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Hafnium, oxygen, neodymium, strontium, and lead isotopic constraints on magmatic evolution of the supereruptive southern Black Mountains volcanic center, Arizona, U.S.A.: A combined LASS zircon–whole-rock study

Susanne M. McDowell1,2,*, Sarah Overton3, Christopher M. Fisher4, William O. Frazier1, Calvin F. Miller1, Jonathan S. Miller3, and Rita C. Economos5†

1Earth and Environmental Sciences, Vanderbilt University, PMB 351805, 2301 Vanderbilt Place, Nashville, Tennessee 37235-1805, U.S.A.
2Department of Geology, Hanover College, 484 Ball Drive, Hanover, Indiana 47243, U.S.A.
3Geology Department, San Jose State University, One Washington Square, San Jose, California 95192, U.S.A.
4School of the Environment, Washington State University, P.O. Box 642812, Pullman Washington 99164-2812, U.S.A.
5Department of Earth and Space Sciences, University of California–Los Angeles, 595 Charles Young Drive East, P.O. Box 951567, Los Angeles, California 90095, U.S.A.

Abstract

The >700 km³ Peach Spring Tuff (PST), erupted at 18.8 Ma from the Silver Creek caldera in the southern Black Mountains volcanic center (SBMVC) of western Arizona, is the only supereruption-scale ignimbrite in the northern Colorado River Extensional Corridor. The SBMVC contains pre- and post-caldera volcanic rocks and caldera-related intrusions (~19–17 Ma) that provide a detailed petrologic record of ignimbrite antecedence and aftermath.

Whole-rock Sr-Nd-Pb-Hf isotopic data combined with complementary zircon O and Hf isotopic data from a suite of pre- through post-PST samples provide robust constraints on (1) how the SBMVC evolved with respect to magmatic sources and processes throughout its ~2 Ma history and (2) the petrogenetic relationships between the PST and slightly younger intracaldera plutons. Both pre- and post-PST units have isotopic ranges (εNd = –8.3 to –11.6, εHf = –8.2 to –14.0, ⁸⁷Sr/⁸⁶Sr = 0.709–0.712, ²⁰⁶Pb/²⁰⁴Pb = 18.19–18.49, ²⁰⁸Pb/²⁰⁴Pb = 15.60–15.62, ²⁰⁸Pb/²⁰⁴Pb = 38.95–39.29) that fall within the spectrum of Miocene Colorado River Extensional Corridor rocks and are consistent with mixing of substantial fractions of Proterozoic (Mojave) crust and juvenile material derived from regional enriched mantle. Compared to the PST, which has relatively uniform isotopic ratios (εNd = –11.4 to –11.7, εHf = –13.8 to –14.3, ⁸⁷Sr/⁸⁶Sr = 0.709–0.712, ²⁰⁶Pb/²⁰⁴Pb = 18.20–18.29, ²⁰⁸Pb/²⁰⁴Pb = 15.60–15.62, ²⁰⁸Pb/²⁰⁴Pb = 39.02–39.33), individual pre- and post-PST units are isotopically more variable and generally more primitive. Consistent with whole-rock isotopes, zircon εHf (–8 to –14) and oxygen δ¹⁸O (+4.5 to +7.2‰) for most pre- and post-PST units also have wider ranges and more mantle-like values than those of the PST (–12 to –15, +6.1 to +7.1‰). Moreover, zircon isotopic compositions decrease in post-PST samples. A few zircons from post-PST intrusions have δ¹⁸O values lower than mantle values (<+5‰), suggesting incorporation of hydrothermally altered rock.

Whole-rock and zircon elemental and isotopic analyses indicate that (1) most pre- and post-PST units are less evolved and less homogenized than the PST itself; (2) intrusions in the Silver Creek caldera are petrogenetically distinct from the PST and therefore represent discrete magmatic pulses, not unerupted PST mush; (3) enriched mantle input increased in the SBMVC following the paroxysmal PST eruption; (4) post-PST history of the SBMVC was characterized by periodic influx of magmas with varying juvenile fractions into pre-existing mushy or solidified intrusions, resulting in variable and incomplete hybridization; and (5) melting and assimilation of hydrothermally altered crust played a relatively minor role in the generation and evolution of magmas in the SBMVC.

Keywords: Volcanic center, petrogenesis, zircon, oxygen isotopes, Sr isotopes, Hf isotopes, Nd isotopes, Pb isotopes, supereruption

Introduction

The southern Black Mountains volcanic center (SBMVC), located in the northern Colorado River Extensional Corridor (CREC) of northwestern Arizona, comprises the >700 km³ Peach Spring Tuff (PST); its source, the Silver Creek caldera; and well-exposed pre- to post-PST volcanic units and intracaldera intrusions that were emplaced over a period of 2 m.y. (Ferguson et al. 2013; Pamukcu et al. 2013; McDowell et al. 2014). The completeness of the SBMVC’s magmatic record and the recent finding that the age of part of the intracaldera intrusion complex is indistinguishable from that of the PST (McDowell et al. 2014)
make it an attractive widespread interest: (1) How do volcanic centers that produce large-volume explosive eruptions evolve with respect to magmatic source(s), composition, and processes (e.g., Lipman 2007; Tappa et al. 2011; Watts et al. 2011, 2012)? (2) What are the petrographic relationships between volcanic rocks and spatially associated subvolcanic intrusions (e.g., Bachmann and Bergantz 2004; Bachmann et al. 2007; Glazner et al. 2008)? More specifically, what are the relationships between very large ignimbrites and the approximately contemporaneous plutons in their source calderas (e.g., Lipman 1984; Bachmann and Bergantz 2008; Zimmerer and McIntosh 2012a, 2012b; Mills and Coleman 2013)? In the case of the SBMVC, are the intracaldera intrusions unerupted remnants of supereruption magmas, or do they represent discrete magmatic pulses?

