

# Petrogenesis and tectonic setting of the peralkaline Pine Canyon caldera, Trans-Pecos Texas, USA

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## Abstract

The Pine Canyon caldera is a small (6–7 km diameter) ash-flow caldera that erupted peralkaline quartz trachyte, rhyolite, and high-silica rhyolite lavas and ash-flow tuffs about 33–32 Ma. The Pine Canyon caldera is located in Big Bend National Park, Texas, USA, in the southern part of the Trans-Pecos Magmatic Province (TPMP). The eruptive products of the Pine Canyon caldera are assigned to the South Rim Formation, which represents the silicic end member of a bimodal suite (with a “Daly Gap” between 57 and 62 wt.% SiO<sub>2</sub>); the mafic end member consists primarily of alkali basalt to mugearite lavas of the 34–30 Ma Bee Mountain Basalt. Approximately 60–70% crystallization of plagioclase, clinopyroxene, olivine, magnetite, and apatite from alkali basalt coupled with assimilation of shale wall rock ( $M_a/M_c=0.3-0.4$ ) produced the quartz trachyte magma. Variation within the quartz trachyte–rhyolite suite was the result of ~70% fractional crystallization of an assemblage dominated by alkali feldspar with subordinate clinopyroxene, fayalite, ilmenite, and apatite. High-silica rhyolite is not cogenetic with the quartz trachyte–rhyolite suite, and can be best explained as the result of ~5% partial melting of a mafic granulite in the deep crust under the fluxing influence of fluorine. Variation within the high-silica rhyolite is most likely due to fractional crystallization of alkali feldspar, quartz, magnetite, biotite, and monazite. Lavas and tuffs of the South Rim Formation form A-type rhyolite suites, and are broadly similar to rock series described in anorogenic settings both in terms of petrology and petrogenesis. The Pine Canyon caldera is interpreted to have developed in a post-orogenic tectonic setting, or an early stage of continental rifting, and represents the earliest evidence for continental extension in the TPMP.

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## 1. Introduction and geologic setting

The South Rim Formation (SRF) consists of peralkaline quartz trachyte, rhyolite, and high-silica rhyolite lavas and tuffs that erupted about 33–32 Ma from the Pine Canyon caldera and several postcaldera vents that form the Chisos Mountains in Big Bend National Park

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(BBNP), Texas, USA (Fig. 1) (Maxwell et al., 1967; Ogley, 1978; Barker et al., 1986; Urbanczyk and White, 2000; Miggins et al., 2004). The SRF represents the silicic end-member of a bimodal suite in BBNP; the mafic end-member consists of alkali basalt to mugearite lavas of the Chisos Group, which includes the 34–30 Ma Bee Mountain Basalt as well as older (47–34 Ma), similar lavas (Schucker, 1986; Schucker and Nelson, 1988; Henry and Davis, 1996).

BBNP is located in the southern part of the Trans-Pecos Magmatic Province (TPMP), one of several middle Tertiary igneous provinces proximal to late Tertiary to Quaternary basins of the Rio Grande rift (Fig. 2; Barker, 1977, 1987; Dickerson and Muehlberger, 1994; Chapin et al., 2004). The TPMP is divided into an eastern alkalic belt and a western metaluminous belt; most alkalic magmatism occurred in the eastern belt, including peralkaline volcanic centers such as the Pine Canyon caldera, the Buckhorn caldera (Parker,

1986), and the Paisano volcano (Parker, 1983), as well as a chain of nepheline trachyte and phonolite intrusions (Potter, 1996). Metaluminous volcanic rocks occur throughout the TPMP, and are closely related both spatially and temporally to peralkaline volcanic centers in the eastern belt (e.g., the Davis Mountains volcanic field; Henry et al., 1994). Mafic rocks are widespread in the southern TPMP (the Big Bend area), but are very rare elsewhere in the TPMP (Barker, 1987).

Magmatism in the TPMP began about 48 Ma, immediately following the end of the Laramide orogeny in west Texas, and continued until about 16 Ma, during Basin and Range extension (Henry and McDowell, 1986). Although it is generally accepted that the earliest magmatism took place in a compressional (orogenic) stress regime, and that the latest magmatism took place in an extensional (intraplate) stress regime, the timing of the change is controversial. On the basis of paleostress

