megacryst, but does not correspond to the composition of the zircon1 core or its position within the host garnet (Fig. 9, Table 1). The rim composition differs between RBTS- and WMBTS-hosted zircon. Zircon1 rims are
homogeneous in Hf from the outer margin against the host garnet to the inner margin of the zircon rim against the unreacted core. Further, the zircon1 rim compositions are distinct from the zircon2 rims, even on grains located immediately adjacent to the megacrysts, such as Matrix1 from WMBTS (Figs. 5b, 8c). These data imply that with regard to Hf, the zircon1 rim composition was buffered throughout its formation and in a domain coextensive with the garnet host. Third, the steep HREE profile, lack of Ce anomaly, and overall lower concentration of HREE of the zircon1 rims is distinctive and anomalous. If zircon1 rims formed exclusively from dissolution-reprecipitation, the rim compositions should be consistent with the original core, which is not the case. If the rims formed in equilibrium with garnet under typical metamorphic conditions, the HREE profile of the zircon rim should be consistent with the HREE profile of the co-existing garnet (e.g. Rubatto 2002; Hoskin and Schaltegger 2003; Harley et al. 2007). A transect across the co-existing garnet megacryst via LA-ICPMS (see Data Supplement Figure 2, Table 3) yielded a flat HREE profile, which suggests that either zircon is not in equilibrium with this garnet or that the conditions that formed these rims favor REE partitioning between the reacting phases. An alternative explanation is the addition of components to form new zircon from a material relatively depleted in REE compared to zircon. The local volumetric increase, recorded by the distinctive radial fractures surrounding nearly all zircon1 grains, confirms some amount of growth (i.e. addition of new material). New material sourced externally to the garnet (e.g. a fluid) would require transport of at least Zr and Hf across many cm of intact garnet while maintaining all the geochemical characteristics described above. We therefore conclude that the contribution of new material and the fluid associated with the metasomatic reactions are both locally derived from the host garnet.

Hydrogen and Na can be minor substituents in garnet under HP/UHP conditions. Hydrogen enters the garnet structure as OH or $\mathrm{H}_{4} \mathrm{O}_{4}$ to at least 2500ppm (as $\mathrm{H}_{2} \mathrm{O}$ ) at UHP (Gong et al. 2013) whereas garnet typically contains only tens to hundreds of ppm at crustal pressure (Maldener et al. 2003). Similarly, significant Na enters the garnet structure at up to $0.22 \mathrm{wt} \%$ $\mathrm{Na}_{2} \mathrm{O}$ at several GPa in mantle examples (Sobolev and Lavrent'ev 1971) yet elevated Na is found in crustal HP/UHP garnet only to a limited extent (e.g. Schertl et al. 1991). The disparity between the possible and the typically observed H and Na content in HP/UHP garnet may indicate that these substituents exited the garnet on decompression. We suggest that HP/UHP garnet that has incorporated significant H and Na may experience metasomatic effects during decompression from the release of endogenous alkali-bearing fluid when these substituents exit the garnet structure. Such an endogenous fluid may have participated in the reactions that produced the metamorphic rims in zircon1.

Growth of zircon within garnet requires mass transfer of zircon components, particularly Zr and Hf. Typical garnet at crustal pressure ( $<1 \mathrm{GPa}$ ) contains tens of ppm Zr (e.g. Fraser et al. 1997, Degeling et al. 2001). However, experiments have shown that garnet can incorporate up to 6000 ppm Zr at pressures of 5 to 7 GPa (Dwarzski et al. 2006), indicating increased solubility of Zr (and presumably, Hf) in garnet under UHP conditions. The order of magnitude difference in Zr solubility in garnet between UHP and crustal conditions may provide a source for such mass transfer to have occurred between garnet and the included zircons, if such a pressure excursion occurred and diffusivity was sufficient.

The coarse rutile precipitates in the phosphatic garnet megacrysts also indicate a period of longrange diffusivity of another tetravalent cation (Ti) in octahedral coordination. Under typical crustal and UHT conditions, Ti in garnet substitutes for Si in tetrahedral coordination (Kawasaki and Motoyoshi 2007). However, at elevated pressure (>1GPa), Ti in garnet is almost entirely in octahedral coordination (Ackerson et al. 2013). Precipitation of coarse rutile blades and bicrystals in the phosphatic garnet megacrysts may have proceeded by open-system precipitation mechanisms as described by Proyer et al. (2013).

The composition of the myriad ca. $1 \mu \mathrm{~m}$ zircon crystals in the phosphatic garnet megacrysts is unknown due to analytical limitations for very small volumes, but their broad distribution and relatively uniform size and morphology suggest precipitation from an originally higher- Zr host garnet. If so, the addition of new material to the metamorphic rims of the included detrital zircon would be merely another aspect of the process of zircon precipitation from the bulk garnet. If not, the micro-zircons are matrix inclusions and each phosphatic garnet overgrew a pre-existing distribution of micro-zircons. However, this would require a pre-existing concentration of micro-zircons on the order of $10^{8} / \mathrm{cm}^{3}$ over volumes on the order of $10 \mathrm{~s}^{\text {of }} \mathrm{cm}^{3}$, with evidence for this distribution having been preserved only within the phosphatic garnet megacrysts.

To summarize, the rims on zircon1 show evidence of two metamorphic mechanisms. First, dissolution-reprecipitation reactions are indicated by the CL-dark reaction front enriched in Th,
$\mathrm{U}, \mathrm{Y}$, and P adjacent to the unreacted core. Second, the extensive fracturing of the surrounding garnet host indicates local volumetric increase of zircon (i.e. growth). No unusual fracturing is observed around any other inclusions in garnet. Because simple mixing between zircon and garnet does not entirely explain the anomalous chemistry of the zircon1 rims, we interpret that these rim compositions were produced by both metamorphic mechanisms: dissolutionreprecipitation reaction that removed and relocated xenotime component (and potentially HREE?) from the rims and of the addition of components from garnet. The uniform composition of the metamorphic rims (Fig. 7) indicates that both metamorphic processes were operating simultaneously.

In zircon2, the accumulation of $\mathrm{U}, \mathrm{Y}, \mathrm{P}$, and Th at the core-rim boundary provides clear evidence of dissolution-reprecipitation reactions similar to those in the megacrysts, but there is no certain evidence of growth. The metamorphic rims have generally higher Hf (Fig. 9) and much lower Th/U (Fig. 11b) than the cores, but they lack the distinctive signatures of fixed Hf and no measurable Th. Some rims are consistent with equilibration with garnet, whereas others suggest equilibration with a metamorphic fluid. These data indicate that the rim compositions are controlled by local changes in mineralogy and the presence and availability of fluids and melt over 30 million years of metamorphism.

## Chronology of events

The oscillatory CL zoning and compositions of zircon cores from both populations indicate a magmatic or volcanogenic source of detrital grains that were subsequently metamorphosed. In
zircon1, the cores are dominantly Paleozoic and range from 447 to $404 \mathrm{Ma}(\mathrm{n}=28)$. The population lacks Grenville dates, which typically dominate the detrital zircon signature in lithologies from this region (e.g. Cawood and Nemchin 2001; Murphy et al. 2004; van Staal et al. 2009). In contrast, zircon 2 cores yield a broad range of concordant dates. Proterozoic dates are common and range from 1726 to 562 Ma (Fig. 11; Table 2). Paleozoic dates range from 533 to $415 \mathrm{Ma}(\mathrm{n}=17)$, most of which cluster near 475 Ma . The older dates are broadly consistent with the signature of the Laurentian margin (see Data Supplement Figure 3), but may also include contributions from other terranes - the sample size is too small to fully address provenance. The Paleozoic dates in both populations are interpreted as zircon shed from nearby magmatic arcs during the Taconic through early Acadian ( 475 to 404 Ma ). The youngest concordant zircon core date pins deposition to 404 Ma .

The timing of the reaction producing the CL-dark boundary between the core and rim cannot be dated directly. However, the metamorphic rims beyond the band are commonly large enough to analyze via LASS and geochemistry is essential in deciphering the metamorphic mechanism(s) that produced the zircon rims. The HREE profiles at the oldest zircon1 locations (400 and 396 Ma ) are significantly steeper than the younger concordant zircon1 ( 385 to 373 Ma ). These data suggest that the unique conditions and reactions (endogenous fluids and growth from garnet) that formed the zircon1 rims with the steepest HREE profiles were perhaps short in duration ( 400 to 396 Ma ) and that the analyses with more typical REE profiles signal a return to granulite to amphibolite facies metamorphism by 395 Ma . The youngest dates ( 377 and 373

Ma ) are geochemically consistent with igneous growth, suggesting the presence of melt during this interval.

The composition of zircon2 rims also support granulite to amphibolite facies conditions by 395 Ma. Half of the REE profiles are similar to zircon2 cores and lack the steep HREE profiles observed in some of zircon1 rims. The other REE profiles from zircon2 rims indicate garnet stability. The long duration of metamorphism ( 394 to 365 Ma ) and varied compositions (Fig. 10a) are consistent with zircon response to local changes in mineralogy and fluid/melt composition and/or availability over this interval, which generally agrees with regional constraints for the timing of the high-temperature Acadian orogeny (e.g. Pyle and Spear 2002; Cheney et al. 2006, Gatewood et al. 2015). The fluid that catalyzed the production of metamorphic rims on zircon2 may have been sourced from a variety of reactions associated with the high-temperature Acadian, including the melt-producing reactions that ultimately produced the restitic schist.

The restitic nature of the schist requires that melt was extracted, but the effect of melting on garnet and zircon varies among these samples. The pristine, intact megacryst in WMBTS indicates that some garnet megacrysts persisted through melting without modification, but resorption of the garnet megacrysts in RBTS and the presence of epidote along fractures within these megacrysts indicate a response to the presence of fluid and/or melt. The oldest dates and the steepest HREE profiles of metamorphic zircon are included within the pristine megacryst and suggest net growth of zircon, not net dissolution. The younger metamorphic rim dates in
both zircon1 and zircon2 are consistent with either modification of zircon via metasomatic dissolution-reprecipitation or some component of igneous growth after 395 Ma . Some new growth of metamorphic zircon may have occurred in zircon2, but it can only be confirmed in zircon1 where the presence of radial fractures of the host garnet indicates net growth of zircon. Although many of the zircon2 rims were likely produced from metasomatic fluids associated with melting, the precise timing of melt production cannot be directly determined from the zircon data.

## IMPLICATIONS

## Metamorphic growth and modification of zircon

Recent Zr budget studies demonstrate the limited capacity for crystallization of new zircon (i.e. overgrowths) within common metamorphic systems (Degeling et al. 2001; Kohn et al. 2015). Yet, concordant rims on zircon recording metamorphic events are common in polymetamorphic systems. Metasomatism by dissolution-reprecipitation has emerged as an alternative to overgrowth as a mechanism for producing datable metamorphic rims on zircon (Tomaschek et al. 2003; Geisler et al. 2007). Zircon1 and zircon2 yield abundant evidence of dissolutionreprecipitation mechanisms in the formation of metamorphic zircon rims. However, the radial fractures around zircon1 also indicate volumetric expansion (new growth), and thus an unusual setting where both processes have been confirmed.

Many examples of dissolution-reprecipitation mechanisms in zircon exhibit the lobate boundary between core and rims (e.g. Vonlanthen et al. 2012). In addition to these features, the zircons in this study also have a thin CL-dark band found at the core-rim boundary. The CL-dark band is tied to trace-element accumulations at the reaction front and has not been observed in other zircon studies, with the exception of the diamondiferous UHP locality near Xanthi, in the Central Rhodope, Greece (cf. Fig. 11e; Krenn et al. 2010). One of the most distinctive features of the trace-element accumulation at the edge of the unreacted core is the sharp accumulation of Th and $U$. Thorium is much more spatially restricted than $U$ and appears to be excluded from the rest of the rim. These observations are similar to laboratory experiments with dissolutionreprecipitation reactions in xenotime, where Harlov and Wirth (2012) observed an accumulation of Th along the reaction front and an exclusion from the rest of the rim domain. Quantification of the Th accumulation (hence the quantity of reacted zircon, if its original Th content is known) and evaluation of the Th budget in the metamorphic rim may allow for evaluation of the relative contribution of dissolution-reprecipitation and growth processes in metamorphic zircon.

These data prompt questions about the fidelity of metamorphic zircon. What do these dates mean? Do they record metamorphic events? The data demonstrate that most rim analyses are concordant, which suggests that the dates can be related to the timing of metasomatism. The composition also provides insight regarding the conditions of metasomatism. For example, the rim dates from zircon2 suggest that zircon grew in equilibrium with garnet for portions of the metamorphic history and in equilibrium with non-garnet stable fluids for other portions.

Collectively, these data indicate that the matrix phase assemblage was changing over the 30 Myr interval. The relatively small number of rim analyses (19) compared with core (119) suggests that more detailed information regarding the metamorphic evolution of the phase assemblage would require measuring a more reactive phase where larger portions of the mineral retain information about metamorphism. Monazite is an excellent chronometer to address these questions - particularly the timing of melt-generation-but the lack of monazite within the pristine megacrysts suggests that a record derived solely from monazite will be incomplete. Because zircon is present in all petrographic contexts, it remains an useful target for constructing the entire metamorphic history, though perhaps at broader strokes.