To address these questions with respect to the SBMVC, we apply a combination of whole-rock Sr-Nd-Hf-Pb and in situ zircon O and Hf isotopic analysis. Because isotopes of Sr, Nd, Pb, and Hf are not appreciably fractionated as a consequence of closed-system processes, their ratios remain effectively constant in the products of closed-system crystallization and melt segregation on the timescales involved. Only open-system events, like magma mixing and crustal assimilation, can create isotopic variability within a magma. Moreover, radiogenic isotopic ratios constrain source composition and age. Previous studies have shown that Proterozoic, Mesozoic, and Miocene-age rocks in the Mojave Desert region, which includes the SBMVC, have distinctive Sr, Nd, and Pb isotopic signatures (e.g., Bennett and DePaolo 1987; Farmer et al. 1989; Wooden and Miller 1990; Feuerbach et al. 1993; Miller and Wooden 1994; Falkner et al. 1995; Metcalf et al. 1995; Miller et al. 2000; Bachl et al. 2001; Erickson et al. 2004). The isotopic characteristics established by these studies serve as regional benchmarks against which we can compare the isotopic compositions of the SBMVC and with which we can constrain sources and open-system processes such as assimilation and magma mixing.

The introduction of high-precision, high-resolution analytical techniques has permitted determination of isotopic ratios in situ in minerals. Hafnium and oxygen isotopic compositions of zircons offer particularly valuable insights into magmatic origins and evolution. More sensitively than whole-rock analyses, in situ Hf isotope data provide constraints on magmatic sources, degree of magmatic heterogeneity, and open-system processes (e.g., Hawkesworth and Kemp 2006; Kemp et al. 2006, 2007, 2010; Drew et al. 2013). Oxygen isotope ratios determined in situ in zircon shed complementary light on magmatic characteristics and processes; in particular, they document varying input from crustal materials that have interacted with surface water (e.g., Bindeman and Valley 2001; Valley et al. 2005; Hawkesworth and Kemp 2006; Bindeman et al. 2007; Kemp et al. 2007; Watts et al. 2011, 2012). We combine our comprehensive isotopic data with new and existing whole-rock and zircon elemental data to characterize representative volcanic and intrusive units in the SBMVC. We then apply the constraints offered by the data set to investigate magmatic sources and processes and plutonic-volcanic connections.

**GEOLOGICAL CONTEXT**

The 70 to 100 km wide northern Colorado River Extensional Corridor (CREC) is a zone of north-northwest-trending crustal blocks bounded by normal faults at the eastern edge of the Basin and Range in western Arizona, southern Nevada, and southeastern California (Fig. 1; Faulds et al. 1990, 2001). It formed between ~20 and 12 Ma when lithospheric extension, preceded and accompanied by intermediate to silicic magmatism, dismembered Proterozoic- and Mesozoic-age continental crust (Faulds et al. 1990, 2001; Varga et al. 2004). Evidence for the region’s tectonic and volcanic upheaval during the middle Miocene is well preserved within the northern CREC as thick sequences (>3 km) of volcanic and sedimentary strata and dissected coeval plutons (e.g., Faulds et al. 1990; Falkner et al. 1995; Bachl et al. 2001; Miller and Miller 2002; Metcalf 2004; Walker et al. 2007; Lang et al. 2008).

The southern Black Mountains produced the most voluminous eruption in the northern CREC: the “supereruption” of the Peach Spring Tuff (PST) at 18.8 Ma (Lidzbarski et al. 2012; Ferguson et al. 2013; Pamukcu et al. 2013). The PST ignimbrite is widely recognized in southeastern California, southern Nevada, and western Arizona (Young and Brennan 1974; Glazner et al. 1986; Buesch and Valentine 1986) (Fig. 1a). Its source, the Silver Creek caldera, was dismembered during post-PST extension, with a smaller fragmented now exposed across the Colorado River in the Sacramento Mountains, California (Ferguson et al. 2013).

Although the PST represents by far the largest eruption in the southern Black Mountains, it was bracketed by ~2 million years of volcanic activity (Pearthree et al. 2010; McDowell et al. 2012, 2014; Table 1). The Silver Creek caldera and its environs (Fig. 1) provide a temporal record of pre- to post-PST magmatism in the vicinity of the caldera (Lang 2001; Lang et al. 2008; McDowell et al. 2014).

**STAGES OF SBMVC MAGMATISM**

We divide SBMVC magmatism into three stages based on this and previous studies (e.g., Lang et al. 2008; Pearthree et al. 2010; Pamukcu et al. 2013; McDowell et al. 2014): (1) initial, predominantly intermediate-composition, effusive volcanism; (2) the dominantly silicic PST eruption; and finally (3) compositionally diverse, small-volume volcanism and epizonal intrusions (Fig. 2).
FIGURE 1. (a) Extent of the 18.8 Ma rhyolitic Peach Spring Tuff and location of its source, the Silver Creek Caldera (Ferguson et al. 2013; Pamukcu et al. 2013). BR = Basin and Range, CP = Colorado Plateau, CREC = Colorado River Extensional Corridor, SM = Sacramento Mountains, BM = Black Mountains, CM = Cerbat Mountains, HM = Hualapai Mountains, SCC = Silver Creek Caldera. Box shows approximate extent of the Southern Black Mountains Volcanic Center (SBMVC). (b) Map of SBMVC within area of box shown in a. Sample locations are shown with their unit numbers (italicized, following designations in Table 1). Box shows area of c. BM = Black Mountains, CM = Cerbat Mountains, HM = Hualapai Mountains. (c) Geology and sample locations in the Oatman-Silver Creek area, southern Black Mountains. The Silver Creek caldera and its immediate environs includes intracaldera PST, post-PST intrusions, and pre- and post-PST volcanics (geology from Ferguson et al. 2013).
(1) Pre-PST magmatism is dominated by thick, phenocryst-rich (~10–40%), biotite and plagioclase) trachytic, trachyandesitic, and trachyandesitic lavas that overlie Precambrian basement and are exposed from Union Pass to the southwestern Black Mountains (Fig. 1; Ransome 1923; Thorson 1971; DeWitt et al. 1986; Faulds et al. 1999; Lang 2001; Murphy 2004; Lang et al. 2008; Pearthree et al. 2010). These intermediate-composition lavas exceed ~1 km thickness throughout the southern 40 km of the Black Mountains. Approximately 15 km north of Silver Creek caldera (Fig. 1), the same lavas thin to less than 200 m (Lang et al. 2008; Ferguson et al. 2013; Murphy 2004; Murphy et al. 2013). This suggests a total volume of order of 103 km3. Faulds et al. (1999) obtained biotite 40Ar/39Ar dating for pre-PST lava of 19.19 ± 0.06 and 19.59 ± 0.03 Ma. CA-TIMS U-Pb dating of zircons extracted from Alcyone trachyte yielded a weighted mean age of 19.01 ± 0.2 Ma (McDowell et al. 2014). The Alcyone trachyte comprises a thick sequence of lavas at the base of the pre-PST section (Ransome 1927; Thorson 1971; DeWitt et al. 1986). Units higher in the section include the Gold Road rhyolite (Ransome 1927; Thorson 1971; DeWitt et al. 1986); thinner mafic to intermediate lavas including the Wrigley Mine basaltic trachyandesite and Esperanza trachyte (Pearthree et al. 2010), exposed to the southeast of the Silver Creek caldera and near Union Pass (Fig. 1, Pearthree et al. 2010; Ferguson et al. 2013; Murphy et al. 2013); and the Cook Canyon rhyolite, an ignimbrite ranging from ~10–100 m in thickness that was produced by the largest explosive eruption in the SBMVC other than the PST (Buesch and Valentine 1986; Murphy 2004; Murphy et al. 2013).