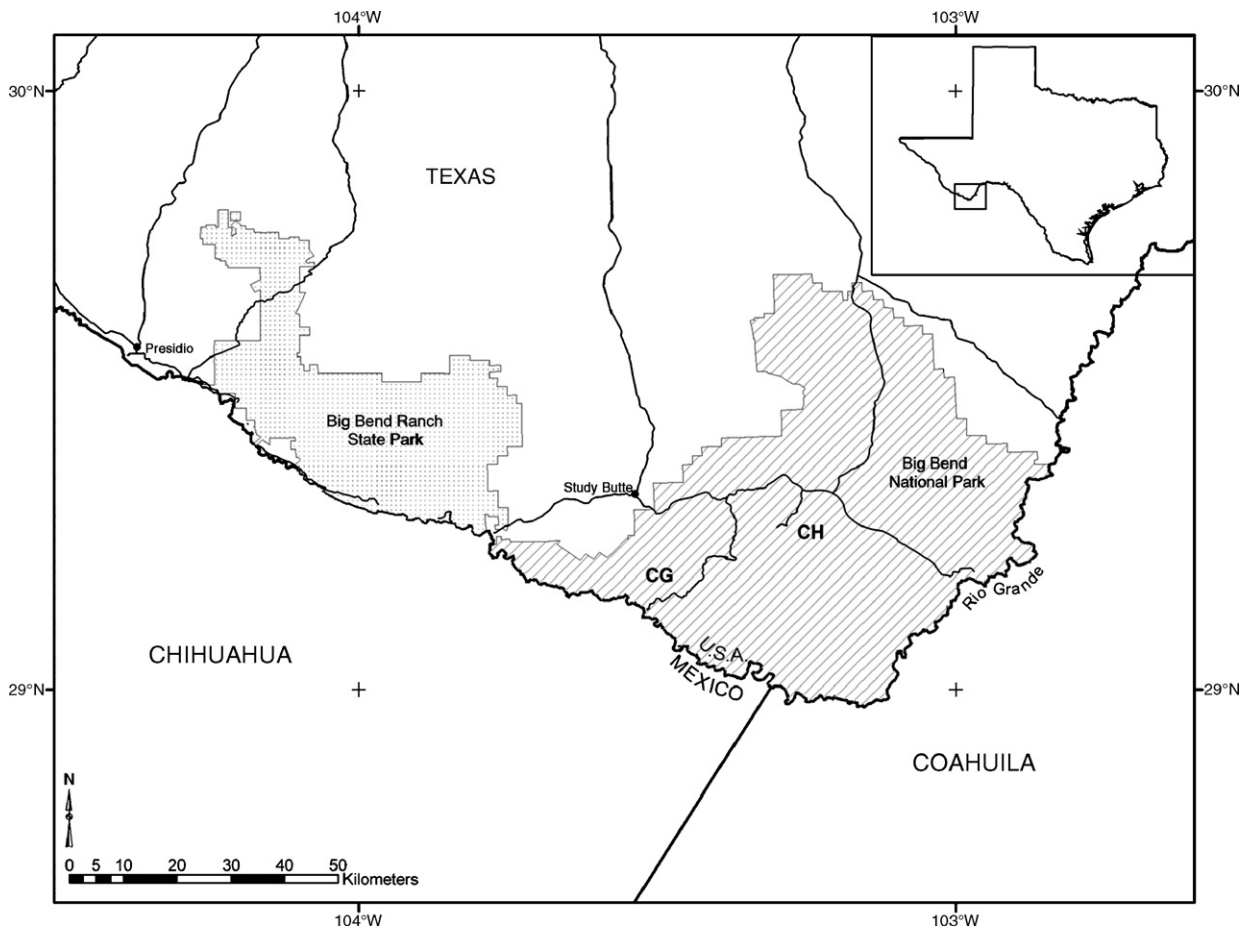


Fig. 1. Location of Big Bend National Park, Texas. Areas within the park referred to in the text include the Chisos Mountains (CH) and the Castolon Graben (CG).

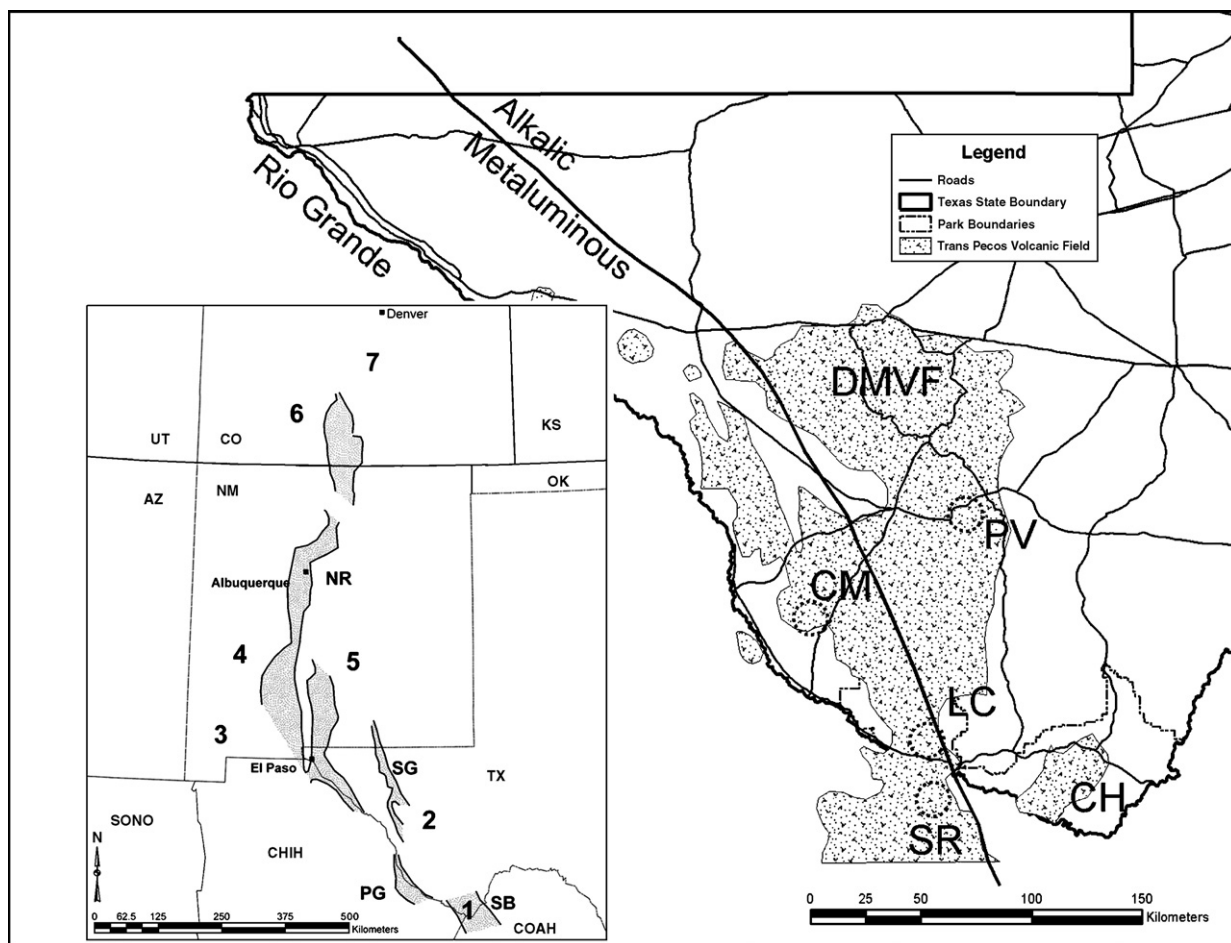


Fig. 2. The Trans-Pecos Magmatic Province (TPMP) with the approximate boundary between the eastern alkalic belt and western metaluminous belt; the shaded area indicates the extent of volcanic rocks in the TPMP (Barker, 1977). Also shown for reference are the national and state part boundaries and roads (see Fig. 1). Volcanic centers include: CH, Chisos Mountains; CM, Chinati Mountains; DMVF, Davis Mountains volcanic field; LC, Leyva Canyon volcano; PV, Paisano volcano; SR, Sierra Rica. The inset map shows the locations of middle to late Tertiary basins of the Rio Grande Rift and selected middle Tertiary volcanic centers. Volcanic centers include: (1) Chisos Mountains, (2) Davis Mountains, (3) Boot Heel, (4) Mogollon–Datil, (5) Sierra Blanca, (6) San Juan Mountains, and (7) central Colorado; basins include: NR, northern Rio Grande rift; SG, Salt Graben; PG, Presidio Graben; and SB, the “Sunken Block” (Dickerson and Muehlberger, 1994; Chapin et al., 2004).

analysis of dikes and veins in the TPMP, Henry et al. (1991) suggested that a compressional regime persisted until 31 Ma, and that magmatism prior to 31 Ma occurred in a subduction-related, continental volcanic arc. However, recent work in southern New Mexico and central Colorado, has suggested that extension began in the region about 36 Ma, and that related magmatism was the result of passive continental rifting over a foundering subducted slab (Lawton and McMillan, 1999; McMillan et al., 2000; Chapin et al., 2004; McIntosh and Chapin, 2004). Alkalic rocks such as peralkaline quartz trachyte and rhyolite are generally considered to be characteristic of intraplate magmatism (Bowden, 1974), but have been documented at convergent margins (e.g., D’Entrecasteaux Islands, New Guinea: Smith et al., 1977; Mayor

Island, New Zealand: Houghton et al., 1992). Within volcanic arcs, however, peralkaline magmatism is usually still attributed to extension either during the waning stages of orogeny, or immediately after, in a post-orogenic tectonic regime (Bonin, 1988; Stolz et al., 1993; Bonin et al., 1998; Bonin, 2004; Cadoux et al., 2005).