Rims with high common- Pb and/or discordance suggest that the conditions responsible for forming metamorphic zircon can be complex. The presence of high common Pb may be related to the composition of the metasomatic fluid, the P-T conditions of metasomatism, or the potential contributions of constituents from other phases (e.g. phosphatic garnet) to grow new zircon. We do not have enough data to resolve among these possibilities, but detailed atomic scale analysis of the reaction boundary itself (e.g. APT analysis) may provide insight regarding the distribution and possible source of common- Pb . Discordant analyses may reflect the incomplete removal of radiogenic Pb from this original zircon or mixing of different domains (e.g. core and rim), but this falls beyond the resolution of the techniques employed in this study. Further improvements in spatial resolution will permit analysis of thin domains and will likely resolve some of the ambiguities presented here.

## Regional implications

The near absence of older zircon cores within the garnet megacrysts, as compared to the adjacent matrix, presents an interesting problem. One explanation is that the phosphatic garnet megacrysts grew in a tightly restricted setting in a protolith that did not contain the same Proterozoic component of zircon present in their matrix. An alternative explanation is that the garnet preferentially resorbed Proterozoic zircon during growth because they had accumulated more radiation damage and were therefore more labile than other zircon grains in the detrital population. In this case, the zircon clusters found in some garnet specimens (Fig. 3d) represent locally high concentrations of zircon components within the garnet and may reflect resorbed detrital zircon.

The LASS dates on zircon cores and rims indicate that the original deposition concluded by ca. 404 Ma and that metamorphism began shortly thereafter-by c. 400 Ma . The timing and geochemistry of these analyses suggest three important things. First, the detrital zircon cores record an approaching island arc (or arcs) proximal to Laurentia active ca. 447 to 404 Ma . Second, zircon1 rims record some of the earliest metamorphism (ca. 400 Ma ) associated with the conventional Acadian may have been at HP/UHP conditions. Third, these grains record continued metamorphism from 395 Ma until the end of the Acadian (ca. 365 Ma ), suggesting that these rocks record nearly the entire history of Acadian metamorphism in the region.

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## Figure Captions

FIGURE 1: Geologic maps of study area. a) Regional map showing geologic context of the
Goshen Dome; adapted from Karabinos et al. (1998). b) The Goshen Dome, cored by the Collinsville Gneiss. The Cobble Mountain Formation contains restitic garnet-kyanite schist near the western margin, located within domains previously mapped as granulite and amphibolite gneisses. Yellow dots mark sample locations. Map modified from Hatch and Warren (1981).

Figure 2: RBTS. a) Plane polarized light photomicrograph. X-ray composition maps of b) Ca $\mathrm{K} \alpha$ and c) Mn K $\alpha$. Red dots mark locations of analyzed zircons; red arrow marks the location of the d) quantitative profile showing $\mathrm{Mg} \#\left(\mathrm{X}_{\mathrm{Prp}} /\left(\mathrm{X}_{\mathrm{Prp}}+\mathrm{X}_{\mathrm{Alm}}\right)\right)$, $\mathrm{X}_{\mathrm{Sps}}, \mathrm{X}_{\mathrm{Grs}}$, and $\mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$ versus distance across the garnet in $\mu \mathrm{m}$.

FIGURE 3: RBTS. a) Plane polarized light photomicrograph of zircon inclusion wholly contained within garnet, showing radial fractures. Sub- $\mu \mathrm{m}$ apatite precipitates and oriented rutile needles cloud the host garnet. b) Backscattered electron (BSE) image of a zircon inclusion within garnet with radial fractures and abundant $\mu \mathrm{m}$-scale zircon crystals (bright flecks) in the host garnet. c) Plane polarized light photomicrograph of rutile precipitates; many are twinned. d) BSE image of zircon needles and blades in garnet.

Figure 4: a) Compositional profile near-core to rim of garnet RBTS-B (adjacent to garnet RBTS)
shows Mg\# ( $\left.\mathrm{X}_{\text {Prp }} /\left(\mathrm{X}_{\text {Prp }}+\mathrm{X}_{\mathrm{Alm}}\right)\right), \mathrm{X}_{\mathrm{Sps}}, \mathrm{X}_{\mathrm{Grs} \text {, }}$ and $\mathrm{wt} \% \mathrm{P}_{2} \mathrm{O}_{5}$. Sub- $\mu \mathrm{m}$ hydroxylapatite inclusions are abundant to the left of the red dashed line (near the core) and conspicuously absent to the right of the line (towards the rim), where intrinsic $w t \% \mathrm{P}_{2} \mathrm{O}_{5}$ increases and XGrs drops to ca. 0.03 . b) Plane polarized light photomicrograph showing location of compositional profile. Intrinsic $\mathrm{P}_{2} \mathrm{O}_{5}$ is anticorrelated to the presence of apatite inclusion trails.

FIgURE 5: WMBTS. a) Plane polarized light photomicrograph. X-ray composition maps of $\mathbf{b}$ ) $\mathbf{C a}$ $\mathrm{K} \alpha$ and $\mathbf{c}$ ) $\mathrm{Mn} \mathrm{K} \alpha$. Red dots mark locations of analyzed zircon1; two matrix zircons are indicated in yellow. Red arrow marks the location of the d) quantitative profile showing $\mathrm{Mg} \#$ $\left(X_{\text {Prp }} /\left(X_{\text {Prp }}+X_{\text {Alm }}\right)\right), X_{\text {Sps }}, X_{\text {Grs }}$, and $w t \% \mathrm{P}_{2} \mathrm{O}_{5}$.

FIgURE 6: G12B10. X-ray composition maps of a) $\mathrm{Al} \mathrm{K} \alpha$ and b) $\mathrm{Ca} \mathrm{K} \alpha$. Red dots mark locations of analyzed zircon. c) Cross-polarized light photomicrograph. d) Plane-polarized light photomicrograph; mineral abbreviations: $\mathrm{qtz}=$ quartz, $\mathrm{grt}=$ garnet, $\mathrm{chl}=$ chlorite, $\mathrm{pl}=$ plagioclase, $\mathrm{bt}=$ biotite, $\mathrm{crd}=$ cordierite, $\mathrm{ky}=$ kyanite. Darkest minerals are rutile and ilmenite. All images are the same scale.

Figure 7: Representative zircon1 grains. a) From RBTS: cathodoluminescence (CL), laser ablation split stream (LASS) spot locations and corresponding ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb} / 238 \mathrm{U}$ dates, Hf $\mathrm{M} \alpha$, and $\mathrm{U} \mathrm{M} \beta$ maps. b) From WMBTS: CL, LASS spot locations and corresponding ${ }^{207} \mathrm{~Pb}-$
corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates, $\mathrm{Hf} \mathrm{M} \alpha$, Th $\mathrm{M} \alpha, \mathrm{U} \mathrm{M} \beta$, and $\mathrm{Y} \mathrm{L} \alpha$ maps; red arrows point to CL-dark, Th, U, Y, P enriched band at the margin of the unreacted core. c) From WMBTS: CL and Hf M $\alpha$ map. $\mathrm{U} \mathrm{M} \beta$ maps are not corrected for (minor) $\mathrm{Th} \mathrm{M} \gamma$ overlap due to much lower Th concentration and restricted spatial distribution Th vs. U. Note the characteristic CL-dark band between the unreacted core and the metamorphic rim and the homogeneity in Hf on the rims. Italicized dates are discordant; black LASS spots have high common- Pb .

Figure 8: Matrix zircon from G12B, G12G, and WMBTS. a) Cathodoluminescence (CL) and Xray composition maps ( $\mathrm{Hf} \mathrm{M} \alpha$, Th $\mathrm{M} \alpha, \mathrm{U} \mathrm{M} \beta, \mathrm{Y} \mathrm{L} \alpha$, and $\mathrm{P} \mathrm{K} \alpha$ ) of a characteristic zircon found within kyanite in the matrix of G12B10; 20- $\mu \mathrm{m}$ scale on all images in this row. Hafnium is homogeneous in the rim and distinct from the core composition. The boundary between unreacted core and metamorphic rim is marked by a CL-dark band enriched in Th, $\mathrm{U}, \mathrm{Y}$ and P . b) CL images of zircon grains from the matrix of G12B10 and G12G3. Circles mark laser ablation split stream (LASS) analysis spots with corresponding ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates. Magmatic core domains labeled. Red arrows point to CL-dark, Th, U, Y, P enriched band at the margin of the unreacted core. Grains 12 and 30 are within chlorite; grain 48 is within rutile. (c) Matrix grain 1 from WMBTS (see Fig. 5 for location) shown in CL and backscattered electron (BSE). Red boxes mark the location of WDS-EPMA maps (Hf M $\alpha$, Th $\mathrm{M} \alpha, \mathrm{U} \mathrm{M} \beta$, and $\mathrm{Y} L \alpha$ ). Note that the CL-dark band between the unreacted core and the metamorphic rims is also enriched in Hf, Th, U, and Y. Two bands of U and Y are also evident; see text for details.

FIGURE 9: Zircon included in garnet megacrysts in a) RBTS ( $\mathrm{n}=13$ grains). b) WMBTS ( $\mathrm{n}=13$
grains). (c) Matrix ( $\mathrm{n}=14$ grains). Vertical gray lines separate analyses from different grains. Color-filled symbols are zircon core domains (typically 2 analyses per grain). The adjacent white-filled symbols (typically 2 analyses per grain) are the rim compositions directly next to the core. Dashed lines show the mean of core compositions; solid lines show the mean of rim compositions. Colored shading represents $1 \sigma$ of the mean.

Figure 10: A. Rare earth element profiles from zircon1. Dashed lines are analyses with high common- Pb . Gray field marks a range of magmatic zircon compositions from igneous sources. B. $\mathrm{Th} / \mathrm{U}$ vs. ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb}-{ }^{238} \mathrm{U}$ dates of zircon1; dates reflect $2 \sigma$ uncertainty.

Figure 11: A. Rare earth element profiles from zircon2. The gray shaded region marks a range of magmatic zircon compositions from igneous rocks. B. Th/U vs. ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb}-{ }^{238} \mathrm{U}$ dates from zircon2; dates reflect $2 \sigma$ uncertainty.

## Data Supplement Text

Figure 1: Cathodoluminescence (CL) images of zircon analyzed in this study. Circles mark the location of spot analyses and colored numbers are the ${ }^{207} \mathrm{~Pb}$ corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates (in Ma). The grain number for each sample is shown in white.

Figure 2: Locations of garnet transects for geochemical analysis via laser ablation. The transect start is marked with a red circle; the end is marked with a red square.

Figure 3: Kernel density estimation of ${ }^{207} \mathrm{~Pb}$-corrected ${ }^{206} \mathrm{~Pb} /{ }^{238} \mathrm{U}$ dates from zircon cores. Circles below the $x$-axis are the dates. Mixed spot analyses were excluded.

## Data Tables

1: Electron microprobe analyses of zircon. Data were collected at UMass-Amherst.
2: Zircon geochronology and geochemistry analyses. Full analytical results. Data were collected at UC Santa Barbara.

3: Transects across garnet analyzed via laser ablation analysis. Full analytical results. Data were collected at UC Santa Barbara.

Table 1: Electron probe micro-analysis results from cores and rims in both zircon populations.

|  | $\mathbf{n}$ | $\mathbf{H f O}_{2}$ | $\mathbf{1 \sigma}$ | $\mathbf{T h O}_{2}$ | $\mathbf{1 \sigma}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| RBTS - core | 26 | 1.19 | 0.16 | 0.032 | 0.023 |
| RBTS - rim | 26 | 1.62 | 0.07 | 0.002 | 0.004 |
| WMBTS - core | 26 | 1.23 | 0.19 | 0.070 | 0.046 |
| WMBTS - rim | 25 | 1.54 | 0.05 | 0.003 | 0.006 |
| Matrix - core | 29 | 1.22 | 0.16 | - | - |
| Matrix - rim | 30 | 1.41 | 0.11 | - | - |

$\mathrm{n}=$ number of analyses
Detection limits at $99 \%$ confidence level: $0.016 \mathrm{wt} \% \mathrm{HfO}_{2}$ and $0.003 \mathrm{wt} \% \mathrm{ThO}_{2}$ for RBTS and WMBTS core and rim measurements. Analysis on SX-100 with multi-point backgrounds (Allaz et al., 2011; Probe for EPMA, Probe Software Inc.). $\mathrm{HfO}_{2}$ matrix zircon analyses by SX-50 at lower precision, which is sufficient to confirm heterogeneity apparent from X-ray composition maps.

Table 2: $\mathrm{U}-\mathrm{Pb}$ and rare earth element data of concordant ages from all samples, classified by core, overgrowth and sample (Excel document).