(2) The PST consists of a >0.5 km thick, phenocryst-rich intracaldera trachyte that fills Silver Creek caldera, and outflow that includes trachyte at the top of some proximal exposures but is dominated by high-silica rhyolite (Pamukcu et al. 2013; Ferguson et al. 2013; Frazier 2013). Outflow PST is exposed over an area of 32 000 km2 (Fig. 1; Buesch 1991; Ferguson et al. 2013). 40Ar/39Ar dating of PST sanidine yielded an age of 18.78 ± 0.02 Ma (Buesch 1991; Ferguson et al. 2013). Multiple biotite 40Ar/39Ar dates for pre-PST sanidine and mafic dikes (McDowell et al. 2014) are within error of PST U-Pb zircon and Ar/Ar (18.84 ± 0.15 Ma).

(3) Post-PST magmatism is represented by epizonal intrusions and small-volume lavas and tuffs. Intrusions include two intra- and pericaldera stocks with a total area of exposure ~30 km2, the Moss porphyry (mostly quartz monzonite and quartz monzonite) and the Times porphyry (granite), and compositionally diverse porphyry dikes and small plugs that are exposed both within the caldera and within a radius of 10 km (Ransome 1923; Thorson 1971; DeWitt et al. 1986; McDowell et al. 2014). Most dikes and plugs are silicic, but some dikes have intermediate compositions or are composite. The stocks intrude the PST and display clear evidence for magma mingling and likely hybridization, including magmatic enclaves and rounded, rimmed feldspars (McDowell et al. 2014). Magmatic enclaves and rounded phenocrysts of feldspar and quartz are also locally present in the intermediate and silicic dikes (McDowell et al. 2014). U-Pb CA-TIMS zircon ages for the Moss porphyry (18.76 ± 0.11 and 18.84 ± 0.15 Ma) are within error of PST U-Pb zircon and Ar/Ar sanidine ages; Times porphyry and composite dikes that we interpret to be associated with the Moss and Times intrusions range from 18.7 to 18.5 Ma, and a large intracaldera dike is 18.2 Ma (McDowell et al. 2014, zircon CA-TIMS U-Pb).

Post-PST volcanic rocks in the southern Black Mountains consist of ~18.7 to 16.9 Ma intermediate to silicic ignimbrites, block-and-ash flow deposits, lava flows, and volcanogenic sediments (Fig. 1; Faulds et al. 1999; Murphy 2004; Lang et al. 2008; Pearthree et al. 2010; Murphy et al. 2013; McIntosh and...
Ferguson, unpublished Ar ages). In this study we investigate two of these units: a prominent, glassy ~18.5 Ma silicic lava (McDowell et al. 2014) and its magmatic enclaves, and a 17.5 Ma intermediate-composition lava containing 2–3 cm euhedral feldspar phenocrysts (McIntosh and Ferguson, unpublished Ar ages).

**METHODS**

**Whole-rock analysis**

**Elemental compositions.** Analyses of 19 representative pre- and post-PST samples from the SBMVC were carried out by Activation Laboratories in Ancaster, Ontario, by INAA, ICP, and ICP-MS (Table 2). Fifteen of these were previously reported in McDowell et al. (2014). For this study, we sent four additional samples to Activation Laboratories and include these in Table 2. We also include analyses of 10 PST samples for which we obtained whole-rock isotopic compositions (eight pumice and fiamme, two enclaves). A total of 33 elemental analyses of PST pumice and fiamme are plotted in Figure 2 (from Pamukcu et al. 2013; Frazier 2013).

**Isotopic compositions.** We determined whole-rock isotope compositions (Sr, Hf, Nd, and Pb) for the same 19 samples as for elemental analysis, along with 8 PST pumice samples and two enclaves from PST, at the WSU Radiogenic Isotope and Geochronology Laboratory (RIGL) at Washington State University (Table 3). Approximately 0.25 g of each powdered sample were placed in polytetrafluoroethylene vessels, dissolved in ~7 mL 10:1 HF:HNO₃, and immediately dried at 120 °C to eliminate silica. Samples were then redissolved in ~7 mL 10:1 HF:HNO₃ and placed in steel-jacketed Parr vessels at 150 °C for 5–7 days. The solutions were dried down and redissolved overnight in a mixture of 6 M HCl/H₃BO₃ to convert to chlorides and minimize the production of fluoride species. Samples were dried down again and redissolved in Parr vessels at 150 °C for 24 h in 6 M HCl until sample solutions were clear. These solutions were dried yet again, then redissolved in a mixture of 1 M HCl and 0.1 M HF. High-field-strength elements (including Hf), REE (including Nd), and Sr were initially separated on single cation exchange columns loaded with AG 50W-X12 resin (200–400 mesh). Following the method of Patchett and Tatsumoto (1981), Hf was eluted at the beginning of the procedure in 1 M HCl/0.1 M HF, followed by elution of Sr in 2.5 M HCl and finally bulk REE separation in 6 M HCl. Ti was removed from the Hf fraction, a crucial step, as excess Ti has been shown to alter the measured Hf isotopic composition (Blichert-Toft et al. 1997). Any remaining Yb and Lu in the Hf aliquot were removed in a third stage of column chemistry using 0.18 mL of AG 50W-X12 resin. Sr aliquots were subsequently purified using 0.18 mL Sr-spec resin and HNO₃ (e.g., Gaschnig et al. 2011). Nd was separated from other REEs using LN Spec resin (Gaschnig et al. 2011).
To minimize Pb blanks, we dissolved additional aliquots of each sample specifically for Pb analysis and, following the approach of Prytulak et al. (2006), separated Pb from solution using Biorad AG1-X8 anion resin. Pb aliquots were specifically for Pb analysis and, following the approach of Prytulak et al. (2006), separated Pb from solution using Biorad AG1-X8 anion resin. Pb aliquots were then spiked with Tl, to correct for mass fractionation as described by Gaschnig et al. (2011).