The petrogenesis of peralkaline rocks and the origin of the “Daly Gap” between mafic and silicic magmas has been the subject of debate for many years, and three leading petrogenetic models have emerged: (1) Protracted fractional crystallization of transitional to alkali basalt (e.g., Baker et al., 1977; Parker, 1983; Mungall and Martin, 1995; Civetta et al., 1998); (2) Low-degree partial melting of alkali-rich mafic rock, followed by

fractional crystallization (Bailey and Macdonald, 1970; Lowenstern and Mahood, 1991; Hay and Wendlandt, 1995; Hay et al., 1995a,b; Bohrson and Reid, 1997, 1998); and, (3) Partial melting of crustal rock or fractional crystallization combined with alkali and trace element enrichment via a volatile phase (Bailey and Macdonald, 1975; Macdonald et al., 1987; Bailey and Macdonald, 1987; Davies and Macdonald, 1987). In this paper, we examine the petrogenesis of a suite of peralkaline quartz trachyte, rhyolite, and high-silica rhyolite that erupted from the Oligocene Pine Canyon caldera. The close spatial and temporal relationship between peralkaline silicic magmas and mafic magmas in the Big Bend area provides an excellent opportunity to evaluate the role of mafic magmatism in the origin of peralkaline magmas. Detailed knowledge of the petrogenesis of the SRF is also applied to help interpret the tectonic setting of the TPMP at 33–32 Ma.

## 2. Analytical methods

We present sixty new analyses of samples of lava and tuff from the South Rim Formation. All samples were powdered to –200 mesh in a pre-contaminated tungsten-carbide shatterbox grinder. Thirty-seven of these were analyzed for both major- and trace-elements by ICP-OES and ICP-MS techniques following a lithium metaborate/tetraborate fusion dilution at Activation Laboratories, Ancaster, Ontario (Code 4Lithorsearch). The remaining twenty-three were analyzed by electron-dispersive X-ray fluorescence spectroscopy (ED-XRF) at Sul Ross State University, Alpine, Texas; see White and Urbanczyk (2001) for a detailed description of the procedure. Mineral chemistry was obtained by electron probe microanalysis (EPMA) at the University of Texas at El Paso on a Cameca SX50 instrument; a description of the procedure can be found in White et al. (2005). Whole-rock and representative mineral analyses are available on line; see the journal's homepage <http://www.elsevier.com/locate/lithos> under "Electronic Supplements".

## 3. Stratigraphy and petrology

### 3.1. Chisos Group

Maxwell et al. (1967) assigned volcanic units and intercalated sedimentary rocks in the Big Bend area that are located above late Cretaceous and early Tertiary sedimentary rocks, but below a major unconformity marking the end of sedimentary deposition, to the Chisos Formation (promoted to Group by Henry and

Davis, 1996). The Chisos Group consists of the 47–34.5 Ma Alamo Creek Basalt (ACB), the 34.5 Ma Ash Spring Basalt (ASB), the 34–30 Ma Bee Mountain Basalt (BMB), the 33 Ma Mule Ears Spring Tuff (MEST), and the 32 Ma Tule Mountain Trachyandesite (TMT) (Henry and McDowell, 1986; Schucker and Nelson, 1988; Henry and Davis, 1996). ASB, BMB, and volcaniclastic sedimentary rocks are the only units in the Chisos Group that crop out in the Pine Canyon area (Maxwell et al., 1967; Ogley, 1978). The BMB is the most widespread volcanic formation in the Chisos Group (Barker et al., 1986), and consists of numerous flows of aphyric to porphyritic alkali basalt to mugearite lavas that erupted over a large area, cropping out from the Chisos Mountains westward into Big Bend Ranch State Park (Schucker, 1986; Henry and Davis, 1996). At least three flows of BMB lava have been identified between the MEST and TMT, and at least one flow has been described above the TMT, indicating activity to at least 32 Ma (Henry and Davis, 1996) and possibly as late as 29 Ma (Schucker and Nelson, 1988).

### 3.2. South Rim Formation (SRF)

The peralkaline quartz trachyte, rhyolite, and high-silica rhyolite lavas and tuffs that crop out in the Chisos Mountains were assigned by Maxwell et al. (1967) to the South Rim Formation (SRF), along with similar peralkaline high-silica rhyolite lavas and tuffs that crop out to the southwest of the Chisos in the Castolon graben. Benker (2005) divided the SRF in the Chisos Mountains into three informal members that correspond to the three episodes of Pine Canyon volcanism described by Barker et al. (1986): the Pine Canyon Rhyolite Member (PCR), the Boot Rock Member (BRM), and the Emory Peak Rhyolite Member (EPR).

#### 3.2.1. Pine Canyon Rhyolite Member (PCR)

The Pine Canyon Rhyolite ("Brown Rhyolite" of Maxwell et al., 1967) represents the caldera-forming ignimbrite of the Pine Canyon caldera, a small (6–7 km diameter) downsag caldera (Walker, 1984) that formed about 33–32 Ma (Barker et al., 1986). The PCR defines a circular pattern coincident with the caldera itself and ranges in thickness from ~300 m along the northern and eastern margins of the caldera to ~20 m along the southwest margin of the caldera (Ogley, 1978; Drenth and Finn, 2004). PCR ranges in lithology from a lithic-free, densely welded vitrophyre to a coarsely lithic welded ash-flow tuff that weathers to a distinctive brown color. PCR samples studied consist primarily of sparsely phyrlic, partially

devitrified, eutaxitic vitrophyre. Anorthoclase (Or<sub>35</sub>) is the dominant phenocryst, comprising about 5 vol.% of the sample. Minor (<1 vol.%) phenocrysts include sodic hedenbergite (Wo<sub>46</sub>Fs<sub>54</sub>), ilmenite (Ilm<sub>98</sub>), aenigmatite, ferrichterite, fayalite, and apatite. The presence of both aenigmatite and ferrichterite suggest equilibration at low temperatures (<750 °C) and low oxygen fugacities (Charles, 1975; Scaillet and Macdonald, 2001). Oxygen fugacities for sample 99802, calculated from clinopyroxene–quartz–ilmenite equilibria with QUILF95 (Andersen et al., 1993) over a temperature range of 680 to 740 °C at 1 kbar of pressure, are 1.7 to 1.9 log units below the FMQ buffer. These results are consistent with the aenigmatite–ilmenite equilibrium model presented by White et al. (2005), which suggests crystallization between FMQ-1.7 and FMQ-2.0 in a quartz-saturated melt with a Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> activity of 1.0.