Figure 1


Figure 2


Figure 3

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a
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Figure 4


Figure 5


Figure 6


Figure 7


Figure 8


Figure 9


Figure 10


Figure 11


| Grt | Output_1_16 | WMBTS z4 | MIX | 0.913 | 16.00 | 0.44 | 0.057 | 0.001 | 390 | 8 | 0.98 | 399 | 6 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Grt | Output_1_17 | WMBTS z4 | MIX | 0.731 | 15.55 | 0.36 | 0.056 | 0.001 | 401 | 8 | 0.99 | 404 | 5 |
| Grt | Output_1_18 | WMBTS z4 | C | 0.769 | 14.11 | 0.31 | 0.055 | 0.001 | 442 | 9 | 1.01 | 436 | 4 |
| Grt | Output_1_19 | WMBTS z4 | C | 0.369 | 14.37 | 0.29 | 0.056 | 0.001 | 434 | 9 | 1.01 | 429 | 2 |
| Grt | Output_1_20 | WMBTS z4 | C | 0.774 | 14.47 | 0.32 | 0.056 | 0.001 | 431 | 8 | 1.01 | 427 | 4 |
| Grt | Output_1_21 | WMBTS z5 | MIX | 0.539 | 15.89 | 0.34 | 0.056 | 0.001 | 393 | 8 | 0.99 | 397 | 4 |
| Grt | Output_1_22 | WMBTS z5 | C | 0.795 | 14.29 | 0.32 | 0.056 | 0.001 | 436 | 9 | 1.00 | 437 | 5 |
| Grt | Output_1_24 | WMBTS z6 | C | 0.591 | 14.86 | 0.31 | 0.055 | 0.001 | 420 | 8 | 1.01 | 417 | 4 |
| Grt | Output_1_25 | WMBTS z6 | MIX | 0.451 | 12.80 | 0.32 | 0.057 | 0.001 | 485 | 10 | 1.01 | 482 | 9 |
| Grt | Output_1_28 | WMBTS z8 | MIX | 0.880 | 15.49 | 0.35 | 0.055 | 0.001 | 403 | 8 | 1.01 | 399 | 5 |
| Grt | Output_1_29 | WMBTS z9 | C | 0.557 | 14.56 | 0.30 | 0.055 | 0.001 | 428 | 8 | 1.01 | 425 | 3 |
| Grt | Output_1_31 | WMBTS z10 | MG | 0.290 | 16.19 | 0.38 | 0.056 | 0.001 | 385 | 8 | 0.98 | 395 | 5 |
| Grt | Output_2_01 | WMBTS Spot 15 | C | 0.856 | 14.52 | 0.34 | 0.055 | 0.001 | 429 | 8 | 1.00 | 429 | 4 |
| Grt | Output_2_03 | WMBTS Spot 17 | C | 0.796 | 14.06 | 0.31 | 0.055 | 0.001 | 443 | 9 | 1.02 | 435 | 4 |
| Grt | Output_2_04 | WMBTS Spot 18 | C | 0.812 | 14.78 | 0.33 | 0.055 | 0.001 | 422 | 8 | 1.00 | 421 | 4 |
| Grt | Output_2_05 | WMBTS Spot 19 | C | 0.882 | 14.73 | 0.34 | 0.055 | 0.001 | 423 | 8 | 1.00 | 424 | 4 |
| Grt | Output_2_07 | WMBTS Spot 21 | C | 0.882 | 14.62 | 0.32 | 0.055 | 0.001 | 427 | 8 | 1.01 | 423 | 3 |
| Ma | Output_2_09 | WMBTS Spot 23 | C | 0.510 | 5.98 | 0.13 | 0.072 | 0.002 | 997 | 19 | 1.00 | 993 | 8 |
| Ma | Output_2_10 | WMBTS Spot 24 | C | 0.994 | 7.70 | 0.43 | 0.068 | 0.002 | 785 | 15 | 0.99 | 794 | 32 |
| Ma | Output_2_11 | WMBTS Spot 25 | C | 0.846 | 5.95 | 0.14 | 0.072 | 0.001 | 1001 | 19 | 1.01 | 994 | 7 |
| Ma | Output_2_12 | WMBTS Spot 26 | C | 0.824 | 6.10 | 0.14 | 0.072 | 0.002 | 978 | 19 | 1.00 | 982 | 7 |
| Ma | Output_2_13 | WMBTS Spot 27 | C | 0.778 | 5.91 | 0.14 | 0.073 | 0.002 | 1008 | 20 | 1.00 | 1006 | 9 |
| Grt | Output_2_15 | WMBTS Spot 29 | C | 0.826 | 15.02 | 0.33 | 0.055 | 0.001 | 415 | 8 | 0.99 | 419 | 4 |
| Grt | Output_2_16 | WMBTS Spot 30 | C | 0.859 | 15.31 | 0.35 | 0.056 | 0.001 | 407 | 8 | 0.99 | 410 | 4 |
| Grt | Output_2_17 | WMBTS Spot 31 | C | 0.867 | 13.93 | 0.34 | 0.055 | 0.001 | 447 | 9 | 1.01 | 441 |  |
| Grt | Output_2_18 | WMBTS Spot 32 | C | 0.804 | 14.70 | 0.33 | 0.055 | 0.001 | 424 | 8 | 1.00 | 422 | 4 |
| Ma | Output_1_01 | G12G3_zrn 20um | C | 0.892 | 6.32 | 0.05 | 0.072 | 0.001 | 945 | 8 | 0.98 | 962 | 5 |
| Ma | Output_1_03 | G12G3_zrn 20um | C | 0.962 | 4.46 | 0.06 | 0.085 | 0.001 | 1304 | 16 | 1.00 | 1306 | 7 |
| Ma | Output_1_04 | G12G3_zrn 20um | C | 0.995 | 4.63 | 0.10 | 0.083 | 0.001 | 1261 | 25 | 1.00 | 1263 | 15 |
| Ma | Output_1_07 | G12G3_zrn 20um | C | 0.746 | 5.13 | 0.04 | 0.079 | 0.001 | 1148 | 9 | 1.00 | 1154 | 6 |
| Ma | Output_1_08 | G12G3_zrn 20um | C | 0.813 | 3.89 | 0.03 | 0.094 | 0.001 | 1472 | 13 | 0.99 | 1488 | 7 |
| Ma | Output_1_09 | G12G3_zrn 20um | C | 0.981 | 12.69 | 0.27 | 0.059 | 0.001 | 488 | 10 | 0.97 | 502 | 9 |
| Ma | Output_1_11 | G12G3_zrn 20um | C | 0.865 | 4.23 | 0.04 | 0.085 | 0.001 | 1372 | 13 | 1.01 | 1351 | 7 |
| Ma | Output_1_12 | G12G3_zrn 20um | C | 0.845 | 5.22 | 0.04 | 0.078 | 0.001 | 1128 | 9 | 0.99 | 1140 | 5 |
| Ma | Output_1_13 | G12G3_zrn 20um | C | 0.753 | 5.05 | 0.04 | 0.078 | 0.001 | 1165 | 9 | 1.00 | 1168 | 7 |
| Ma | Output_1_14 | G12G3_zrn 20um | C | 0.867 | 5.07 | 0.04 | 0.079 | 0.001 | 1160 | 10 | 0.99 | 1171 | 8 |


| Ma | Output_1_15 | G12G3_zrn 20um | C | 0.828 | 3.29 | 0.03 | 0.103 | 0.001 | 1717 | 14 | 1.01 | 1699 | 8 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ma | Output_1_16 | G12G3_zrn 20um | C | 0.833 | 3.59 | 0.03 | 0.103 | 0.001 | 1575 | 14 | 0.97 | 1625 | 8 |
| Ma | Output_1_17 | G12G3_zrn 20um | C | 0.894 | 3.33 | 0.03 | 0.104 | 0.001 | 1695 | 17 | 1.00 | 1702 | 10 |
| Ma | Output_1_18 | G12G3_zrn 20um | C | 0.838 | 6.17 | 0.06 | 0.073 | 0.001 | 966 | 9 | 0.99 | 982 | 7 |
| Ma | Output_1_19 | G12G3_zrn 20um | C | 0.790 | 5.95 | 0.06 | 0.072 | 0.001 | 1001 | 10 | 0.99 | 1007 | 8 |
| Ma | Output_1_20 | G12G3_zrn 20um | C | 0.843 | 3.88 | 0.03 | 0.094 | 0.001 | 1476 | 13 | 0.99 | 1491 | 8 |
| Ma | Output_1_21 | G12G3_zrn 20um | C | 0.910 | 4.08 | 0.04 | 0.090 | 0.001 | 1413 | 14 | 0.99 | 1424 | 9 |
| Ma | Output_1_22 | G12G3_zrn 20um | C | 0.876 | 3.60 | 0.03 | 0.102 | 0.001 | 1571 | 13 | 0.98 | 1618 | 6 |
| Ma | Output_1_23 | G12G3_zrn 20um | C | 0.598 | 13.02 | 0.16 | 0.056 | 0.001 | 478 | 6 | 1.01 | 474 | 6 |
| Ma | Output_1_24 | G12G3_zrn 20um | C | 0.892 | 4.43 | 0.04 | 0.084 | 0.001 | 1313 | 11 | 1.00 | 1310 | 7 |
| Ma | Output_1_25 | G12G3_zrn 20um | C | 0.937 | 4.51 | 0.05 | 0.084 | 0.001 | 1290 | 15 | 1.00 | 1286 | 8 |
| Ma | Output_1_26 | G12G3_zrn 20um | C | 0.892 | 4.34 | 0.04 | 0.084 | 0.001 | 1340 | 11 | 1.01 | 1323 | 8 |
| Ma | Output_1_27 | G12G3_zrn 20um | C | 0.931 | 5.20 | 0.06 | 0.082 | 0.001 | 1128 | 14 | 0.97 | 1172 | 9 |
| Ma | Output_1_28 | G12G3_zrn 20um | C | 0.997 | 6.78 | 0.45 | 0.072 | 0.001 | 882 | 57 | 0.97 | 909 | 51 |
| Ma | Output_1_30 | G12G3_zrn 20um | C | 0.882 | 7.06 | 0.06 | 0.070 | 0.001 | 852 | 8 | 0.98 | 875 | 8 |
| Ma | Output_1_31 | G12G3_zrn 20um | C | 0.887 | 4.24 | 0.05 | 0.091 | 0.001 | 1361 | 16 | 0.98 | 1394 | 13 |
| Ma | Output_1_32 | G12G3_zrn 20um | C | 0.811 | 3.67 | 0.04 | 0.096 | 0.001 | 1553 | 15 | 1.00 | 1551 | 8 |
| Ma | Output_1_33 | G12G3_zrn 20um | C | 0.913 | 5.89 | 0.06 | 0.071 | 0.001 | 1013 | 10 | 1.02 | 990 | 6 |
| Ma | Output_1_34 | G12G3_zrn 20um | C | 0.867 | 11.96 | 0.17 | 0.057 | 0.001 | 518 | 7 | 1.01 | 515 | 7 |
| Ma | Output_1_35 | G12G3_zrn 20um | C | 0.675 | 13.05 | 0.16 | 0.056 | 0.001 | 476 | 6 | 1.00 | 476 | 6 |
| Ma | Output_1_38 | G12G3_zrn 20um | C | 0.784 | 4.85 | 0.05 | 0.084 | 0.001 | 1202 | 13 | 0.97 | 1240 | 10 |
| Ma | Output_1_39 | G12G3_zrn 20um | C | 0.839 | 4.36 | 0.06 | 0.085 | 0.001 | 1333 | 18 | 1.00 | 1328 | 12 |
| Ma | Output_1_40 | G12G3_zrn 20um | C | 0.880 | 3.80 | 0.04 | 0.094 | 0.001 | 1508 | 16 | 1.00 | 1508 | 9 |
| Ma | Output_1_41 | G12G3_zrn 20um | C | 0.835 | 5.83 | 0.05 | 0.073 | 0.001 | 1021 | 9 | 1.00 | 1018 | 8 |
| Ma | Output_1_42 | G12G3_zrn 20um | C | 0.615 | 5.90 | 0.05 | 0.073 | 0.001 | 1009 | 9 | 1.00 | 1010 | 7 |
| Ma | Output_1_43 | G12G3_zrn 20um | C | 0.794 | 6.53 | 0.08 | 0.070 | 0.001 | 918 | 10 | 0.99 | 924 | 8 |
| Ma | Output_1_44 | G12G3_zrn 20um | C | 0.851 | 4.03 | 0.05 | 0.090 | 0.001 | 1430 | 16 | 1.00 | 1430 | 9 |
| Ma | Output_1_05 | G12G3_zrn3 15um | C | 0.923 | 3.38 | 0.08 | 0.103 | 0.002 | 1671 | 41 | 1.00 | 1673 | 11 |
| Ma | Output_1_06 | G12G3_zrn3 15um | C | 0.896 | 3.27 | 0.09 | 0.103 | 0.002 | 1726 | 46 | 1.01 | 1703 | 16 |
| Ma | Output_1_07 | G12G3_zrn3 15um | C | 0.890 | 3.85 | 0.09 | 0.090 | 0.002 | 1495 | 33 | 1.01 | 1470 | 9 |
| Ma | Output_1_08 | G12G3_zrn3 15um | C | 0.951 | 6.51 | 0.19 | 0.070 | 0.001 | 921 | 26 | 0.99 | 928 | 14 |
| Ma | Output_1_09 | G12G3_zrn3 15um | C | 0.915 | 6.02 | 0.16 | 0.073 | 0.002 | 990 | 25 | 0.99 | 996 | 11 |
| Ma | Output_1_10 | G12G3_zrn3 15um | C | 0.918 | 6.11 | 0.15 | 0.072 | 0.001 | 976 | 23 | 0.99 | 986 | 8 |
| Ma | Output_1_11 | G12G3_zrn3 15um | C | 0.950 | 6.06 | 0.14 | 0.073 | 0.001 | 983 | 22 | 0.99 | 994 | 8 |
| Ma | Output_1_12 | G12G3_zrn3 15um | C | 0.962 | 6.49 | 0.20 | 0.071 | 0.002 | 923 | 28 | 0.99 | 937 | 17 |
| Ma | Output_1_15 | G12G3_zrn3 15um | C | 0.979 | 4.59 | 0.11 | 0.085 | 0.002 | 1268 | 29 | 0.99 | 1284 | 9 |