Notes: Samples PSK-6a, PSK-7, and PSK-14 analyzed by WSU lab; all others by XRAL. *PSK-6a is from the same lava (Esperanza trachyte) as PSK-11; no elemental analysis is available for PSK-11. *NAD38. * Total Fe as Fe\text{O}_3. * Loss on ignition. * Total oxides as analyzed (prior to normalization). * nd = LOI determined.

In situ zircon analyses (oxygen and Lu-Hf)

We performed in situ oxygen isotope and Lu-Hf isotope measurements on zircon from representative pre- to post-PST units: five pre-PST volcanic samples, 13 intrusive post-PST samples, and three volcanic post-PST samples (Supplemental Tables 1 and 2). Zircon grains were separated from whole rock using standard methods, including crushing, density separation by water table and heavy liquids, magnetic susceptibility separation by Frantz magnetic separator, and hand-picking. Grains were then mounted in epoxy and polished to their approximate centers and imaged using SEM cathodoluminescence on the JEOL JSM 5600 scanning electron microscope (SEM) at the Microanalysis Center shared by the U.S. Geological Survey and Stanford University.

Oxygen isotopes. Following the methods of Trail et al. (2007), we carried out a total of 467 O isotope analyses (93 pre-PST, 312 post-PST intrusive, 62 post-PST volcanic) at UCLA using the Cameca IMS 1270 in multi-collection mode (C\text{O} as primary beam spot size ~20–25 μm). Analyses were calibrated using zircon standard R33, which yielded an in-run reproducibility of 0.48‰. δ18O was calculated using TSMOW (Baertschi 1976). Cited precisions are the geometric mean of at least 3 analyses per sample using VSMOW (Baertschi 1976). Cited precisions are the geometric mean of at least 3 analyses per sample using VSMOW (Baertschi 1976).
Hf/\text{Pb}\) of 0.282015. The full data set is
Hf/\text{Pb}\) of 0.282293
177\text{U} age of 596
Pb/\text{238}\text{U}.

Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/).

Notes: Samples PSK-6a, PSK-7, and PSK-14 analyzed by WSU lab; all others by XRAL.

Continued

Notes: Sample AM-16-25127, Supplemental Appendices. Deposit items are free

mean of the within-spot standard error and the in-run reproducibility on R33. The full data set is reported in Supplemental Appendix 2.

Lu-Hf isotopes. Following analyses for O isotopic composition, the mounts were lightly repolished and the age and Lu-Hf isotope composition was determined on a subset of the same grains at RIGL. We conducted a total of 239 analyses of four

SIMS age (McDowell et al. 2014).

To constrain the age and Hf isotopic composition of the source materials, a small subset of analyses targeted inherited cores (Table 4). When possible, we selected ablation sites that overlapped with previous O isotopic analysis locations. Care was taken to avoid placing the laser beam over multiple CL zones. Analyses were calibrated using zircon standards R33 and FC1. The mean 176\text{Hf}/177\text{O} for FC1 and R33 [0.282181 ± 3 (2 SD), n = 73; 0.282754 ± 4 (2 SD), n = 112] are in close agreement with the solution MC-ICPMS values of 0.282184 ± 16 (Woodhead and Hergt 2005) and 0.282764 ± 14 (Fisher et al. 2014). Reference zircons 91500 and GI-1 were analyzed as secondary standards for both U-Pb age and Lu-Hf isotopic composition and are in good agreement with published reference values. Eleven LASS analyses of 91500 yielded a weighted mean 187\text{Lu}/187\text{Hf} age of 1068 ± 12 Ma (2 SE) and a mean 187\text{Hf}/187\text{O} of 0.282293 ± 37 (2 SD) (Schoene et al. 2006; Blichert-Toft 2008), while 10 LASS analyses of GI-1 yielded a weighted mean 187\text{Lu}/187\text{Hf} age of 956 ± 9 Ma (2 SE) and a mean 187\text{Hf}/187\text{O} of 0.282015 ± 35 (2 SD) (Morel et al. 2008). Analyses of all reference materials are reported in detail in Supplement Appendix 3.

Continued on next page

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RESULTS

Whole-rock geochemistry documents SBMVC magmatic evolution from predominantly intermediate-composition effusive volcanism (pre-PST), to a high-volume high-silica explosive event (PST), and finally to compositionally diverse volcanic and intrusive magmatism (post-PST). Pre-PST volcanic rocks have 48 to 70 wt% SiO$_2$; post-PST intrusions, 50 to 80 wt% and post-PST volcanic rocks, 48 to 75 wt% (Lang et al. 2008; Pearthree et al. 2010; Frazier 2013; McDowell et al. 2014; Fig. 2; Tables 1 and 2). True mafic rocks (basalts and gabbros) are relatively rare, and, except for PST, Times porphyry, and minor dikes and stocks, rhyolites, and granites are also uncommon. The dominant SBMVC intermediate rocks are rich in total alkalies and especially in K$_2$O and almost all are basaltic trachyandesite, trachyandesite, and trachydacite or trachyte in the classification scheme of Le Bas et al. (1986). Most samples fall in the trachyte plus trachydacite field and are trachytes according to the criterion normative Qz/(Qz+Pl+Or) < 0.2, and therefore for simplicity we use the term “trachyte” as a general descriptor. Pre- and post-PST units are environmentally distinct from the PST, which has lower Sr and Ba and higher Zr and Rb at a given SiO$_2$ than its magmatic predecessors and successors (Fig. 2).