### 3.2.2. Boot Rock Member (BRM)

The Boot Rock Member (Wasp Spring Flow-Breccia and Lost Mine Rhyolite of Maxwell et al., 1967) consists of a series of quartz trachyte to rhyolite lavas, ignimbrites, and maar surge deposits that erupted from intra- and extra-caldera postcaldera vents about 32.17 ± 0.9 Ma (Barker et al., 1986; Urbanczyk and White, 2000; Miggins et al., 2004). Inside the caldera structure, the BRM overlies the PCR without a sharp contact, and includes megabreccia, welded ash-flow tuff, surge deposits, and quartz trachyte lava. BRM welded ash-flow tuffs, lavas, and similar intrusive rocks studied consist of <10 vol.% phenocrysts of sanidine (Or<sub>39</sub>) with subordinate (<1 vol.%) hedenbergite (Wo<sub>44</sub>Fs<sub>55</sub>) and ilmenite (Ilm<sub>96–97</sub>), and with rare magnetite (Mgt<sub>37</sub>) and aenigmatite. Trace amounts of apatite and zircon are present in many samples. For sample PC-06, an intrusion of quartz trachyte (~67.7 wt.% SiO<sub>2</sub>), an Andersen and Lindsley (1988) two-oxide temperature and log *f*O<sub>2</sub> of 768 °C and –16.7 (FMQ-1.5) was determined.

### 3.2.3. Emory Peak Rhyolite Member (EPR)

The Emory Peak Rhyolite Member (Burro Mesa Rhyolite of Maxwell et al., 1967) consists of a series of quartz-bearing rhyolitic welded to rheomorphic ash-flow tuffs that erupted from intra- and extra-caldera postcaldera vents at 31.93 ± 0.13 Ma (Barker et al., 1986; Miggins et al., 2004). Intrusive rocks petrographically and geochemically identical to the EPR form a series of east and northeast trending dikes that cross-cut the Chisos Group, PCR, and BRM. EPR samples studied consist of welded, devitrified ash-flow tuff and

rheomorphic tuff, some of which have large (up to 10 cm), rounded inclusions of basalt similar to BMB. Sanidine (Or<sub>41</sub>) and quartz are the dominant phenocrysts; minor phenocrysts include magnetite (Mgt<sub>53</sub>), fluorian (2.21 wt.% F) biotite (annite), monazite, and zircon. Vapor-phase fluorian arfvedsonite (1.50 wt.% F) is a ubiquitous groundmass phase in the rheomorphic tuff. The presence of biotite in this assemblage suggests equilibration at low temperatures (<700 °C) under reducing conditions and close to H<sub>2</sub>O saturation (Scaillet and Macdonald, 2001). For oxygen fugacities defined by the FMQ buffer, the assemblage annite + sanidine + magnetite is in equilibrium at 680–690 °C at ~1 kbar of total pressure (Dachs, 1994).

### 3.3. Burro Mesa Formation

Units in the Castolon graben include the Wasp Springs Tuff Member (WST) and the Burro Mesa Rhyolite Member (BUM), which erupted between 29.40 ± 0.17 and 28.96 ± 0.14 Ma (Miggins et al., 2004). The BUM includes aphyric comendite lava and ash-flow tuff (Lower Burro Mesa, LBM), and phyrlic comendite lava and ash-flow tuff (Upper Burro Mesa, UBM); on Burro Mesa, a mugearite lava flow similar to BMB lavas occurs between the LBM and UBM (Henry et al., 1989; Holt, 1998; Adams, 2004). Recent work in the Castolon area has demonstrated that outcrops of the BUM do not represent erosional remnants of EPR-correlative flows that originated in the Chisos Mountains, as stated by earlier workers (Maxwell et al., 1967; Ogle, 1978), but instead represent several individual lava dome volcanoes (Henry et al., 1989; Holt, 1998; Barker, 2000; Parker, 2002; Adams, 2004). We consider neither the WST nor the BUM to be part of the SRF; instead, these are included as informal members in the (new) Burro Mesa Formation, following Benker (2005).

## 4. Geochemistry

### 4.1. Classification

Samples of the South Rim Formation (SRF) and representative samples of Chisos Group mafic lavas (Henry and Davis, 1996; Adams, 2004) were classified using the total alkalis versus silica (TAS) diagram (Fig. 3; Le Maitre et al., 2002). Most SRF samples have an agpaite index (A.I. = mol Na + K / Al) greater than unity and/or groundmass arfvedsonite or aenigmatite, which indicates that these rocks are peralkaline. The presence of arfvedsonite and/or aenigmatite in some rocks despite

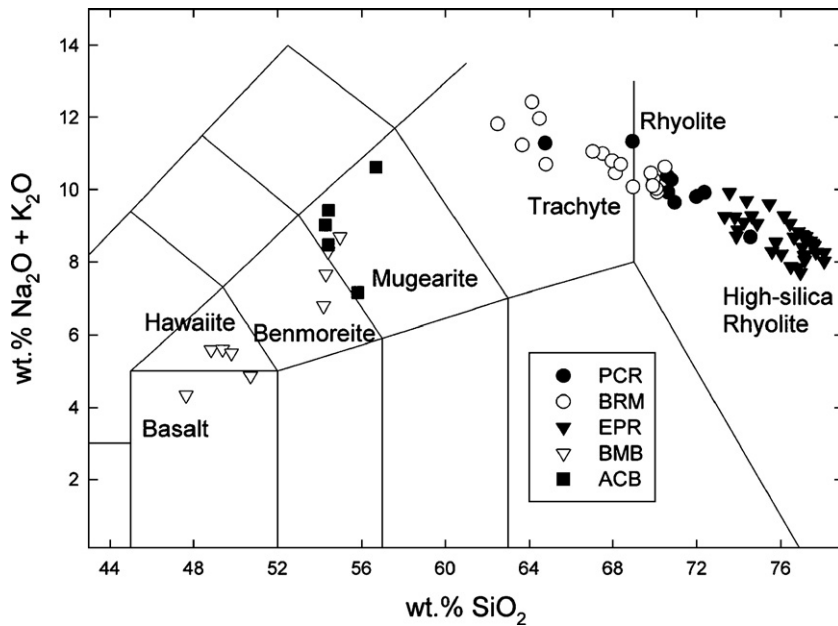


Fig. 3. South Rim Formation data from this report and Chisos Group data from Henry and Davis (1996) and Adams (2004) plotted on a total alkalis–silica (TAS) diagram (Le Maitre et al., 2002). Members of the South Rim Formation include the Pine Canyon Rhyolite Member (PCR), the Boot Rock Member (BRM), and the Emory Peak Rhyolite Member (EPR); representative formations of the Chisos Group include the Bee Mountain Basalt (BMB) and the Alamo Creek Basalt (ACB).

values of A.I. < 1.0 suggests that many of these samples have lost alkali components. The Pine Canyon Rhyolite (PCR) represents the most peralkaline unit (A.I. = 1.03–1.21) and most samples classify as rhyolite or comendite (borderline pantellerite). The Boot Rock Member (BRM) is less peralkaline (A.I. = 0.93–1.13) and most samples classify as quartz trachyte or comenditic trachyte and comendite. The Emory Peak Rhyolite (EPR) is the least peralkaline unit (A.I. = 0.89–1.09) and classifies as high-silica rhyolite or comendite. Chisos Group lavas plot between basalt (~45 wt.% SiO<sub>2</sub>) and mugearite (~57 wt.% SiO<sub>2</sub>), which results in a “Daly Gap” between Chisos Group and SRF suites.