| Ma | Output_1_16 | G12G3_zrn3 15um | C | 0.966 | 4.46 | 0.10 | 0.084 | 0.002 | 1306 | 29 | 1.01 | 1296 | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ma | Output_1_17 | G12G3_zrn3 15um | C | 0.980 | 5.68 | 0.24 | 0.078 | 0.002 | 1040 | 42 | 0.97 | 1074 | 28 |
| Ma | Output_1_18 | G12G3_zrn3 15um | C | 0.976 | 4.35 | 0.10 | 0.084 | 0.002 | 1338 | 31 | 1.02 | 1312 | 10 |
| Ma | Output_1_19 | G12G3_zrn3 15um | C | 0.972 | 5.26 | 0.13 | 0.081 | 0.002 | 1116 | 27 | 0.98 | 1149 | 11 |
| Ma | Output_1_20 | G12G3_zrn3 15um | D-R | 0.879 | 16.58 | 0.49 | 0.053 | 0.001 | 378 | 11 | 1.02 | 370 | 8 |
| Ma | Output_1_21 | G12G3_zrn3 15um | MIX | 0.934 | 15.46 | 0.39 | 0.055 | 0.001 | 404 | 10 | 1.01 | 402 | 5 |
| Ma | Output_1_23 | G12G3_zrn3 15um | C | 0.898 | 3.80 | 0.09 | 0.093 | 0.002 | 1509 | 37 | 1.01 | 1496 | 11 |
| Ma | Output_1_24 | G12G3_zrn3 15um | C | 0.993 | 4.48 | 0.24 | 0.090 | 0.002 | 1288 | 67 | 0.97 | 1337 | 43 |
| Ma | Output_1_25 | G12G3_zrn3 15um | C | 0.896 | 3.75 | 0.09 | 0.092 | 0.002 | 1528 | 35 | 1.02 | 1497 | 10 |
| Ma | Output_1_26 | G12G3_zrn3 15um | C | 0.956 | 6.63 | 0.18 | 0.072 | 0.002 | 903 | 24 | 0.97 | 932 | 14 |
| Ma | Output_1_27 | G12G3_zrn3 15um | C | 0.865 | 7.81 | 0.23 | 0.067 | 0.002 | 775 | 22 | 0.99 | 788 | 15 |
| Ma | Output_1_28 | G12G3_zrn3 15um | C | 0.907 | 6.84 | 0.22 | 0.068 | 0.002 | 880 | 28 | 1.01 | 874 | 18 |
| Ma | Output_1_29 | G12G3_zrn3 15um | C | 0.954 | 4.35 | 0.12 | 0.088 | 0.002 | 1330 | 35 | 0.99 | 1348 | 13 |
| Ma | Output_1_01 | G12B10_z 15um | MIX | 0.903 | 16.34 | 0.35 | 0.056 | 0.001 | 382 | 8 | 0.97 | 395 | 5 |
| Ma | Output_1_07 | G12B10_z 15um | C | 0.923 | 4.85 | 0.09 | 0.083 | 0.002 | 1205 | 23 | 0.98 | 1235 | 8 |
| Ma | Output_1_08 | G12B10_z 15um | C | 0.966 | 4.88 | 0.10 | 0.082 | 0.002 | 1199 | 23 | 0.98 | 1221 | 9 |
| Ma | Output_1_09 | G12B10_z 15um | C | 0.970 | 6.28 | 0.13 | 0.073 | 0.001 | 951 | 20 | 0.98 | 976 | 9 |
| Ma | Output_1_10 | G12B10_z 15um | D-R | 0.900 | 16.71 | 0.33 | 0.056 | 0.001 | 374 | 7 | 0.97 | 388 | 4 |
| Ma | Output_1_12 | G12B10_z 15um | C | 0.962 | 3.74 | 0.07 | 0.096 | 0.002 | 1527 | 29 | 0.99 | 1543 | 9 |
| Ma | Output_1_14 | G12B10_z 15um | D-R | 0.888 | 16.78 | 0.32 | 0.054 | 0.001 | 373 | 7 | 0.99 | 377 | 4 |
| Ma | Output_1_16 | G12B10_z 15um | MIX | 0.886 | 15.60 | 0.31 | 0.054 | 0.001 | 401 | 8 | 1.00 | 399 | 4 |
| Ma | Output_1_21 | G12B10_z 15um | D-R | 0.876 | 15.97 | 0.33 | 0.055 | 0.001 | 391 | 8 | 0.98 | 398 | 5 |
| Ma | Output_1_26 | G12B10_z 15um | Patch | 0.740 | 15.48 | 0.30 | 0.055 | 0.001 | 403 | 8 | 1.00 | 402 | 5 |
| Ma | Output_1_27 | G12B10_z 15um | Patch | 0.731 | 15.71 | 0.30 | 0.055 | 0.001 | 398 | 7 | 1.00 | 398 | 4 |
| Ma | Output_1_28 | G12B10_z 15um | Patch | 0.937 | 16.30 | 0.32 | 0.054 | 0.001 | 384 | 7 | 1.00 | 382 | 4 |
| Ma | Output_1_29 | G12B10_z 15um | C | 0.932 | 7.85 | 0.18 | 0.066 | 0.001 | 772 | 17 | 0.99 | 781 | 10 |
| Ma | Output_1_32 | G12B10_z 15um | C | 0.870 | 4.08 | 0.08 | 0.093 | 0.002 | 1406 | 27 | 0.99 | 1433 | 9 |
| Ma | Output_1_33 | G12B10_z 15um | C | 0.972 | 3.75 | 0.07 | 0.092 | 0.002 | 1532 | 29 | 1.02 | 1494 | 8 |
| Ma | Output_1_35 | G12B10_z 15um | D-R | 0.895 | 15.91 | 0.29 | 0.054 | 0.001 | 393 | 7 | 1.01 | 390 | 4 |
| Ma | Output_1_36 | G12B10_z 15um | C | 0.914 | 7.21 | 0.13 | 0.070 | 0.001 | 834 | 15 | 0.97 | 860 | 6 |
| Ma | Output_1_44 | G12B10_z 15um | C | 0.860 | 13.05 | 0.29 | 0.056 | 0.001 | 476 | 10 | 1.01 | 474 | 7 |
| Ma | Output_1_46 | G12B10_z 15um | C | 0.965 | 9.42 | 0.21 | 0.060 | 0.001 | 652 | 14 | 1.01 | 643 | 7 |
| Ma | Output_1_47 | G12B10_z 15um | D-R | 0.796 | 16.76 | 0.32 | 0.055 | 0.001 | 373 | 7 | 0.98 | 382 | 4 |
| Ma | Output_1_49 | G12B10_z 15um | C | 0.941 | 4.59 | 0.11 | 0.084 | 0.002 | 1268 | 29 | 0.99 | 1280 | 14 |
| Ma | Output_1_51 | G12B10_z 15um | MIX | 0.845 | 16.61 | 0.35 | 0.055 | 0.001 | 377 | 8 | 0.99 | 382 | 5 |
| Ma | Output_1_57 | G12B10_z 15um | C | 0.928 | 3.81 | 0.07 | 0.096 | 0.002 | 1500 | 28 | 0.99 | 1514 | 9 |


| Ma | Output_1_59 | G12B10_z 15um | C | 0.995 | 14.12 | 0.44 | 0.056 | 0.001 | 441 | 13 | 1.00 | 442 | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ma | Output_1_65 | G12B10_z 15um | C | 0.871 | 11.60 | 0.22 | 0.059 | 0.001 | 533 | 10 | 0.99 | 537 | 4 |
| Ma | Output_1_67 | G12B10_z 15um | C | 0.969 | 5.21 | 0.11 | 0.083 | 0.002 | 1124 | 22 | 0.97 | 1171 | 10 |
| Ma | Output_1_70 | G12B10_z 15um | C | 0.924 | 4.48 | 0.08 | 0.085 | 0.002 | 1299 | 23 | 1.00 | 1298 | 7 |
| Ma | Output_1_72 | G12B10_z 15um | D-R | 0.812 | 15.98 | 0.29 | 0.056 | 0.001 | 390 | 7 | 0.98 | 400 | 4 |
| Ma | Output_1_74 | G12B10_z 15um | D-R | 0.868 | 16.37 | 0.30 | 0.056 | 0.001 | 382 | 7 | 0.98 | 391 | 3 |
| Ma | Output_1_75 | G12B10_z 15um | MIX | 0.898 | 15.75 | 0.29 | 0.056 | 0.001 | 396 | 7 | 0.98 | 404 | 4 |
| Ma | Output_1_76 | G12B10_z 15um | D-R | 0.883 | 15.87 | 0.30 | 0.055 | 0.001 | 394 | 7 | 1.00 | 393 | 3 |
| Ma | Output_1_77 | G12B10_z 15um | Patch | 0.819 | 17.15 | 0.32 | 0.055 | 0.001 | 365 | 7 | 0.99 | 371 | 4 |
| Ma | Output_1_79 | G12B10_z 15um | C | 0.919 | 8.62 | 0.19 | 0.065 | 0.001 | 706 | 15 | 0.98 | 724 | 8 |
| Ma | Output_1_81 | G12B10_z 15um | C | 0.877 | 4.37 | 0.09 | 0.085 | 0.002 | 1328 | 25 | 1.00 | 1322 | 9 |
| Ma | Output_1_86 | G12B10_z 15um | C | 0.877 | 10.22 | 0.19 | 0.059 | 0.001 | 602 | 11 | 1.01 | 597 | 5 |
| Ma | Output_1_87 | G12B10_z 15um | C | 0.864 | 10.99 | 0.20 | 0.058 | 0.001 | 562 | 10 | 1.00 | 561 | 4 |
| Ma | Output_1_88 | G12B10_z 15um | D-R | 0.812 | 17.15 | 0.36 | 0.054 | 0.001 | 365 | 7 | 0.99 | 370 | 4 |
| Ma | Output_1_89 | G12B10_z 15um | C | 0.946 | 15.06 | 0.29 | 0.055 | 0.001 | 415 | 8 | 1.01 | 412 | 4 |
| Ma | Output_1_90 | G12B10_z 15um | D-R | 0.875 | 15.90 | 0.31 | 0.055 | 0.001 | 393 | 8 | 0.99 | 396 | 4 |
| Ma | Output_1_91 | G12B10_z 15um | C | 0.975 | 6.30 | 0.13 | 0.072 | 0.001 | 948 | 18 | 0.99 | 963 | 7 |
| Ma | Output_1_93 | G12B10_z 15um | C | 0.860 | 6.08 | 0.12 | 0.072 | 0.001 | 981 | 20 | 1.00 | 984 | 8 |
| Ma | Output_1_96 | G12B10_z 15um | C | 0.733 | 5.92 | 0.14 | 0.074 | 0.002 | 1005 | 22 | 0.99 | 1013 | 14 |
| Ma | Output_1_101 | G12B10_z 15um | C | 0.921 | 5.83 | 0.12 | 0.073 | 0.001 | 1020 | 20 | 1.01 | 1012 | 10 |
| Ma | Output_1_102 | G12B10_z 15um | D-R | 0.815 | 14.33 | 0.26 | 0.057 | 0.001 | 434 | 8 | 0.97 | 448 | 4 |
| Ma | Output_1_103 | G12B10_z 15um | C | 0.900 | 5.72 | 0.11 | 0.073 | 0.001 | 1040 | 20 | 1.01 | 1033 | 7 |
| Ma | Output_1_104 | G12B10_z 15um | C | 0.916 | 5.76 | 0.11 | 0.073 | 0.001 | 1032 | 19 | 1.01 | 1025 | 8 |
| Ma | Output_1_01 | G12B8_z 15um | C | 0.895 | 3.40 | 0.06 | 0.103 | 0.001 | 1659 | 27 | 1.00 | 1668 | 10 |
| Ma | Output_1_03 | G12B8_z 15um | C | 0.906 | 5.82 | 0.09 | 0.073 | 0.001 | 1022 | 15 | 1.01 | 1016 | 6 |
| Ma | Output_1_04 | G12B8_z 15um | C | 0.964 | 5.97 | 0.10 | 0.072 | 0.001 | 999 | 16 | 1.00 | 995 | 8 |
| Ma | Output_1_07 | G12B8_z 15um | C | 0.951 | 5.72 | 0.08 | 0.074 | 0.001 | 1039 | 15 | 1.00 | 1041 | 6 |
| Ma | Output_1_08 | G12B8_z 15um | C | 0.930 | 6.40 | 0.10 | 0.070 | 0.001 | 936 | 14 | 1.01 | 929 | 6 |
| Ma | Output_1_11 | G12B8_z 15um | C | 0.973 | 3.72 | 0.07 | 0.093 | 0.001 | 1541 | 27 | 1.02 | 1513 | 11 |
| Ma | Output_1_12 | G12B8_z 15um | C | 0.972 | 3.60 | 0.07 | 0.095 | 0.001 | 1586 | 32 | 1.01 | 1560 | 13 |
| Ma | Output_1_13 | G12B8_z 15um | C | 0.967 | 3.57 | 0.07 | 0.098 | 0.001 | 1594 | 29 | 1.00 | 1593 | 14 |
| Ma | Output_1_14 | G12B8_z 15um | C | 0.967 | 3.95 | 0.07 | 0.093 | 0.001 | 1451 | 26 | 0.99 | 1468 | 12 |
| Ma | Output_1_17 | G12B8_z 15um | C | 0.841 | 6.51 | 0.10 | 0.071 | 0.001 | 921 | 14 | 0.99 | 929 | 6 |
| Ma | Output_1_19 | G12B8_z 15um | C | 0.824 | 10.57 | 0.18 | 0.059 | 0.001 | 583 | 10 | 1.01 | 577 | 6 |
| Ma | Output_1_20 | G12B8_z 15um | D-R | 0.876 | 15.43 | 0.23 | 0.055 | 0.001 | 405 | 6 | 1.00 | 406 | 3 |
| Ma | Output_1_21 | G12B8_z 15um | C | 0.943 | 5.48 | 0.10 | 0.079 | 0.001 | 1076 | 19 | 0.97 | 1116 | 10 |