Sr, Nd, and Hf isotopic ranges for pre-PST units ({$^{87}$Sr/$^{86}$Sr})$_{i}$ = 0.7093 to 0.7110, $\varepsilon$Nd = −8.3 to −11.6, and $\varepsilon$Hf = −8.2 to −14.0) are similar to those of post-PST volcanics and intrusions ({$^{87}$Sr/$^{86}$Sr})$_{i}$ = 0.7091 to 0.7124, $\varepsilon$Nd = −8.4 to −10.4, and $\varepsilon$Hf = −8.8 to −13.1) (Table 3, Fig. 3). Times and Moss magmatic enclaves (SCM-27b and MPE1, respectively) have the most primitive isotopic ratios (e.g., highest $\varepsilon$Hf and $\varepsilon$Nd). Throughout
Table 3. Whole-rock isotopic compositions (Pb, Nd, Hf, Sr)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Unit</th>
<th>Pb</th>
<th>Nd</th>
<th>Hf</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIT-2 16</td>
<td>Post-PST (Cordwood Lava)</td>
<td>18.4259</td>
<td>0.0038</td>
<td>15.6134</td>
<td>0.0032</td>
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<td>Malic Dike</td>
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<td>0.0023</td>
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<tr>
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<td>0.0039</td>
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<td>15.9896</td>
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<td>Times Porphyry (Leucogranite)</td>
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<td>0.0038</td>
<td>15.6048</td>
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<td>15.6087</td>
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* εHf calculated using present day CHUR: 18Nd/143Nd = 0.512638 (Bouvier et al. 2008).
* εNd calculated using present day CHUR: 143Nd/144Nd = 0.704527 (Bouvier et al. 2008).
* Ratios calculated from ICP-MS trace element data.
* Sample from same unit as PSK-6a in Table 2 (no elemental analysis available for PST-1); location: 34° 58’50.0” N, 114° 23’23.0” W.
the sample suite, \(\varepsilon_{Hf}\) shows a strong positive correlation with \(\varepsilon_{U}\). All pre- and post-PST units have Pb isotopic ratios within the ranges \(206\text{Pb}/204\text{Pb} = 18.19–18.49\), \(207\text{Pb}/204\text{Pb} = 15.60–15.62\), and \(208\text{Pb}/204\text{Pb} = 38.95–39.29\). PST samples are more uniform isotopically and generally have lower \(\varepsilon_{Nd}\) and \(\varepsilon_{Hf}\) and higher \(\varepsilon^{87}\text{Sr}/\varepsilon^{86}\text{Sr}\) than the other SBMVC rocks \(\varepsilon^{87}\text{Sr}/\varepsilon^{86}\text{Sr} = 0.7108\) to 0.7121 (with one higher outlier, see discussion), \(\varepsilon_{Nd} = –11.4\) to –11.6, and \(\varepsilon_{Hf} = –13.8\) to –14.2). Pb isotope ratios are similar to those of the rest of the SBMVC \(206\text{Pb}/204\text{Pb} = 18.20–18.29\), \(207\text{Pb}/204\text{Pb} = 15.60–15.62\), and \(208\text{Pb}/204\text{Pb} = 39.09–39.32\). Collectively, SBMVC units have isotopic signatures consistent with those determined for other Miocene intrusive and volcanic units within the northern CREC (e.g., Miller and Wooden 1994; Metcalf et al. 1995; Falkner et al. 1995; Miller et al. 2000; Bachl et al. 2001; Ericksen et al. 2004) (Fig. 3).

Zircon \(\delta^{18}O\) in the majority of pre-PST, PST, and post-PST units falls within the range +5 to +7.3‰, with several higher outliers between \(\delta^{18}O = +7.8\) to +8.8 (one extreme outlier has \(\delta^{18}O = +12.2\)) and lower outliers between +4.2 to +5.0 (Fig. 4). Broadly, zircon \(\delta^{18}O\) decreases from older to younger units: average \(\delta^{18}O = +6.8\) in the oldest sample, ~19 Ma Alcyone trachyte, whereas average \(\delta^{18}O = +5.6\) in the youngest samples, ~18.2 Ma silicic porphyry dikes (Fig. 4). PST values, excluding one lower outlier at 4.5‰, range from 5.6 and 7.2‰ and average 6.4‰.

The 239 LASS zircon spots interpreted to be of Miocene age yielded \(\varepsilon_{U}\) values that range from –6 to –16 (Fig. 4). Overall, \(\varepsilon_{Hf}\) is higher in post-PST units than in pre-PST units. The oldest sample, Alcyone trachyte, and the PST have the lowest values (near –14). All samples younger than PST have some zircons with \(\varepsilon_{Hf} > –10\), whereas all analyzed zircons from PST or pre-PST units have \(\varepsilon_{Hf} < –10\).

Six LASS analyses of zircons from five samples clearly reveal inheritance: their \(206\text{Pb}/204\text{U}\) and \(207\text{Pb}/204\text{Pb}\) ages are 1.51–1.62 and 1.66–1.75 Ga, respectively, and \(\varepsilon_{Hf}\) values are –30 to –34 (Table 4). For most paired O and Hf analyses, obtained from the same areas of single zircon grains, \(\varepsilon_{Hf}\) correlates negatively with \(\delta^{18}O\) (Table 5; Fig. 5a). This correlation breaks down for zircons with the lowest, near- and sub-mantle, \(\delta^{18}O (<5.5‰)\). All of the low- \(\delta^{18}O\) zircon analyses are from post-PST intrusive units, with exception of the single outlier PST grain.

Ranges of measured \(\varepsilon_{Hf}\) values in individual samples (excluding analyses that we interpret to have partly or entirely encountered inherited cores) are 3 to 7 units, in many cases exceeding \(\pm 2\sigma\) analytical uncertainty. Similarly, \(\delta^{18}O\) displays one- to four-unit intrasample variation, also commonly exceeding analytical uncertainty (see Fig. 5b).

### Table 4. Proterozoic zircon (U-Pb ages, Hf, and O isotopic compositions)

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<th>(1\sigma)</th>
<th>(206\text{Pb}/204\text{U} ) age (Ma)</th>
<th>(1\sigma)</th>
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Notes: nd = not determined; 16 additional analyses revealed evidence for Proterozoic zircon during the ablation but are not reported owing to too few ratios to reliably determine either age or Hf isotopic composition.

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**Figure 3.** Whole-rock isotopic compositions of pre- to post-PST SBMVC units (this study); CREC intrusions (Falkner et al. 1995, Bachl et al. 2001, and unpublished Vanderbilt and San Jose State University data). Strontium-neodymium isotopic fields: inferred enriched mantle composition (Feuerbach et al. 1993); Proterozoic and Mesozoic rocks of the region (Bennett and DePaolo 1987; Miller and Wooden 1994; Allen et al. 1995; Kapp et al. 2002). Lead isotopic fields for Mojave and Arizona terranes are from Woody and Miller (1990), and Feuerbach et al. (1998).