Both the Pine Canyon suite and the Emory Peak suite can also be classified as A-type (anorogenic) magmas (Loiselle and Wones, 1979; Whalen et al., 1987). At ~70% SiO<sub>2</sub>, the PCR has high total alkalis (9.5 wt.%), low CaO (0.50 wt.%), very high FeO<sup>T</sup>/MgO (150), and elevated concentrations of high field-strength elements (HFSE) (e.g., 1850 ppm Zr, 225 ppm Nb). EPR is also characterized by high total alkalis (7–9 wt.%), low CaO (<0.50 wt.%), high FeO<sup>T</sup>/MgO (up to 360), and somewhat elevated concentrations of HFSE (e.g., 700–900 ppm Zr, 100–150 ppm Nb). On tectonic discrimination diagrams (not presented), both suites plot in the Within Plate Granite (Y vs. Nb, Y+Nb vs. Rb; Pearce et al., 1984) and A-type fields (Zr vs. 10000 Ga/

Al, FeO<sup>T</sup>/MgO vs. Zr+Nb+Ce+Y; Whalen et al., 1987).

#### 4.2. Pearce element ratio diagrams

Harker diagrams are not particularly useful for discriminating trends in these silicic rocks: all major-elements show a monotonous decline with increasing SiO<sub>2</sub> (Benker, 2005). Therefore, we instead present Pearce (1968) element ratio (PER) diagrams. PER diagrams are graphs of  $A/\Omega$  vs.  $B/\Omega$ , where  $A$ ,  $B$ , and  $\Omega$  are all compositional abundances, and  $\Omega$  is a conserved, or incompatible, element. PER diagrams are based on the stoichiometry of rock-forming minerals, and slopes of data distributions are equal to the  $A:B$  ratio of minerals lost or gained during differentiation of a suite of cogenetic rocks (Russell and Nicholls, 1988). Representative PER diagrams that use Zr as the conserved-element denominator (following Bradshaw, 1992) are presented in Fig. 4. Two obvious suites within the South Rim Formation can be seen in these diagrams: one that includes the Pine Canyon Rhyolite (PCR), the Boot Rock Member (BRM), and the Lone Mountain (PJ-01) and Little Nugent (PC-06) intrusions (Pine Canyon suite); and another that includes the Emory Peak Rhyolite (EPR), and the Hayes Ridge (PC-05), K-Bar (KB-01), Panther Pass (PP-03), Appetite Peak (AP-

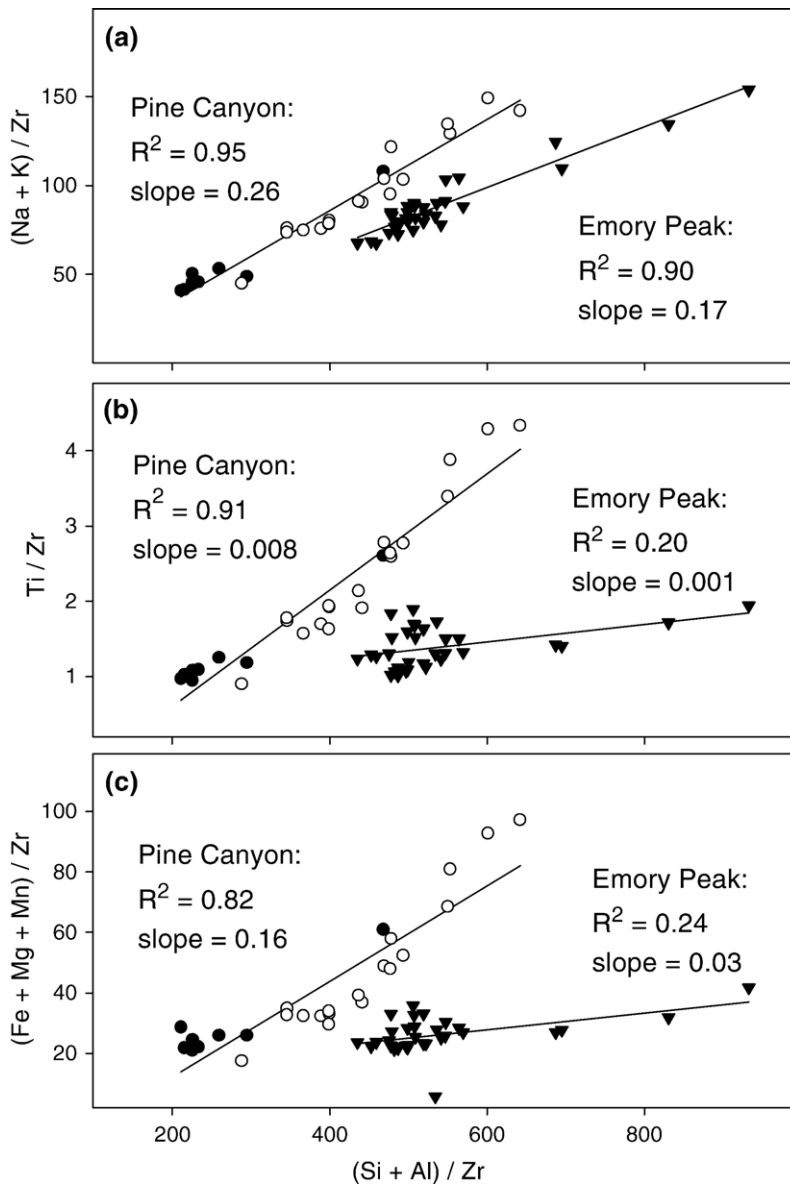


Fig. 4. Pearce (1968) element ratio (PER) diagrams for the South Rim Formation using Zr as the conserved-element denominator (Bradshaw, 1992). Symbols are the same as in Fig. 3.

01), and Lost Mine Trail (LM-02) intrusions (Emory Peak suite).

It can be inferred from the PER diagrams that it is unlikely that the high-silica rhyolite Emory Peak suite evolved via fractional crystallization from the Pine Canyon suite. However, closed system processes may be able to explain compositional variation within each suite. The Pine Canyon suite demonstrates an increase in  $SiO_2$  from  $\sim 62$  to  $\sim 72$  wt.% with a decrease in  $(Si + Al) / Zr$  and all major element oxides (Benker, 2005). The similarity between the calculated (Stanley and

Russell, 1990) alkali feldspar fractionation slope (0.25) and observed slope (0.26) in Fig. 4a, coupled with the dominant presence of alkali feldspar as a phyrlic phase in these rocks, strongly suggests that fractional crystallization of an assemblage dominated by alkali feldspar with minor clinopyroxene and Fe–Ti oxides (Fig. 4b,c) played a dominant role in the petrogenesis of the quartz trachyte–rhyolite suite. There is much less systematic variation in the Emory Peak suite, especially with respect to Fe, Mg, Mn, and Ti, which may be due to the crystallization of zircon, an accessory phase observed in

the EPR. Only the alkali metals strongly correlate with silicon and aluminum, declining with a slope of 0.17, which would be consistent with fractional crystallization of an assemblage of quartz and alkali feldspar.