| Ma | Output_1_22 | G12B8_z 15um | C | 0.965 | 6.68 | 0.10 | 0.070 | 0.001 | 897 | 13 | 0.99 | 909 | 6 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ma | Output_1_23 | G12B8_z 15um | Patch | 0.982 | 14.97 | 0.50 | 0.056 | 0.001 | 416 | 14 | 0.97 | 428 | 16 |
| Ma | Output_1_24 | G12B8_z 15um | C | 0.912 | 9.78 | 0.16 | 0.062 | 0.001 | 627 | 10 | 0.98 | 639 | 6 |
| Ma | Output_1_26 | G12B8_z 15um | MIX | 0.860 | 15.83 | 0.26 | 0.057 | 0.001 | 394 | 6 | 0.97 | 407 | 4 |
| Ma | Output_1_27 | G12B8_z 15um | C | 0.884 | 6.24 | 0.11 | 0.071 | 0.001 | 959 | 16 | 1.01 | 955 | 11 |
| Ma | Output_1_28 | G12B8_z 15um | C | 0.916 | 3.72 | 0.07 | 0.096 | 0.001 | 1533 | 27 | 0.99 | 1542 | 11 |
| Ma | Output_1_29 | G12B8_z 15um | C | 0.951 | 3.64 | 0.06 | 0.095 | 0.001 | 1570 | 25 | 1.01 | 1551 | 10 |
| Ma | Output_1_30 | G12B8_z 15um | C | 0.948 | 3.71 | 0.06 | 0.096 | 0.001 | 1536 | 25 | 1.00 | 1541 | 10 |
| Ma | Output_1_31 | G12B8_z 15um | C | 0.776 | 13.23 | 0.22 | 0.056 | 0.001 | 470 | 8 | 1.02 | 462 | 5 |
| Ma | Output_1_32 | G12B8_z 15um | C | 0.776 | 13.16 | 0.21 | 0.057 | 0.001 | 472 | 7 | 0.99 | 475 | 5 |
| Ma | Output_1_33 | G12B8_z 15um | C | 0.866 | 13.42 | 0.22 | 0.056 | 0.001 | 463 | 7 | 1.01 | 461 | 5 |
| Ma | Output_1_34 | G12B8_z 15um | C | 0.867 | 13.12 | 0.23 | 0.056 | 0.001 | 474 | 8 | 1.01 | 471 | 6 |
| Ma | Output_1_35 | G12B8_z 15um | C | 0.720 | 13.23 | 0.22 | 0.056 | 0.001 | 470 | 8 | 1.01 | 464 | 5 |
| Ma | Output_1_36 | G12B8_z 15um | C | 0.858 | 13.00 | 0.22 | 0.056 | 0.001 | 478 | 8 | 1.02 | 470 | 6 |
| Ma | Output_1_37 | G12B8_z 15um | C | 0.910 | 4.37 | 0.07 | 0.083 | 0.001 | 1331 | 21 | 1.02 | 1308 | 9 |
| Ma | Output_1_40 | G12B8_z 15um | Patch | 0.875 | 15.71 | 0.27 | 0.057 | 0.001 | 397 | 7 | 0.97 | 411 | 5 |
| Ma | Output_1_41 | G12B8_z 15um | MIX | 0.959 | 13.76 | 0.27 | 0.056 | 0.001 | 452 | 9 | 1.00 | 453 | 6 |

Flagged for Pb -common
C = core
$\mathrm{D}-\mathrm{R}=$ dissolution-reprecipitation
MG = metamorphic growth of new material
$\mathrm{MIX}=$ mixing 2+ domains
Patchy $=$ textural pattern
Grt = within garnet megacryst
$\mathrm{Ma}=$ within matrix


| 391 | 7 | 476 | 18 | 1357 | 472 | 97 | 5763 | 5 | 3600 | 0 | 24 | 0 | 3 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 402 | 5 | 443 | 23 | 715 | 134 | 29 | -4350 | 7 | 2400 | 0 | 8 | 0 | 2 |
| 441 | 4 | 428 | 17 | 788 | 557 | 120 | -15417 | 5 | 5620 | 0 | 42 | 0 | 9 |
| 434 | 2 | 432 | 14 | 1360 | 1128 | 247 | 9000 | 5 | 5960 | 0 | 75 | 0 | 8 |
| 431 | 4 | 441 | 16 | 1241 | 1170 | 260 | 7112 | 6 | 5200 | 0 | 57 | 0 | 7 |
| 394 | 3 | 442 | 21 | 827 | 150 | 34 | 4311 | 4 | 2550 | 0 | 8 | 0 | 3 |
| 436 | 4 | 463 | 19 | 1159 | 785 | 176 | 3172 | 4 | 3990 | 0 | 36 | 0 | 3 |
| 420 | 3 | 432 | 19 | 761 | 444 | 94 | 5905 | 4 | 4510 | 0 | 28 | 0 | 6 |
| 485 | 7 | 480 | 34 | 271 | 4 | 3 | 50088 | 47 | 1994 | 0 | 0 | 0 | 0 |
| 403 | 4 | 410 | 21 | 620 | 223 | 50 | 7803 | 4 | 2700 | 1 | 9 | 0 | 4 |
| 428 | 2 | 425 | 14 | 1356 | 1526 | 312 | 16543 | 5 | 5180 | 0 | 60 | 0 | 7 |
| 386 | 5 | 460 | 38 | 951 | 33 | 8 | 5637 | 12 | 502 | 0 | 1 | 0 | 1 |
| 429 | 5 | 424 | 9 | 902 | 701 | 143 | 10242 | 7 | 5300 | 0 | 45 | 0 | 5 |
| 443 | 4 | 413 | 12 | 400 | 227 | 48 | 3833 | 6 | 2753 | 0 | 25 | 0 | 3 |
| 422 | 4 | 425 | 11 | 524 | 353 | 73 | 5166 | 5 | 3400 | 0 | 31 | 0 | 4 |
| 423 | 5 | 422 | 12 | 543 | 308 | 63 | 2172 | 5 | 3070 | 0 | 26 | 0 | 3 |
| 427 | 4 | 409 | 7 | 1117 | 1344 | 257 | 2105 | 10 | 8650 | 0 | 68 | 0 | 7 |
| 997 | 9 | 978 | 16 | 97 | 76 | 35 | 22786 | 12 | 806 | 0 | 29 | 0 | 3 |
| 784 | 39 | 864 | 21 | 262 | 66 | 25 | 10600 | 8 | 620 | 1 | 21 | 0 | 2 |
| 1001 | 10 | 991 | 10 | 203 | 127 | 56 | -14542 | 10 | 1078 | 0 | 36 | 0 | 3 |
| 978 | 10 | 992 | 13 | 97 | 45 | 20 | -10914 | 9 | 438 | 0 | 21 | 0 | 1 |
| 1008 | 12 | 1006 | 17 | 69 | 45 | 20 | -18200 | 12 | 499 | 0 | 20 | 0 | 1 |
| 415 | 4 | 427 | 10 | 643 | 705 | 135 | 4407 | 11 | 4310 | 0 | 28 | 0 | 5 |
| 408 | 4 | 437 | 12 | 521 | 175 | 36 | 8048 | 6 | 3710 | 0 | 14 | 0 | 5 |
| 447 | 6 | 414 | 15 | 298 | 146 | 30 | 2033 | 6 | 3120 | 0 | 17 | 0 | 4 |
| 424 | 4 | 426 | 12 | 554 | 438 | 87 | 10316 | 6 | 9970 | 0 | 29 | 1 | 14 |
| 947 | 7 | 998 | 7 | 762 | 311 | 137 | 11717 | 8 | 528 | 0 | 6 | 0 | 0 |
| 1304 | 15 | 1311 | 3 | 2650 | 935 | 536 | 42065 | 14 | 3350 | 0 | 22 | 0 | 3 |
| 1261 | 24 | 1274 | 5 | 2930 | 982 | 535 | 50074 | 17 | 3650 | 0 | 24 | 1 | 6 |
| 1149 | 8 | 1166 | 9 | 340 | 137 | 68 | 7653 | 8 | 1004 | 0 | 22 | 0 | 1 |
| 1475 | 12 | 1502 | 7 | 309 | 374 | 238 | 4150 | 11 | 4850 | 0 | 31 | 0 | 9 |
| 489 | 10 | 560 | 10 | 2610 | 438 | 80 | 6056 | 34 | 2640 | 6 | 61 | 8 | 58 |
| 1368 | 12 | 1319 | 8 | 283 | 156 | 108 | 3561 | 13 | 1318 | 1 | 22 | 1 | 12 |
| 1129 | 8 | 1155 | 6 | 632 | 174 | 90 | 10929 | 4 | 682 | 0 | 10 | 0 | 0 |
| 1165 | 8 | 1157 | 10 | 267 | 85 | 45 | 4230 | 2 | 542 | 0 | 7 | 0 | 0 |
| 1161 | 9 | 1179 | 7 | 463 | 131 | 71 | 11033 | 12 | 627 | 0 | 9 | 0 | 0 |