**DISCUSSION**

**Whole-rock Sr-Nd-Hf-Pb isotopes**

Whole-rock isotopic ratios serve to constrain contributions from potential sources for Miocene magmas in the CREC (Fig. 3). The Proterozoic crust of this region is characterized by high to very high $^{87}\text{Sr}/^{86}\text{Sr}$ (>0.710, up to 0.80 and higher) and low to very low $^{187}\text{Os}/^{188}\text{Os}$ (~–15 to ~–22); Paleoproterozoic rocks in general, especially the more silicic rocks, are concentrated in the upper and lower portions of these ranges of values, respectively, whereas Mesoproterozoic rocks fall in the lower and upper portions (Bennett and DePaolo 1987; Miller and Wooden 1994). We are unaware of published whole-rock Hf isotope data for Proterozoic rocks in this area, but, based on the $^{187}\text{Os}/^{188}\text{Os}$ correlations of the Crustal and Terrestrial Arrays (Vervoort et al. 1999, 2011) and present day $^{187}\text{Os}$ of Proterozoic rocks in and near the CREC, we estimate that their $^{187}\text{Os}$ values range from ~–17 to ~–33. Numerous studies have concluded that juvenile, mantle-derived magmas in the CREC and environs older than ~12 Ma, were derived from ancient enriched lithospheric mantle ($^{187}\text{Os}/^{188}\text{Os} < ~0.705$; e.g., Daley and DePaolo 1992; DePaolo and Daley 2000; Feuerbach et al. 1993; Metcalf et al. 1995 (also see Metcalf et al. op. cit. for a rare exception)). More silicic igneous rocks of Mesozoic and Cenozoic age span the Nd-Sr, and presumably Hf, isotopic range between what is thought to be the enriched regional lithospheric mantle and Proterozoic crust (Fig. 3) and are generally interpreted to reflect hybridization processes involving these two sources (e.g., Miller and Wooden 1994; Allen et al. 1995; Bachl et al. 2001).

Lead isotope ratios for almost all mid-Miocene and older rocks in this region fall above the Northern Hemisphere Regression Line (elevated $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ relative to $^{206}\text{Pb}/^{204}\text{Pb}$). Wooden and coworkers (Wooden et al. 1988; Wooden and Miller 1990; see also Feuerbach et al. 1998) have identified two Pb isotopic provinces: the Mojave province to the west is characterized by higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ than the Arizona province (Fig. 3). The boundary between the two provinces is thought to lie within the CREC, very near the SBMVC.

Sr and Nd isotope ratios for SBMVC samples overlap with those of other Miocene units within the CREC ($\text{Sr} = 0.709$ to 0.714, $^{143}\text{Nd}/^{144}\text{Nd} = –8$ to ~–15) (Fig. 3d). Like other CREC igneous units, isotopic signatures of SBMVC volcanics and intrusions suggest that they are mixtures of juvenile and crustal components, derived, respectively, from the regional enriched lithospheric mantle and the Proterozoic crust. The wide range of isotopic compositions implies a wide range of proportions of the two types of contributing materials. The less evolved compositions (lower Sr, higher $^{143}\text{Nd}$) permit a very high proportion of juvenile material, but the range of suggested compositions of purely juvenile magmas leaves unclear whether the less isotopically evolved SBMVC rocks could be derived entirely from the mantle or have a substantial crustal component. A great majority of analyzed samples lie in a swath between plausible mantle and crustal sources, which we interpret to indicate hybridization involving large, varying crustal and mantle fractions. Isotopic data for Mesozoic igneous units in and near the CREC overlap with those of the SBMVC (e.g., Miller and Wooden 1994; Geyer et al. 1995) and could therefore represent plausible crustal sources that do not require hybridization with juvenile material. However, because the southern Black Mountains lack exposures of Mesozoic rocks, and extensive zircon dating has found no evidence of Mesozoic inheritance (McDowell et al. 2014; Lidzbarski et al. 2012; Lidzbarski 2014; this study), we infer that Mesozoic-age crust did not serve as a significant contributor to SBMVC magmas.

Lead isotope ratios strongly suggest that SBMVC magmas were derived from the regional lithosphere (crust and mantle). More specifically, uniformly high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ indicate origin within Mojave, not Arizona, province lithosphere (Fig. 3).

The PST, including both trachyte and rhyolite, and Alcyone trachyte have isotopic compositions that suggest the largest Paleoproterozoic crustal components among all sampled units. One outflow PST rhyolite pumice has much higher Sr, of
### Table 5. Paired O and Hf isotopic analyses of zircon

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(Continued on next page)
0.723; this sample, like other PST rhyolites, has very low Sr concentration (17 ppm), and we attribute the high Sr to slight contamination through incorporation of a few percent of Proterozoic crust with much higher $^{87}$Sr/$^{86}$Sr and Sr concentration (Miller and Wooden 1994), perhaps as a lithic fragment. Other pre- and post-PST extrusive and intrusive units display a wider range of whole-rock isotopic values and have more primitive isotopic compositions. The paucity of $\delta^{18}$O values suggests that magmatic sources comprised both ancient crustal and juvenile mantle-derived material (Fig. 4; Table 5), with the highest values of $\sim$–6.6 representing growth from entirely juvenile magma and all others indicating highly variable amounts of hybridization.

Oxygen isotopic compositions of zircon are mostly $\sim$+5.6, somewhat heavier than expected for crystals grown from juvenile, mantle-derived magmas but mostly toward the lower end of the typical crustal zircon range. This further supports the inference that SBMVC magmas were hybrids that combined substantial proportions of juvenile mantle-derived and crustal components. The paucity of $\delta^{18}$O values $>\sim$7 to $+8\%$ (Fig. 4; Supplemental Appendix 2) suggests limited input from metasedimentary sources (e.g., the abundant paragneisses of the Mojave terrane). A few relatively low $\delta^{18}$O analyses ($\delta^{18}$O = $+4–5\%$) from a silicic porphyry dike and Times porphyry zircons may reflect limited melting and assimilation of hydrothermally altered rock during the SBMVC’s post-PST magmatic stage (e.g., Bindeman and Valley 2001), but the dearth of these values suggests that, unlike the large-volume continental magmatic centers along the Yellowstone-Snake River Plain trend (Bindeman and Valley 2001; Watts et al. 2011; Drew et al. 2013), this process played a relatively minor role in the development and evolution of the PST and other SBMVC magmas.