#### 4.3. Trace-element geochemistry

Trace element variation diagrams are presented in Fig. 5, which use Nb as a differentiation index. Despite being higher in silica, the Emory Peak suite is depleted in all incompatible trace elements compared

to the Pine Canyon suite, and with the exception of Ga there is little obvious systematic variation within the Emory Peak suite. Systematic variation is observed within the Pine Canyon suite: with increasing Nb, all incompatible trace elements exhibit an approximately three-fold increase in concentration, Sr declines from 13 to 7 ppm, and Ba declines from 106 to 9 ppm. Incompatible trace-element ratios vary between each suite, but remain fairly constant within suites: for example, Zr/Hf is  $40.6 \pm 2.0$  for the Pine Canyon suite and  $32.1 \pm 3.8$  for the Emory Peak suite, and Rb/Nb is

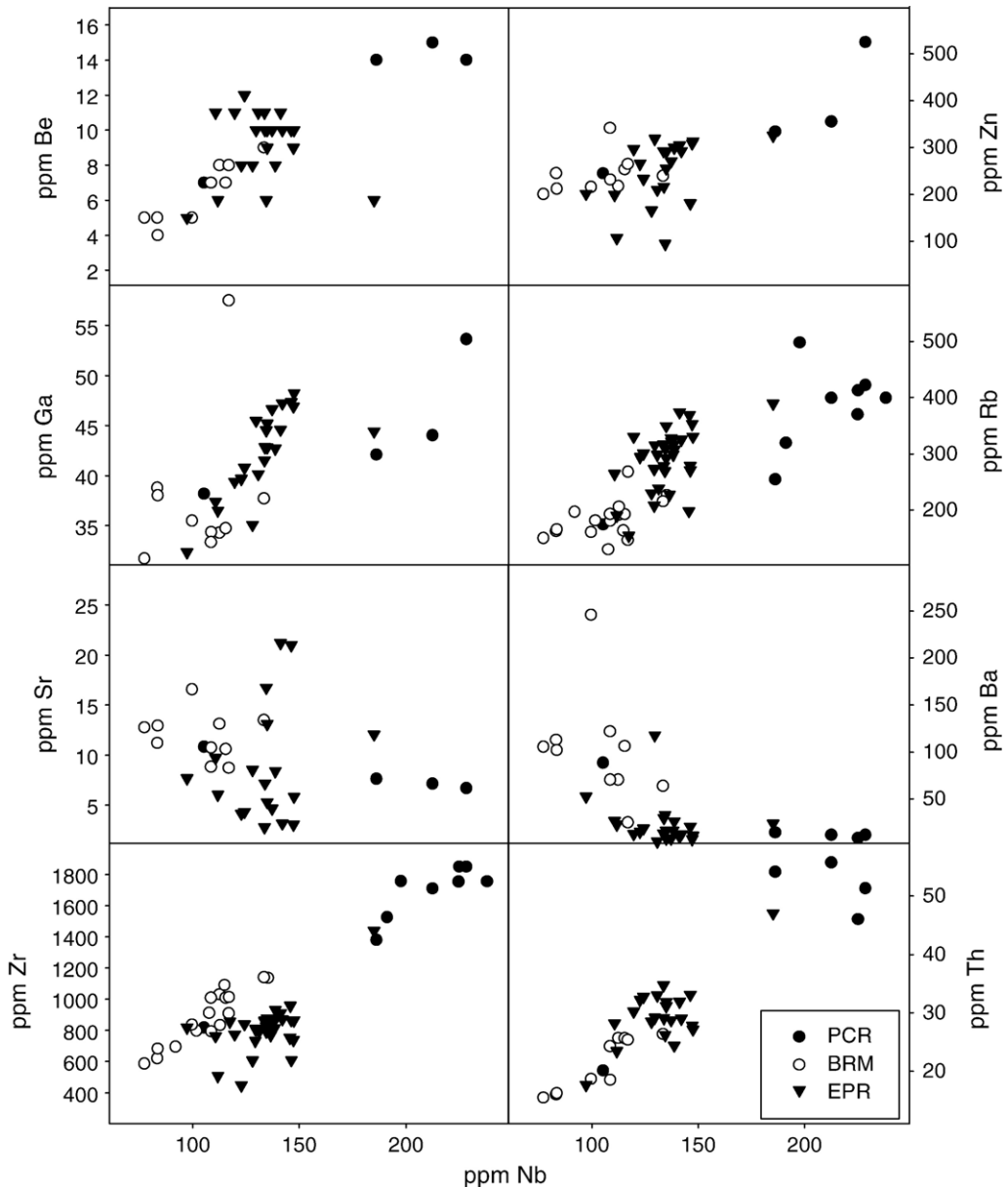


Fig. 5. Trace-element variation diagrams for the South Rim Formation using Nb as a differentiation index. Symbols are the same as in Fig. 3.



$1.7 \pm 0.2$  (Pine Canyon suite) and  $2.2 \pm 0.6$  (Emory Peak). For comparison, incompatible trace element ratios for the Bee Mountain Basalt (Henry and Davis, 1996; Adams, 2004) are  $41.5 \pm 2.0$  (Zr/Hf) and  $1.45 \pm 0.48$  (Rb/Nb).

REE plots of representative analyses (normalized following Boynton, 1984) are presented in Fig. 6. Again despite being higher in silica, the Emory Peak suite is

depleted in REE compared to the Pine Canyon suite: Ce is enriched by 210–754 $\times$  chondrite in the Pine Canyon suite compared to 43–439 $\times$  chondrite in the Emory Peak suite, and Yb is enriched by 26–76 $\times$  chondrite in the Pine Canyon suite versus 30–83 $\times$  chondrite in the Emory Peak suite. Chondrite-normalized values for Ce/Yb and La/Sm remain fairly constant within the Pine Canyon suite at  $8.0 \pm 0.4$  and  $4.2 \pm 0.3$ , respectively