| 1712 | 12 | 1674 | 8 | 159 | 78 | 61 | 3743 | 2 | 1033 | 0 | 6 | 0 | 1 |
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| 1584 | 13 | 1670 | 9 | 201 | 137 | 103 | 3010 | 3 | 1880 | 0 | 8 | 0 | 2 |
| 1695 | 15 | 1692 | 7 | 159 | 85 | 67 | 3597 | 2 | 1084 | 0 | 7 | 0 | 1 |
| 968 | 8 | 1004 | 12 | 186 | 77 | 35 | 730 | 13 | 469 | 0 | 13 | 0 | 0 |
| 1001 | 10 | 1000 | 16 | 239 | 93 | 45 | 2920 | 3 | 507 | 0 | 14 | 0 | 1 |
| 1480 | 12 | 1499 | 10 | 145 | 63 | 45 | 2823 | 3 | 1055 | 0 | 14 | 0 | 1 |
| 1413 | 13 | 1424 | 8 | 214 | 72 | 52 | 5794 | 3 | 807 | 0 | 12 | 0 | 1 |
| 1580 | 12 | 1659 | 4 | 1417 | 90 | 62 | 28833 | 14 | 823 | 0 | 2 | 0 | 0 |
| 477 | 6 | 443 | 23 | 172 | 107 | 24 | 1797 | 7 | 826 | 0 | 14 | 0 | 1 |
| 1312 | 10 | 1301 | 4 | 837 | 388 | 243 | 12975 | 12 | 1920 | 0 | 21 | 0 | 2 |
| 1289 | 14 | 1285 | 6 | 739 | 285 | 176 | 14913 | 6 | 1490 | 24 | 108 | 12 | 58 |
| 1337 | 10 | 1298 | 6 | 707 | 274 | 180 | 13785 | 34 | 1435 | 0 | 17 | 0 | 1 |
| 1134 | 13 | 1239 | 5 | 1455 | 639 | 381 | 43750 | 9 | 3000 | 0 | 18 | 0 | 5 |
| 882 | 55 | 988 | 32 | 753 | 130 | 72 | 8917 | 11 | 960 | 0 | 10 | 0 | 1 |
| 854 | 7 | 927 | 10 | 486 | 395 | 177 | 3638 | 20 | 3640 | 2 | 65 | 3 | 24 |
| 1366 | 15 | 1439 | 11 | 250 | 115 | 82 | 3788 | 8 | 884 | 0 | 23 | 0 | 3 |
| 1553 | 13 | 1549 | 8 | 421 | 6 | 4 | 9731 | 3 | 918 | 0 | 1 | 0 | 0 |
| 1010 | 9 | 946 | 8 | 536 | 270 | 128 | 5345 | 20 | 518 | 0 | 7 | 0 | 1 |
| 518 | 7 | 499 | 17 | 433 | 79 | 25 | 1688 | 7 | 1056 | 0 | 7 | 0 | 2 |
| 476 | 5 | 465 | 27 | 155 | 80 | 17 | 803 | 3 | 740 | 0 | 22 | 0 | 0 |
| 1207 | 12 | 1298 | 13 | 95 | 24 | 16 | 3955 | 4 | 894 | 0 | 4 | 0 | 1 |
| 1332 | 16 | 1322 | 18 | 70 | 20 | 13 | 1123 | 6 | 763 | 0 | 3 | 0 | 1 |
| 1507 | 15 | 1504 | 8 | 209 | 150 | 112 | 6190 | 11 | 936 | 0 | 25 | 0 | 2 |
| 1020 | 9 | 1019 | 11 | 230 | 54 | 26 | 2709 | 15 | 495 | 0 | 6 | 0 | 1 |
| 1010 | 8 | 1012 | 15 | 195 | 46 | 22 | 3510 | 12 | 518 | 0 | 6 | 0 | 1 |
| 919 | 10 | 929 | 14 | 182 | 56 | 23 | 2285 | 11 | 409 | 0 | 8 | 0 | 0 |
| 1430 | 14 | 1428 | 8 | 424 | 203 | 147 | 4408 | 8 | 3400 | 10 | 87 | 3 | 23 |
| 1674 | 20 | 1676 | 10 | 202 | 115 | 91 | 2873 | 3 | 1860 | 0 | 8 | 0 | 2 |
| 1719 | 27 | 1671 | 19 | 133 | 66 | 55 | 1566 | 2.3 | 1203 | 0 | 6 | 0 | 1 |
| 1490 | 14 | 1431 | 11 | 281 | 41 | 33 | 4376 | 2.7 | 878 | 0 | 4 | 0 | 0 |
| 921 | 19 | 925 | 16 | 398 | 125 | 54 | -3400 | 3.8 | 324 | 0 | 10 | 0 | 0 |
| 991 | 15 | 1007 | 15 | 262 | 95 | 45 | 489 | 7.8 | 468 | 0 | 12 | 0 | 1 |
| 977 | 11 | 996 | 10 | 545 | 193 | 89 | 4545 | 8.1 | 627 | 0 | 14 | 0 | 1 |
| 984 | 10 | 1001 | 8 | 608 | 212 | 99 | 9475 | 10.3 | 615 | 0 | 14 | 0 | 1 |
| 924 | 21 | 954 | 16 | 523 | 241 | 101 | 5318 | 7.2 | 830 | 0 | 16 | 0 | 1 |
| 1272 | 14 | 1306 | 4 | 1484 | 883 | 523 | 5159 | 9.3 | 2790 | 0 | 30 | 0 | 3 |


| 1304 | 13 | 1289 | 7 | 1211 | 525 | 323 | 12814 | 7.2 | 2250 | 0 | 18 | 0 | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1043 | 35 | 1147 | 17 | 1948 | 1570 | 666 | 5307 | 16.7 | 4520 | 5 | 260 | 15 | 112 |
| 1334 | 16 | 1286 | 6 | 1248 | 623 | 396 | 13630 | 7.8 | 3180 | 0 | 20 | 0 | 5 |
| 1121 | 15 | 1216 | 7 | 1480 | 686 | 389 | 11854 | 8.4 | 3190 | 0 | 20 | 0 | 6 |
| 378 | 8 | 346 | 26 | 1028 | 7 | 1 | 4181 | 7.4 | 193 | 0 | 0 | 0 | 1 |
| 404 | 6 | 395 | 14 | 3020 | 820 | 135 | 6694 | 18.7 | 3030 | 15 | 400 | 25 | 180 |
| 1506 | 20 | 1486 | 13 | 259 | 261 | 189 | 4353 | 10.2 | 1960 | 0 | 36 | 0 | 5 |
| 1300 | 55 | 1427 | 20 | 336 | 234 | 165 | 4237 | 10.8 | 1870 | 0 | 41 | 0 | 3 |
| 1522 | 17 | 1466 | 12 | 277 | 190 | 141 | 4428 | 4.7 | 1710 | 0 | 42 | 0 | 3 |
| 906 | 16 | 997 | 15 | 706 | 50 | 12 | 8243 | 4.7 | 847 | 0 | 2 | 0 | 0 |
| 777 | 15 | 835 | 26 | 199 | 48 | 19 | 1195 | 9.6 | 508 | 0 | 8 | 0 | 0 |
| 880 | 21 | 872 | 26 | 165 | 49 | 19 | 1075 | 6.9 | 473 | 0 | 8 | 0 | 1 |
| 1333 | 22 | 1386 | 9 | 416 | 172 | 123 | 2856 | 8.5 | 3710 | 0 | 28 | 0 | 4 |
| 383 | 5 | 459 | 11 | 1429 | 16 | 5 | 3917 | 3.4 | 576 | 0 | 15 | 2 | 15 |
| 1210 | 12 | 1260 | 9 | 335 | 112 | 64 | 5623 | 9.8 | 1610 | 0 | 3 | 0 | 1 |
| 1202 | 14 | 1233 | 6 | 582 | 101 | 56 | 14765 | 5.3 | 1252 | 0 | 2 | 0 | 1 |
| 955 | 12 | 1002 | 7 | 718 | 55 | 25 | 6880 | 3.3 | 1268 | 0 | 7 | 1 | 6 |
| 375 | 4 | 439 | 11 | 950 | 4 | 2 | 3153 | -0.7 | 238 | 0 | 4 | 1 | 7 |
| 1529 | 14 | 1540 | 5 | 495 | 266 | 197 | 11588 | 3.9 | 886 | 0 | 15 | 0 | 1 |
| 373 | 4 | 378 | 12 | 1010 | 4 | 1 | 4094 | 9.2 | 21 | 0 | 0 | 0 | 0 |
| 400 | 5 | 368 | 13 | 1337 | 31 | 6 | 4989 | 9.1 | 279 | 0 | 8 | 1 | 10 |
| 392 | 5 | 411 | 15 | 582 | 30 | 9 | 2347 | 29 | 520 | 0 | 5 | 0 | 3 |
| 404 | 5 | 406 | 19 | 356 | 58 | 10 | 1648 | 23.6 | 509 | 0 | 5 | 0 | 4 |
| 398 | 4 | 403 | 19 | 374 | 74 | 13 | 2243 | 32.6 | 805 | 0 | 8 | 0 | 7 |
| 384 | 4 | 384 | 10 | 2300 | 177 | 31 | 4883 | 38.9 | 698 | 2 | 17 | 2 | 18 |
| 773 | 12 | 813 | 12 | 295 | 106 | 39 | 4084 | 6.01 | 119 | 0 | 9 | 0 | 1 |
| 1412 | 14 | 1481 | 10 | 186 | 108 | 70 | 3830 | 4.4 | 1235 | 0 | 25 | 0 | 1 |
| 1527 | 14 | 1463 | 4 | 3763 | 1285 | 795 | 48465 | 11.1 | 1590 | 0 | 39 | 0 | 2 |
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| 837 | 7 | 937 | 9 | 639 | 321 | 128 | 8039 | 9.2 | 293 | 0 | 23 | 0 | 1 |
| 477 | 7 | 437 | 21 | 261 | 361 | 73 | 1783 | 9.2 | 1930 | 0 | 44 | 0 | 4 |
| 651 | 9 | 606 | 7 | 1090 | 522 | 146 | 13500 | 8.5 | 1728 | 0 | 19 | 0 | 5 |
| 374 | 4 | 423 | 18 | 494 | 7 | 2 | 1298 | 0.1 | 245 | 0 | 17 | 3 | 37 |
| 1269 | 20 | 1288 | 14 | 156 | 97 | 55 | 5021 | 16.5 | 1099 | 0 | 11 | 0 | 2 |
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| 1503 | 13 | 1539 | 8 | 228 | 80 | 56 | 3955 | 10.3 | 703 | 0 | 6 | 0 | 1 |


| 441 | 11 | 466 | 6 | 5030 | 235 | 45 | 17268 | 24.5 | 2530 | 7 | 111 | 11 | 82 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 533 | 5 | 564 | 10 | 797 | 754 | 183 | 6000 | 2.7 | 1180 | 0 | 27 | 0 | 1 |
| 1133 | 13 | 1260 | 7 | 751 | 83 | 57 | 10893 | 2.7 | 727 | 0 | 6 | 0 | 1 |
| 1299 | 10 | 1304 | 7 | 510 | 273 | 158 | 11690 | 11.2 | 1383 | 0 | 24 | 0 | 2 |
| 391 | 3 | 451 | 16 | 1294 | 10 | 6 | 2109 | 280 | 120 | 0 | 7 | 1 | 8 |
| 382 | 3 | 439 | 12 | 2248 | 12 | 8 | 2864 | 1530 | 165 | 0 | 7 | 1 | 11 |
| 397 | 4 | 457 | 13 | 1625 | 32 | 14 | 4115 | 6.1 | 180 | 0 | 10 | 1 | 11 |
| 394 | 4 | 408 | 10 | 1340 | 9 | 4 | 2770 | 276 | 68 | 0 | 9 | 1 | 7 |
| 366 | 3 | 420 | 18 | 715 | 47 | 9 | 2486 | 238 | 505 | 0 | 6 | 0 | 3 |
| 707 | 10 | 781 | 12 | 357 | 207 | 76 | 3872 | 14.7 | 594 | 0 | 18 | 1 | 4 |
| 1327 | 14 | 1315 | 11 | 210 | 100 | 63 | 4570 | 9.3 | 845 | 0 | 14 | 0 | 1 |
| 602 | 5 | 581 | 12 | 655 | 798 | 221 | 3791 | 5.1 | 955 | 0 | 68 | 0 | 2 |
| 561 | 4 | 545 | 10 | 1156 | 1691 | 472 | 7353 | 6.9 | 1022 | 0 | 120 | 0 | 3 |
| 365 | 5 | 386 | 19 | 482 | 4 | 1 | 1147 | 1 | 124 | 1 | 12 | 1 | 7 |
| 414 | 5 | 392 | 10 | 1331 | 270 | 56 | 5718 | 11.9 | 1004 | 0 | 17 | 0 | 1 |
| 393 | 4 | 403 | 14 | 797 | 65 | 17 | 4316 | 5.8 | 383 | 0 | 6 | 0 | 1 |
| 950 | 10 | 995 | 5 | 1894 | 123 | 53 | 50077 | 8.6 | 1194 | 0 | 6 | 0 | 3 |
| 981 | 11 | 988 | 14 | 150 | 39 | 18 | 3159 | 7.2 | 531 | 0 | 17 | 0 | 0 |
| 1006 | 16 | 1032 | 31 | 41 | 18 | 7 | 617 | 8.4 | 692 | 0 | 9 | 0 | 2 |
| 1019 | 12 | 1009 | 11 | 273 | 87 | 44 | 5270 | 9.5 | 507 | 0 | 14 | 0 | 1 |
| 435 | 4 | 507 | 15 | 593 | 13 | 7 | 2764 | 2.7 | 95 | 0 | 2 | 0 | 0 |
| 1038 | 11 | 1017 | 11 | 265 | 92 | 47 | 3518 | 10.5 | 543 | 0 | 14 | 0 | 1 |
| 1031 | 11 | 1017 | 9 | 389 | 134 | 69 | 5716 | 8.2 | 631 | 0 | 16 | 0 | 1 |
| 1660 | 16 | 1672 | 10 | 131 | 84 | 70 | 3728 | 6.3 | 1249 | 0 | 8 | 1 | 14 |
| 1021 | 8 | 1006 | 8 | 557 | 14 | 8 | 5408 | 8.7 | 2480 | 0 | 4 | 0 | 0 |
| 998 | 11 | 992 | 6 | 778 | 18 | 10 | 7208 | 3.9 | 1910 | 0 | 5 | 0 | 0 |
| 1039 | 8 | 1050 | 5 | 1276 | 13 | 6 | 22805 | 5.8 | 733 | 0 | 2 | 0 | 0 |
| 936 | 8 | 929 | 7 | 884 | 9 | 4 | 10172 | 7.2 | 306 | 0 | 0 | 0 | 0 |
| 1536 | 18 | 1487 | 6 | 463 | 7 | 6 | 9396 | 6 | 382 | 0 | 1 | 0 | 0 |
| 1580 | 24 | 1529 | 8 | 272 | 86 | 58 | 7095 | 4.8 | 1044 | 0 | 10 | 0 | 2 |
| 1593 | 20 | 1592 | 7 | 466 | 880 | 590 | 5830 | 14.3 | 3510 | 0 | 62 | 0 | 11 |
| 1454 | 18 | 1492 | 7 | 416 | 12 | 5 | 9056 | 4.4 | 305 | 0 | 1 | 0 | 0 |
| 921 | 9 | 952 | 13 | 276 | 64 | 30 | 6895 | 6.8 | 464 | 0 | 20 | 0 | 1 |
| 583 | 7 | 569 | 19 | 300 | 87 | 27 | 3428 | 18 | 244 | 0 | 2 | 0 | 1 |
| 405 | 3 | 408 | 10 | 1176 | 66 | 14 | 4481 | 5.4 | 866 | 0 | 1 | 0 | 2 |
| 1081 | 14 | 1176 | 9 | 495 | 489 | 287 | 10384 | 47 | 1970 | 0 | 19 | 1 | 10 |