Increasing average $\epsilon_{Hf}$ and decreasing $\delta^{18}$O in post-

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**Table 5.—Continued**

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Notes: Sample designations follow this protocol: SCMX4_“X”_“Y”; where “X” = Hf spot number and “Y” = O spot number in Supplementary data files. There are no published Hf isotope data for zircons or whole rocks representing the Proterozoic crust or young mafic rocks interpreted to be juvenile in the CREC region. Based on $\epsilon_{Hf}$ thought to represent the juvenile enriched lithospheric mantle (Fig. 3) and the terrestrial $\epsilon_{Hf}$ and $\epsilon_{Hf}$ array (Vervoort et al. 1999, 2011), we estimate that juvenile $\epsilon_{Hf}$ in the CREC is roughly –2 to –8. As discussed above, we estimate that Miocene $\epsilon_{Hf}$ in the Proterozoic Mojave crust is roughly in the range –17 to –33. An alternative estimate for Miocene $\epsilon_{Hf}$ of Paleoproterozoic rocks, based on the calculated $^{176}$Hf/$^{172}$Hf of the six Paleoproterozoic zircons in our data set and typical $^{176}$Lu/$^{177}$Hf of crustal rocks (~0.0125), falls toward the lower end of that range (~16.4 to –20.4). Based upon these estimates, our zircon $\epsilon_{Hf}$ data are consistent with whole-rock data in suggesting that magmatic sources comprised both ancient crustal and juvenile mantle-derived material (Fig. 4; Table 5), with the highest values of $\sim$–6.6 representing growth from entirely juvenile magma and all others indicating highly variable amounts of hybridization.

Zircon $O$ and $Hf$ isotopes

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PST units is broadly consistent with whole-rock isotopic data that indicate increasing input of mantle-derived material into the SBMVC system after the PST eruption. This inference is supported by the relative abundance of post-PST zircons with enriched Mojave mantle-like zircon isotopic compositions (Fig. 5a).

Zircons from PST samples and the Alcyone trachyte have similar ranges of relatively high δ¹⁸O and low ε₁⁸Hf values, consistent with crystallization within an isotopically homogeneous magma body with a relatively large ancient crustal component. In contrast, zircons from most pre- and post-PST units and individual samples have wider isotopic ranges, lower average δ¹⁸O, and higher average ε₁⁸Hf (Figs. 4 and 5). These characteristics indicate crystallization from petrogenetically diverse magmas with greater contributions from juvenile sources than PST, or Alcyone trachyte. The large ranges in δ¹⁸O and ε₁⁸Hf in zircon from many samples, in many cases beyond analytical uncertainty (see Supplemental Appendix 3), demonstrate isotopic disequilibrium. This indicates open-system processes whereby zircons crystallized in isotopically distinct melts prior to mingling and mixing (cf. McDowell et al. 2014).

Like the whole-rock data, zircon isotopic compositions reveal a petrogenetic distinction between the PST and intrusions. Moss porphyry zircon ages are within error of PST age (McDowell et al. 2014), but the two units are isotopically distinct: the Moss porphyry displays a greater range in δ¹⁸O and ε₁⁸Hf than the PST and has a distinctly higher ε₁⁸Hf/WR. The Times porphyry and the dikes exhibit broadly similar averages and trends to those of the Moss porphyry. Thus, whereas effective isotopic homogenization of the PST magma body occurred prior to zircon saturation and crystallization (Frazier 2013), isotopic variability in zircons from the intrusions document mingling and mixing that is also clearly revealed in outcrop and thin section, for example by quenched mafic enclaves and resorbed and rimmed crystals (McDowell et al. 2014).

Integration of zircon and whole-rock Hf isotope data

Comparison and integration of zircon and whole-rock ε₁⁸Hf offers constraints on SBMVC magmatic evolution beyond what can be gleaned from either data set alone (Fig. 5b), providing insights into details of open-system processes.

In rocks that formed from magmas that evolved only by closed-system processes, zircon ε₁⁸Hf should be uniform and statistically identical to initial ε₁⁸Hf in their host rocks. Variation in zircon ε₁⁸Hf that exceeds variability that can be explained by analytical uncertainty for a uniform population suggests evolution involving open-system processes. As noted above, a majority of samples other than PST and Alcyone trachyte meet this criterion for identification of open-system processes. Furthermore, in most rocks globally of intermediate to silicic composition, a great majority of Hf resides in zircon; therefore, mean zircon ε₁⁸Hf should be very close to ε₁⁸Hf in host rocks. Where this is not the case, it reveals not only the influence of open-system processes, but also that a large fraction of whole-rock Hf is not represented by the analyzed zircon. Either the analyzed zircon population was highly non-representative (an important part of the range of compositions was missed), or much of the Hf in the rock is in other phases and has a distinctly different isotopic composition.

The range of zircon ε₁⁸Hf in a majority of samples spans the whole-rock ε₁⁸Hf value and the mean zircon value is close to whole-rock (Fig. 5b). However, in four samples there is a strong apparent mismatch—two magmatic enclaves (one in the Moss porphyry [MPe1], one in the Times porphyry [SCM-27b]), a relatively mafic (trachyandesitic) zone within a composite feldspar porphyry dike (SCM-30), and a post-PST intermediate-composition lava (SIT-2)—in which most or all zircon ε₁⁸Hf values are either lower or higher than ε₁⁸Hf of their host whole rocks. In three cases zircon values are equal to or less than whole-rock, and in the fourth they are equal to or greater than whole rock (Fig. 5b).

In the magmatic enclaves and feldspar porphyry dike, whole-rock ε₁⁸Hf exceeds calculated mean zircon ε₁⁸Hf by ~2 units; ε₁⁸Hf/WR of ~8 to ~10 indicates a larger juvenile component than ε₁⁸Hf/zircon. For individual zircon analyses in these samples, ε₁⁸Hf is 0 to 5 units lower than whole-rock. However, the range of ε₁⁸Hf in magmatic enclave zircons is nearly identical to zircon ε₁⁸Hf ranges in their respective Times and Moss porphyry host rocks (Fig. 5b). We suggest that enclave zircons are likely xenocrysts entrained from the partially crystallized Times and Moss porphyry host magmas during the injection of more mafic, juvenile material. Similarly, the range of zircon ε₁⁸Hf in trachyandesitic sample SCM-30 matches the ε₁⁸Hf range in a more silicic section of the same composite dike (SCM-1b, trachytic), again indicating that the zircon bears the isotopic signature of its original host instead of the more juvenile magma into which it was incorporated. Assuming that our sample set is sufficiently statistically robust, any zircons that grew within the enclaves and dike melts were likely too small to extract via typical mechanical and gravimetric mineral separation methods.