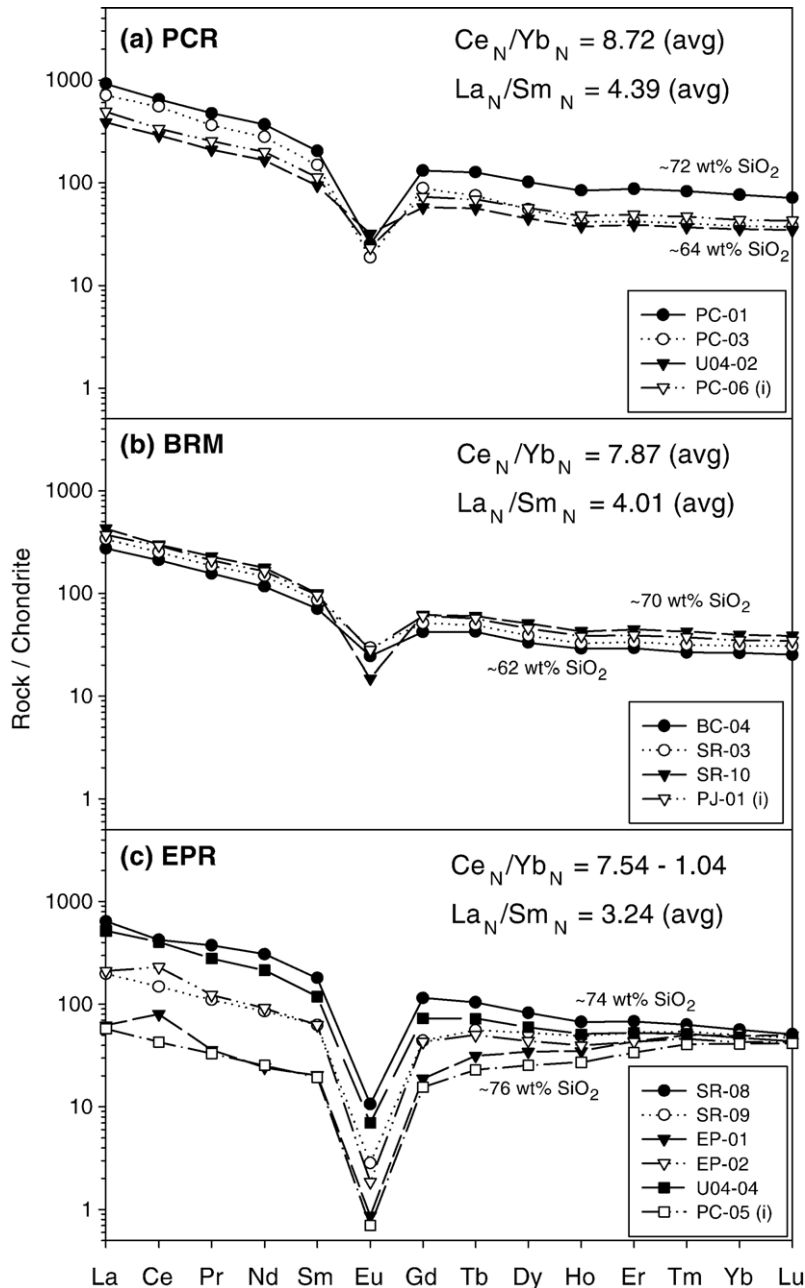


Fig. 6. Rare-earth element diagrams for representative samples from (a) the Pine Canyon Rhyolite Member, (b) the Boot Rock Member, and (c) the Emory Peak Rhyolite Member. All rock samples are normalized to chondrite following Boynton (1984).

(although  $Ce_N/Yb_N$  does jump to 10.8 and 14.1 in two higher-silica samples of PCR). Within the Emory Peak suite,  $La_N/Sm_N$  is lower, but fairly constant, at  $3.2 \pm 0.5$ , whereas  $Ce_N/Yb_N$  systematically decreases from 7.5 to 1.0 with increasing whole-rock silica. Both suites have a negative Eu anomaly that deepens with increasing silica: within the Pine Canyon suite,  $Eu/Eu^*$  decreases from 0.45 to 0.15, and within the Emory Peak suite,  $Eu/Eu^*$  decreases from 0.31 to 0.03. For comparison, normalized rare earth element ratios for the Bee Mountains Basalts (Henry and Davis, 1996; Adams, 2004) are  $7.1 \pm 1.3$  ( $Ce_N/Yb_N$ ),  $3.0 \pm 0.9$  ( $La_N/Sm_N$ ), and 1.1 to 0.8 ( $Eu/Eu^*$ ).

The trace-element data clearly indicate that the high-silica rhyolite of the Emory Peak suite is not related to the quartz trachyte and rhyolite of the Pine Canyon suite via fractional crystallization processes, although fractional crystallization processes may be responsible for variation within the individual suites.

## 5. Petrogenesis

### 5.1. Origin of quartz trachyte via assimilation and fractional crystallization (AFC) of alkali basalt

Major-element mass balance models (Bryan et al., 1969) can both test the hypotheses suggested by PER diagram analysis as well as quantify the relative proportion of the various phases involved during petrogenesis, which can be tested against both the petrography and the trace element data. Major-element mass balance models are presented (Table 1) that test fractional crystallization hypotheses for the origin of quartz trachyte from basalt (Stage 1), and the origin of rhyolite from quartz trachyte (Stage 2). Major-element models suggests that the most primitive peralkaline quartz trachyte of Boot Rock Member presented in this report (BC-04) could be derived via 81% fractional crystallization ( $F=0.19$ ) of an assemblage of plagioclase,

Table 1  
Quartz trachyte–rhyolite major-element mass balance models

	Parent	Daughter						Parent	
<i>Stage 1 FC</i>	H90-50	BC-04	Pl	Cpx	Mgt	Ol	Ap	Calc.	Residuals
SiO <sub>2</sub>	47.65	64.81	54.52	51.81	0.00	38.10	0.00	47.67	-0.02
TiO <sub>2</sub>	2.51	0.43	0.00	1.01	26.49	0.00	0.00	2.88	-0.37
Al <sub>2</sub> O <sub>3</sub>	17.03	14.44	28.26	1.65	2.31	0.00	0.00	17.03	0.00
FeO <sup>T</sup>	12.72	7.20	0.00	9.02	68.46	24.59	0.22	12.57	0.15
MnO	–	–	–	–	–	–	–	–	–
MgO	6.50	0.08	0.00	13.37	2.74	37.32	0.57	6.58	-0.08
CaO	8.62	2.15	12.63	21.85	0.00	0.00	55.67	8.57	0.05
Na <sub>2</sub> O	3.35	5.52	4.41	0.68	0.00	0.00	0.00	3.25	0.10
K <sub>2</sub> O	0.98	5.18	0.18	0.00	0.00	0.00	0.00	1.05	-0.07
P <sub>2</sub> O <sub>5</sub>	0.45	0.06	0.00	0.00	0.00	0.00	43.54	0.51	-0.06
		<i>F</i>						100.11	0.188
Results:		0.185	0.496	0.059	0.104	0.147	0.011		= $\sum r^2$
Normalized:			0.607	0.072	0.127	0.180	0.014		
<i>Stage 2 FC</i>	BC-04	PC-01	Kfs	Cpx	Ilm	Ol	Ap	Calc.	Residuals
SiO <sub>2</sub>	64.81	72.39	66.35	47.41	0.03	28.65	0.00	64.81	0.00
TiO <sub>2</sub>	0.43	0.32	0.00	0.52	50.74	0.12	0.00	0.43	0.00
Al <sub>2</sub> O <sub>3</sub>	14.44	11.67	19.17	0.49	0.00	0.00	0.00	14.38	0.06
FeO <sup>T</sup>	7.20	5.12	0.20	30.62	47.69	65.73	0.22	7.19	0.01
MnO	0.13	0.10	0.00	0.99	1.45	3.99	1.59	0.28	-0.15
MgO	0.08	0.00	0.00	0.30	0.02	1.06	0.56	0.07	0.02
CaO	2.15	0.51	0.35	19.17	0.04	0.43	54.78	2.16	-0.01
Na <sub>2</sub> O	5.52	5.24	7.11	0.49	0.01	0.01	0.00	5.64	-0.12
K <sub>2</sub> O	5.18	4.63	6.83	0.01	0.02	0.01	0.00	5.26	-0.08
P <sub>2</sub> O <sub>5</sub>	0.06	0.02	0.00	0.00	0.00	0.00	42.84	0.04	0.02
		<i>F</i>						100.26	0.047
Results:		0.306	0.562	0.006	0.001	0.091	0.037		= $\sum r^2$
Normalized:			0.806	0.008	0.001	0.131	0.054		