| 898 | 8 | 932 | 5 | 2066 | 165 | 82 | 33870 | 16.1 | 479 | 0 | 34 | 2 | 21 |
| ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 417 | 13 | 466 | 32 | 1413 | 209 | 45 | 9727 | 6.4 | 970 | 0 | 1 | 0 | 0 |
| 628 | 7 | 665 | 11 | 773 | 614 | 172 | 2454 | 8.8 | 940 | 3 | 126 | 20 | 153 |
| 395 | 4 | 472 | 15 | 637 | 53 | 12 | 4086 | 6.6 | 531 | 1 | 26 | 3 | 15 |
| 962 | 11 | 945 | 18 | 195 | 44 | 22 | 2751 | 6.6 | 609 | 0 | 12 | 0 | 1 |
| 1534 | 18 | 1557 | 10 | 141 | 76 | 58 | 835 | 12.7 | 518 | 0 | 11 | 0 | 1 |
| 1569 | 15 | 1532 | 7 | 277 | 163 | 130 | 8651 | 6.5 | 880 | 0 | 13 | 0 | 2 |
| 1537 | 16 | 1547 | 7 | 227 | 264 | 203 | 7533 | 9.7 | 2940 | 0 | 33 | 1 | 11 |
| 470 | 5 | 440 | 22 | 277 | 174 | 39 | 4231 | 5.2 | 2110 | 0 | 57 | 0 | 2 |
| 472 | 5 | 486 | 16 | 274 | 213 | 49 | 2010 | 6.9 | 2370 | 0 | 68 | 0 | 2 |
| 463 | 5 | 449 | 13 | 477 | 370 | 81 | 4383 | 8.2 | 3580 | 0 | 116 | 0 | 3 |
| 474 | 6 | 464 | 17 | 410 | 423 | 97 | 4907 | 11.3 | 3820 | 0 | 126 | 0 | 5 |
| 470 | 5 | 447 | 20 | 324 | 232 | 52 | 2700 | 7.3 | 2210 | 0 | 51 | 0 | 3 |
| 478 | 5 | 432 | 16 | 323 | 345 | 77 | 551 | 6 | 3260 | 0 | 80 | 0 | 7 |
| 1328 | 13 | 1278 | 10 | 182 | 87 | 57 | 8170 | 10.8 | 1072 | 0 | 11 | 0 | 1 |
| 398 | 5 | 479 | 17 | 680 | 82 | 20 | 2404 | 384 | 1240 | 0 | 6 | 1 | 4 |
| 453 | 7 | 452 | 9 | 1242 | 236 | 58 | 11824 | 8.7 | 2280 | 0 | 32 | 1 | 4 |


| Sm (ppm) | Eu <br> (ppm) |  | Gd (ppm) | Tb (ppm) | Dy (ppm) | Ho (ppm) | Er <br> (ppm) | Tm (ppm) | Yb (ppm) | Lu (ppm) | Hf (ppm) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8 |  | 1 | 45 | 19 | 228 | 86 | 433 | 91 | 860 | 171 | 9160 |
| 19 |  | 1 | 117 | 46 | 571 | 212 | 890 | 172 | 1510 | 279 | 10700 |
| 15 |  | 1 | 97 | 37 | 498 | 183 | 789 | 157 | 1500 | 314 | 10960 |
| 17 |  | 1 | 115 | 40 | 532 | 198 | 794 | 154 | 1370 | 248 | 10350 |
| 26 |  | 2 | 122 | 46 | 588 | 223 | 910 | 175 | 1490 | 287 | 10300 |
| 16 |  | 1 | 96 | 38 | 470 | 191 | 860 | 191 | 1970 | 491 | 12100 |
| 5 |  | 0 | 30 | 12 | 157 | 70 | 390 | 105 | 1180 | 343 | 12580 |
| 11 |  | 1 | 22 | 8 | 131 | 64 | 367 | 99 | 1144 | 270 | 9690 |
| 28 |  | 2 | 118 | 46 | 550 | 201 | 948 | 183 | 1540 | 310 | 9100 |
| 18 |  | 1 | 97 | 37 | 473 | 181 | 757 | 159 | 1540 | 311 | 9780 |
| 4 |  | 1 | 26 | 11 | 144 | 60 | 307 | 65 | 685 | 154 | 9390 |
| 46 |  | 5 | 250 | 93 | 1082 | 386 | 1570 | 320 | 2700 | 466 | 8350 |
| 4 |  | 1 | 20 | 9 | 107 | 46 | 281 | 74 | 870 | 238 | 12200 |
| 0 |  | 0 | 1 | 0 | 9 | 9 | 87 | 38 | 660 | 211 | 13000 |
| 15 |  | 1 | 90 | 40 | 472 | 182 | 892 | 170 | 1570 | 312 | 9200 |
| 1 |  | 0 | 4 | 2 | 22 | 7 | 31 | 6 | 60 | 17 | 13370 |
| 0 |  | 0 | 0 | 0 | 6 | 5 | 50 | 22 | 379 | 115 | 13240 |
| 1 |  | 0 | 1 | 1 | 13 | 9 | 78 | 30 | 490 | 149 | 13450 |
| 0 |  | 0 | 1 | 1 | 21 | 17 | 156 | 58 | 948 | 281 | 13800 |
| 0 |  | 0 | 0 | 1 | 16 | 13 | 131 | 52 | 876 | 276 | 12340 |
| 1 |  | 0 | 0 | 0 | 10 | 10 | 109 | 44 | 781 | 217 | 14030 |
| 7 |  | 1 | 48 | 23 | 294 | 117 | 580 | 130 | 1390 | 316 | 10320 |
| 2 |  | 0 | 3 | 2 | 26 | 22 | 223 | 107 | 1660 | 429 | 9870 |
| 14 |  | 1 | 67 | 25 | 304 | 124 | 569 | 118 | 1140 | 242 | 10800 |
| 7 |  | 1 | 46 | 19 | 255 | 101 | 500 | 123 | 1300 | 260 | 10190 |
| 2 |  | 1 | 8 | 5 | 44 | 19 | 113 | 41 | 570 | 169 | 9200 |
| 1 |  | 0 | 1 | 1 | 16 | 16 | 174 | 90 | 1350 | 366 | 10480 |
| 2 |  | 0 | 13 | 4 | 48 | 26 | 223 | 99 | 1530 | 452 | 10900 |
| 4 |  | 0 | 35 | 15 | 176 | 80 | 379 | 84 | 897 | 178 | 10100 |
| 17 |  | 1 | 111 | 41 | 480 | 184 | 782 | 158 | 1460 | 265 | 9560 |
| 9 |  | 1 | 59 | 24 | 288 | 122 | 600 | 131 | 1270 | 262 | 10070 |
| 8 |  | 1 | 47 | 18 | 210 | 84 | 423 | 110 | 1250 | 261 | 10560 |
| 14 |  | 1 | 79 | 33 | 407 | 164 | 679 | 139 | 1290 | 257 | 10710 |


| 5 | 1 | 51 | 19 | 258 | 110 | 570 | 158 | 1840 | 410 | 10060 |
| ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 5 | 1 | 30 | 11 | 144 | 66 | 419 | 137 | 1990 | 497 | 10960 |
| 19 | 1 | 117 | 43 | 525 | 190 | 854 | 174 | 1524 | 272 | 9840 |
| 19 | 1 | 129 | 49 | 568 | 218 | 930 | 177 | 1681 | 310 | 9520 |
| 16 | 2 | 104 | 38 | 460 | 171 | 780 | 185 | 1570 | 309 | 9540 |
| 4 | 1 | 31 | 12 | 156 | 80 | 490 | 159 | 2260 | 546 | 10960 |
| 9 | 1 | 71 | 29 | 349 | 134 | 643 | 145 | 1280 | 230 | 10120 |
| 14 | 1 | 89 | 32 | 381 | 140 | 606 | 134 | 1300 | 256 | 9720 |
| 2 | 2 | 21 | 9 | 105 | 55 | 424 | 158 | 2270 | 561 | 11230 |
| 9 | 1 | 51 | 18 | 227 | 95 | 513 | 132 | 1540 | 322 | 9400 |
| 16 | 1 | 109 | 41 | 469 | 191 | 778 | 158 | 1469 | 264 | 11060 |
| 1 | 0 | 6 | 2 | 22 | 13 | 110 | 42 | 780 | 194 | 10900 |
| 13 | 1 | 95 | 36 | 432 | 168 | 752 | 153 | 1280 | 233 | 16500 |
| 7 | 1 | 54 | 19 | 243 | 99 | 427 | 91 | 819 | 150 | 15440 |
| 10 | 1 | 67 | 24 | 281 | 115 | 507 | 101 | 884 | 163 | 12600 |
| 8 | 1 | 64 | 22 | 275 | 106 | 476 | 101 | 908 | 170 | 15980 |
| 20 | 2 | 148 | 51 | 595 | 229 | 966 | 193 | 1650 | 298 | 10200 |
| 5 | 1 | 23 | 8 | 86 | 30 | 128 | 27 | 252 | 49 | 11300 |
| 3 | 0 | 13 | 5 | 57 | 21 | 99 | 24 | 255 | 54 | 18110 |
| 5 | 1 | 26 | 9 | 97 | 36 | 160 | 36 | 327 | 65 | 16950 |
| 1 | 0 | 9 | 3 | 38 | 15 | 69 | 16 | 154 | 33 | 15900 |
| 2 | 0 | 10 | 3 | 44 | 17 | 72 | 16 | 164 | 33 | 14500 |
| 12 | 2 | 95 | 33 | 401 | 158 | 699 | 131 | 1103 | 205 | 8520 |
| 12 | 1 | 77 | 27 | 328 | 131 | 631 | 139 | 1441 | 281 | 10200 |
| 9 | 1 | 67 | 23 | 275 | 112 | 489 | 100 | 890 | 169 | 11500 |
| 27 | 3 | 174 | 58 | 697 | 264 | 1073 | 214 | 1800 | 321 | 8230 |
|  |  |  |  |  |  |  |  |  |  |  |
| 1 | 0 | 7 | 3 | 34 | 16 | 80 | 21 | 217 | 50 | 10210 |
| 9 | 0 | 55 | 21 | 282 | 115 | 518 | 113 | 1010 | 205 | 13900 |
| 12 | 1 | 60 | 22 | 300 | 116 | 531 | 119 | 1062 | 226 | 14720 |
| 2 | 0 | 15 | 6 | 74 | 32 | 156 | 35 | 338 | 78 | 10270 |
| 21 | 3 | 120 | 36 | 431 | 152 | 663 | 129 | 1127 | 235 | 7990 |
| 56 | 8 | 102 | 25 | 223 | 77 | 367 | 97 | 1096 | 314 | 20400 |
| 19 | 1 | 52 | 13 | 135 | 47 | 199 | 40 | 378 | 74 | 10280 |
| 1 | 0 | 10 | 4 | 51 | 21 | 104 | 23 | 224 | 48 | 12960 |
| 1 | 0 | 10 | 3 | 45 | 19 | 83 | 18 | 179 | 38 | 10810 |
| 2 | 0 | 10 | 4 | 52 | 20 | 98 | 20 | 194 | 42 | 11940 |