In trachyte lava SIT-2, mean zircon ε₁⁸Hf exceeds whole-rock ε₁⁸Hf by ~3 units; the zircon has a more juvenile signature than its more crustal host. SIT-2 is characterized by large, 2–3 cm rounded feldspar glomerocrysts (some with reaction rims), phenocrysts (or xenocrysts) of biotite and sphene with reaction textures, and sparse clinopyroxene and feldspar microlites within a glassy matrix. We surmise that the differences in zircon and whole-rock ε₁⁸Hf reflect the injection of a more evolved magma into, and the partial resorption of, a less evolved feldspar-rich cumulate.

We propose the following reconstruction of the SBMVC’s magmatic evolution based on whole-rock and zircon isotopic constraints in conjunction with field, elemental, and petrographic data (Fig. 6).

1. ~19–18.8 Ma: Eruption of ~10⁴ km³ of intermediate-composition magmas (trachytic and subordinate trachybasaltic and trachyandesitic lavas, Cook Canyon ignimbrite), all produced from a combination of juvenile, enriched-mantle-derived magma and Paleoproterozoic Mojave crustal material. Relative crustal contributions to pre-PST lavas were variable; Alcyone trachyte at the base of the pre-PST lava section records the greatest crustal contribution of analyzed pre-PST units (Figs. 3 and 4).
One pre-PST lava and a PST magmatic enclave provide isotopic evidence for input of magmas with dominantly sources prior to and during the PST episode.

(2) 18.8 Ma: Accumulation, homogenization, and eruption of the >700 km$^3$ PST magma body. The narrow, relatively crust-rich whole-rock and zircon isotopic signatures in rhyolitic and trachytic PST (Figs. 3, 4, and 5) distinguish PST from all other analyzed units in the SBMVC except for the early Alcyone trachyte lava. The uniformity of zircon isotopic compositions suggests that zircon growth postdated mixing.

(3) 18.8–17 Ma: Episodic eruption and intrusion of relatively small volume, elementally and isotopically diverse magmas. Like their magmatic predecessors, post-PST magmas were generated from a combination of enriched mantle- and Paleoproterozoic crust-derived sources. However, they were more isotopically diverse and in general richer in the juvenile component. Intrasample variability in zircon isotopic composition, along with field and petrographic relations, demonstrates open-system processes and suggests that magma recharge periodically reinvigorated the volcanic center, locally disaggregating and assimilating resident crystal mushes or previously crystallized material.

**Implications**

(1) Elemental and isotopic data for the PST and intracaldera plutons indicate that they are petrogenetically distinct: the caldera intrusions are more isotopically heterogeneous and record more juvenile input. Plausibly, the plutons may represent mush from the remains of the base of the PST chamber, rejuvenated and contaminated by more juvenile magma, but the data yield no isotopic evidence for a direct petrogenetic connection between the intracaldera plutons and the phenocryst-rich trachyte that has been interpreted as erupted PST mush.

These findings are in this regard consistent with those from some other Cenozoic, large-eruption producing volcanic centers (such as Questa caldera in the Southern Rocky Mountain volcanic field; see Tappa et al. 2011) where intracaldera plutons are isotopically and temporally distinct from high-volume erupted material. Either the high-volume eruptions evacuated essentially all magma from the chamber, or any remaining material was subject to post-eruption modification, as suggested here.

(2) Previous studies (e.g., Tappa et al. 2011; Lipman 2007) have proposed that ignimbrite-producing felsic volcanic centers exhibit characteristic waxing and waning stages correlating with pre- and post-ignimbrite magmatism, respectively. Other studies (e.g., Annen et al. 2015) also document pre-superserupertion thermal priming of the crust and post-superserupertion diminished magmatic flux. The SBMVC appears to reflect a similar process. Mineral and whole rock isotopic data from the SBMVC reveal that although all SBMVC rocks formed via hybridization between regional enriched mantle magmas and Proterozoic Mojave crust, the supereruptive PST magma body incorporated a larger crustal component and experienced far more thorough hybridization than its magmatic predecessors or successors. This may suggest an increasing thermal flux prior to the PST eruption (consistent with thermal data reported in McDowell et al. 2014 for this system), transferred advectively from the mantle by mafic magmas and leading to more extensive crustal melting during the “waxing” phase of the SBMVC’s history, and the consequent formation of much larger, hotter, more vigorously convecting magma body.

Subsequent diminished mantle flux resulted in abrupt post-PST waning of magmatism. Post-PST volcanic rocks and intrusions have more primitive whole-rock and zircon isotopic compositions than the PST; in the waning stages of magmatic flux within the SBMVC, these isotopic compositions become more primitive through time, indicating a relative increase in the proportion of mantle input to the regional magmatic system.

Increasing mantle fraction in the small-volume magmas was probably a consequence of one or both of two factors: (1) massive partial melting in the subjacent crust rendered it more refractory after the PST eruption, and hence the crust contributed a greatly reduced mass to ascending post-PST mantle-derived magmas; and/or (2) diminished mantle magma flux after the PST eruption resulted in cooling and greatly reduced melting in the crust, such that the modest amounts of magma that reached the upper crust had incorporated smaller crustal components.

**Acknowledgments**

We thank Marsha Lidzbarski for her expertise and assistance in collecting the zircon data presented here, and Charles Ferguson (Arizona Geological Survey) for sharing his extensive knowledge of the southern Black Mountains and of field volcanology in general, and for his assistance in collecting representative samples. Jeff Vervoort, Charles Knaack, Diane Wilford, and Scott Boroughs kindly lent their expertise and facilitated our work at the Washington State Radiogenic Isotope and Geochronology Laboratory. Reviewers Lang Farmer and Peter Lipman and Associate Editor Calvin Barnes provided thorough, careful, constructive comments.

**Figure 6.** Cartoon depicting the magmatic evolution of the SBMVC as indicated by elemental, isotopic, and field data. PMC = Proterozoic Mojave crust component; EM = enriched Mojave lithospheric mantle component.
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**REFERENCES CITED**