| 3 | 0 | 20 | 7 | 92 | 37 | 166 | 35 | 327 | 70 | 9420 |
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| 7 | 1 | 44 | 15 | 176 | 66 | 285 | 55 | 519 | 104 | 9260 |
| 3 | 0 | 20 | 7 | 94 | 35 | 164 | 36 | 336 | 70 | 9420 |
| 2 | 0 | 10 | 3 | 38 | 15 | 73 | 16 | 165 | 34 | 11390 |
| 2 | 0 | 10 | 3 | 43 | 16 | 73 | 17 | 164 | 37 | 11800 |
| 3 | 0 | 22 | 8 | 99 | 39 | 162 | 33 | 312 | 65 | 10560 |
| 3 | 0 | 17 | 5 | 72 | 27 | 124 | 28 | 267 | 55 | 10730 |
| 2 | 0 | 10 | 4 | 53 | 26 | 137 | 33 | 348 | 78 | 12700 |
| 3 | 1 | 18 | 6 | 72 | 30 | 136 | 29 | 278 | 59 | 9490 |
| 6 | 0 | 37 | 14 | 170 | 67 | 294 | 62 | 580 | 110 | 11450 |
| 32 | 3 | 65 | 18 | 162 | 52 | 221 | 46 | 435 | 80 | 11690 |
| 4 | 0 | 26 | 10 | 126 | 50 | 219 | 48 | 445 | 95 | 11140 |
| 14 | 1 | 65 | 23 | 288 | 104 | 476 | 88 | 796 | 160 | 10900 |
| 3 | 0 | 16 | 6 | 79 | 33 | 170 | 39 | 425 | 105 | 10700 |
| 32 | 2 | 101 | 30 | 339 | 126 | 524 | 105 | 885 | 181 | 8710 |
| 5 | 0 | 18 | 6 | 78 | 32 | 134 | 25 | 240 | 43 | 13060 |
| 0 | 0 | 5 | 3 | 56 | 29 | 180 | 55 | 680 | 154 | 13700 |
| 1 | 0 | 7 | 3 | 35 | 16 | 81 | 19 | 224 | 53 | 11640 |
| 3 | 1 | 18 | 6 | 77 | 34 | 173 | 48 | 537 | 124 | 9900 |
| 1 | 0 | 8 | 3 | 57 | 24 | 126 | 28 | 285 | 62 | 13330 |
| 2 | 0 | 16 | 6 | 73 | 31 | 132 | 29 | 287 | 67 | 9090 |
| 3 | 0 | 16 | 6 | 72 | 29 | 132 | 27 | 244 | 54 | 9340 |
| 6 | 1 | 21 | 8 | 82 | 32 | 139 | 29 | 269 | 57 | 10900 |
| 2 | 0 | 11 | 4 | 45 | 18 | 77 | 15 | 141 | 30 | 12730 |
| 2 | 0 | 13 | 4 | 48 | 17 | 74 | 16 | 139 | 28 | 12100 |
| 1 | 0 | 7 | 3 | 37 | 14 | 70 | 14 | 145 | 33 | 11880 |
| 20 | 3 | 95 | 28 | 313 | 117 | 518 | 101 | 922 | 178 | 7110 |
| 6 | 1 | 41 | 15 | 180 | 65 | 305 | 57 | 533 | 99 | 9600 |
| 3 | 0 | 22 | 9 | 112 | 45 | 189 | 37 | 351 | 69 | 9410 |
| 1 | 0 | 13 | 5 | 70 | 28 | 140 | 30 | 300 | 67 | 11760 |
| 1 | 0 | 4 | 2 | 24 | 10 | 53 | 13 | 138 | 27 | 10750 |
| 1 | 0 | 8 | 3 | 39 | 15 | 79 | 16 | 172 | 33 | 11860 |
| 1 | 0 | 10 | 4 | 48 | 21 | 112 | 23 | 238 | 51 | 13050 |
| 2 | 0 | 9 | 4 | 45 | 19 | 104 | 23 | 255 | 49 | 12150 |
| 2 | 0 | 13 | 6 | 67 | 26 | 136 | 30 | 293 | 62 | 12060 |
| 7 | 0 | 53 | 19 | 228 | 94 | 408 | 78 | 757 | 144 | 10800 |


| 7 | 0 | 49 | 17 | 201 | 83 | 381 | 76 | 703 | 137 | 13430 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 140 | 42 | 230 | 61 | 540 | 167 | 700 | 130 | 1190 | 220 | 11190 |
| 12 | 0 | 75 | 24 | 303 | 109 | 481 | 89 | 817 | 148 | 10040 |
| 14 | 1 | 71 | 25 | 298 | 114 | 508 | 96 | 861 | 169 | 11340 |
| 1 | 1 | 6 | 2 | 17 | 5 | 17 | 4 | 26 | 4 | 12800 |
| 50 | 11 | 96 | 23 | 248 | 89 | 490 | 118 | 1420 | 348 | 13600 |
| 8 | 3 | 50 | 16 | 180 | 62 | 293 | 55 | 528 | 104 | 9130 |
| 8 | 2 | 46 | 15 | 170 | 69 | 300 | 56 | 578 | 121 | 9970 |
| 6 | 2 | 38 | 12 | 137 | 54 | 266 | 54 | 531 | 105 | 9460 |
| 1 | 0 | 8 | 4 | 57 | 26 | 145 | 32 | 386 | 76 | 11650 |
| 1 | 0 | 10 | 4 | 41 | 17 | 84 | 17 | 178 | 39 | 12060 |
| 1 | 0 | 11 | 3 | 39 | 16 | 74 | 15 | 165 | 31 | 11070 |
| 11 | 2 | 99 | 30 | 351 | 137 | 565 | 110 | 1058 | 194 | 7900 |
| 13 | 1 | 24 | 3 | 27 | 17 | 140 | 49 | 710 | 202 | 10390 |
| 5 | 0 | 31 | 12 | 150 | 56 | 247 | 52 | 467 | 94 | 10990 |
| 3 | 0 | 22 | 8 | 110 | 41 | 189 | 42 | 405 | 80 | 11910 |
| 5 | 2 | 19 | 7 | 93 | 36 | 178 | 39 | 355 | 69 | 13970 |
| 6 | 0 | 10 | 2 | 14 | 7 | 62 | 27 | 507 | 157 | 12500 |
| 2 | 1 | 15 | 5 | 63 | 26 | 134 | 32 | 338 | 81 | 11720 |
| 1 | 0 | 3 | 1 | 4 | 1 | 1 | 0 | 3 | 1 | 12800 |
| 9 | 2 | 18 | 3 | 20 | 7 | 57 | 20 | 325 | 95 | 11520 |
| 2 | 0 | 4 | 1 | 21 | 9 | 81 | 22 | 360 | 113 | 12400 |
| 7 | 2 | 22 | 4 | 40 | 15 | 74 | 20 | 199 | 44 | 12270 |
| 15 | 5 | 38 | 7 | 70 | 24 | 121 | 25 | 237 | 48 | 11240 |
| 18 | 7 | 59 | 10 | 69 | 24 | 108 | 23 | 222 | 45 | 12100 |
| 2 | 0 | 5 | 1 | 12 | 4 | 16 | 3 | 44 | 10 | 8640 |
| 4 | 0 | 23 | 9 | 106 | 42 | 196 | 42 | 392 | 83 | 10370 |
| 4 | 2 | 23 | 8 | 102 | 40 | 202 | 47 | 480 | 102 | 11780 |
| 0 | 0 | 3 | 1 | 3 | 0 | 1 | 0 | 2 | 1 | 12200 |
| 2 | 1 | 7 | 2 | 23 | 9 | 51 | 14 | 179 | 42 | 11870 |
| 6 | 2 | 42 | 15 | 172 | 64 | 295 | 62 | 552 | 112 | 8530 |
| 8 | 1 | 37 | 12 | 151 | 56 | 264 | 58 | 488 | 104 | 10580 |
| 30 | 1 | 55 | 7 | 35 | 8 | 34 | 12 | 204 | 62 | 12060 |
| 4 | 1 | 26 | 9 | 108 | 40 | 170 | 35 | 312 | 65 | 8850 |
| 0 | 0 | 5 | 1 | 4 | 1 | 6 | 1 | 21 | 6 | 13020 |
| 1 | 0 | 12 | 5 | 59 | 23 | 112 | 24 | 217 | 44 | 11360 |


| 41 | 9 | 67 | 19 | 209 | 73 | 414 | 115 | 1422 | 361 | 12200 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | 1 | 18 | 6 | 91 | 35 | 195 | 46 | 473 | 111 | 12100 |
| 2 | 1 | 11 | 4 | 51 | 21 | 108 | 25 | 268 | 64 | 10230 |
| 5 | 0 | 28 | 10 | 116 | 45 | 203 | 44 | 400 | 77 | 11900 |
| 6 | 1 | 20 | 3 | 18 | 4 | 11 | 2 | 15 | 4 | 12130 |
| 8 | 1 | 18 | 4 | 26 | 5 | 15 | 2 | 15 | 3 | 11490 |
| 12 | 1 | 25 | 5 | 25 | 5 | 17 | 3 | 22 | 5 | 11540 |
| 7 | 1 | 18 | 3 | 16 | 3 | 6 | 1 | 7 | 2 | 12100 |
| 5 | 3 | 22 | 5 | 44 | 16 | 70 | 16 | 157 | 39 | 8970 |
| 3 | 2 | 11 | 3 | 50 | 20 | 96 | 24 | 267 | 66 | 9040 |
| 2 | 0 | 14 | 5 | 64 | 26 | 119 | 26 | 256 | 47 | 9710 |
| 4 | 2 | 23 | 7 | 81 | 30 | 138 | 27 | 277 | 64 | 8870 |
| 5 | 3 | 31 | 9 | 93 | 30 | 138 | 27 | 254 | 57 | 10030 |
| 3 | 1 | 6 | 2 | 12 | 4 | 18 | 4 | 33 | 12 | 12390 |
| 2 | 1 | 13 | 5 | 68 | 30 | 181 | 46 | 541 | 132 | 12720 |
| 2 | 0 | 9 | 3 | 34 | 12 | 57 | 14 | 139 | 29 | 11600 |
| 5 | 1 | 23 | 10 | 119 | 38 | 152 | 27 | 240 | 44 | 14210 |
| 2 | 0 | 10 | 3 | 43 | 17 | 74 | 17 | 168 | 33 | 11300 |
| 4 | 1 | 18 | 6 | 68 | 23 | 96 | 20 | 177 | 36 | 8350 |
| 2 | 0 | 10 | 4 | 50 | 19 | 80 | 17 | 160 | 29 | 13270 |
| 0 | 0 | 3 | 1 | 8 | 3 | 13 | 3 | 27 | 6 | 12110 |
| 2 | 0 | 12 | 4 | 53 | 19 | 83 | 16 | 163 | 29 | 13130 |
| 2 | 0 | 14 | 4 | 54 | 19 | 91 | 19 | 179 | 35 | 13300 |
| 15 | 2 | 43 | 11 | 125 | 44 | 188 | 37 | 334 | 67 | 8280 |
| 2 | 1 | 24 | 13 | 189 | 82 | 435 | 119 | 1241 | 257 | 12400 |
| 2 | 0 | 18 | 10 | 164 | 69 | 381 | 101 | 1188 | 249 | 12210 |
| 0 | 0 | 2 | 2 | 33 | 20 | 154 | 47 | 578 | 175 | 13250 |
| 2 | 0 | 13 | 5 | 38 | 10 | 31 | 5 | 35 | 6 | 14200 |
| 0 | 0 | 1 | 1 | 15 | 9 | 65 | 20 | 233 | 61 | 12640 |
| 4 | 1 | 18 | 6 | 78 | 35 | 163 | 38 | 381 | 91 | 10050 |
| 22 | 4 | 103 | 33 | 370 | 145 | 610 | 124 | 1030 | 211 | 8950 |
| 0 | 0 | 1 | 1 | 15 | 8 | 56 | 17 | 193 | 50 | 12400 |
| 2 | 0 | 6 | 2 | 33 | 14 | 71 | 20 | 213 | 54 | 12130 |
| 4 | 0 | 14 | 4 | 28 | 8 | 27 | 6 | 58 | 14 | 13180 |
| 2 | 0 | 7 | 3 | 52 | 26 | 153 | 40 | 462 | 119 | 14350 |
| 12 | 5 | 57 | 16 | 186 | 72 | 306 | 63 | 592 | 110 | 9110 |


| 23 | 3 | 42 | 7 | 56 | 16 | 64 | 13 | 107 | 20 | 9220 |
| ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 1 | 1 | 8 | 3 | 48 | 29 | 212 | 69 | 990 | 277 | 14600 |
| 130 | 10 | 147 | 17 | 118 | 33 | 131 | 30 | 288 | 57 | 10980 |
| 5 | 3 | 12 | 3 | 36 | 16 | 93 | 27 | 381 | 105 | 13520 |
| 2 | 0 | 11 | 4 | 51 | 21 | 91 | 21 | 211 | 48 | 10880 |
| 1 | 0 | 10 | 3 | 41 | 17 | 78 | 17 | 171 | 38 | 12900 |
| 3 | 1 | 19 | 6 | 82 | 30 | 120 | 27 | 257 | 53 | 12680 |
| 13 | 1 | 82 | 24 | 261 | 99 | 388 | 72 | 684 | 131 | 10700 |
| 4 | 2 | 35 | 12 | 164 | 69 | 297 | 64 | 662 | 141 | 11670 |
| 6 | 4 | 47 | 15 | 209 | 83 | 378 | 78 | 734 | 158 | 9610 |
| 8 | 5 | 63 | 24 | 296 | 121 | 532 | 111 | 1024 | 230 | 10200 |
| 11 | 6 | 88 | 29 | 337 | 131 | 578 | 109 | 1065 | 229 | 9760 |
| 7 | 4 | 49 | 17 | 216 | 79 | 338 | 69 | 649 | 140 | 10010 |
| 13 | 7 | 94 | 28 | 333 | 120 | 472 | 92 | 934 | 189 | 10940 |
| 3 | 0 | 21 | 7 | 89 | 35 | 155 | 34 | 290 | 61 | 9240 |
| 4 | 1 | 23 | 8 | 97 | 41 | 212 | 51 | 581 | 161 | 12500 |
| 6 | 1 | 43 | 17 | 210 | 82 | 412 | 100 | 1160 | 290 | 10780 |