Analysis H90-50 (alkali basalt) adopted from Henry and Davis (1996).

Key to minerals: Pl, plagioclase feldspar; Kfs, alkali feldspar; Ol, olivine; Cpx, clinopyroxene; Mgt, magnetite; Ilm, ilmenite; Qtz, quartz; Ap, apatite. Stage 1 mineral analyses adopted from Schucker (1986) and Nelson et al. (1987). Stage 2 olivine analysis adopted from White et al. (2005), apatite from Deer et al. (1966), all others are from this report. Other symbols:  $F$ =liquid fraction;  $\sum r^2$ =sum of squares of residuals.

clinopyroxene, olivine, magnetite, and apatite from alkali basalt (H90-50; Henry and Davis, 1996). The sum of the squares of the residuals ( $\sum r^2$ ) for this model is acceptable (0.188). This major-element mass balance models is consistent with petrography and mineralogy (Schucker, 1986).

An origin of quartz trachyte via fractional crystallization of alkali basalt is supported by major-element mass balance modelling and some similar incompatible trace element ratios (e.g., Zr/Hf, Ce/Yb). However, there is also trace element evidence that suggests that fractional crystallization alone cannot explain the origin of quartz trachyte, and that open-system processes must also have played a role: (1) incompatible trace-element concentrations (including Nb, Rb, Th, Zr, Hf, and REE) in the most differentiated Chisos Group mafic lavas (~57 wt.% SiO<sub>2</sub>) are similar to those in the least differentiated South Rim Formation quartz trachyte lavas (~62 wt.% SiO<sub>2</sub>), which suggests assimilation of wall-rock depleted with respect to these elements; and (2) K/Rb values for the model parent (H90-50, K/Rb=678) are much higher than for the model daughter (BC-04, K/Rb=286), which argues against fractional crystallization and recommends assimilation of low-K/Rb wall-rock.

DePaolo's (1981) equation for modelling trace-element behavior during combined assimilation and fractional crystallization (AFC) is used to test this hypothesis. Bulk partition coefficients were calculated using minerals and mineral proportions determined by major-element mass balance modelling (see Table 1, Stage 1) and mineral/melt partition coefficients from Paster et al. (1974), Villemant et al. (1981), McKenzie and O'Nions (1991), and Pearce and Norry (1979). The same model parent (H90-50; Henry and Davis, 1996) and daughter (BC-04) magmas used for major-element mass balance modelling was used for trace element AFC modelling. An estimate of average Phanerozoic shale from Condie (1993) was selected as the model assimilant. Shale is considered to be a very likely assimilant because the Big Bend area developed on accreted Phanerozoic crust that includes thick flysch sequences (Cameron et al., 1992; James and Henry, 1993). Model results and calculated bulk partition coefficients are presented in Fig. 7 for (a)  $M_a/M_c$  (mass assimilated/mass crystallized)=0.3 and (b)  $M_a/M_c$ =0.4. These results are arranged and normalized on a spider diagram following Thompson (1982) and show that quartz trachyte may have evolved from alkali basalt via 60–70% crystallization ( $F=0.4$ –0.3) of an assemblage of plagioclase, clinopyroxene, olivine, magnetite, and apatite coupled

with assimilation ( $M_a/M_c=0.3$  to 0.4) of shale wall-rock. However, there are major discrepancies at each of the compatible elements (especially Ba and Sr), where model results are much higher than the model daughter, which may be due to either too-low partition coefficients (e.g.,  $D_{Ba}=2.7$  and  $D_{Sr}=5.0$  would result in a better fit, which could suggest a greater role for plagioclase, and a possible role for alkali feldspar, amphibole, and/or biotite), too-high concentrations in the model assimilant, or a combination of these two possibilities.

### 5.2. Origin of the quartz trachyte–rhyolite suite via fractional crystallization

Major element mass balance modelling (Table 1, Stage 2) suggests that the differentiation of quartz trachyte (BC-04) to peralkaline rhyolite (PC-01) can be explained by 69% fractional crystallization ( $F=0.31$ ) of an assemblage dominated by alkali feldspar (80.6%) with clinopyroxene, ilmenite, fayalite, and apatite. The  $\sum r^2$  for this model is 0.047. Major element model results are consistent with observed petrography and mineralogy, major-element trends shown on the PER diagrams, and incompatible trace element ratios. The fractional crystallization hypothesis is tested with trace element modelling (e.g., Allègre et al., 1977). Bulk partition coefficients were calculated using minerals and mineral proportions determined by major-element mass balance modelling, plus a trace amount (0.0001) of zircon, which was observed as a minor phase in some samples, and mineral/melt partition coefficients from Paster et al. (1974), Pearce and Norry (1979), Fujimaki (1986), Villemant (1988), White (2003), and White et al. (2003).

Unlike most trace-elements that have alkali feldspar/melt partition coefficient that do not vary significantly during differentiation of the quartz trachyte to rhyolite suite, Europium gradually changes from a compatible element ( $D_{Eu}=1.36$ ) in alkali feldspar in the model parent (BC-04) to an incompatible element ( $D_{Eu}=0.65$ ) in the model daughter (PC-01), as estimated using the method (Model Eu-A) described by White (2003). Bulk partition coefficients for samples BC-04 (1.34) and PC-01 (0.78) were calculated using the estimated partition coefficients for alkali feldspar, partition coefficients for clinopyroxene (1.60), ilmenite (0.74), and fayalite (0.02) from Villemant (1988), and apatite (30.0) from Mahood and Stimac (1990), and the model results presented in Table 1 (Stage 2). From these bulk partition coefficients and the value of  $F$  for the model daughter predicted by the major element model (0.306), a linear

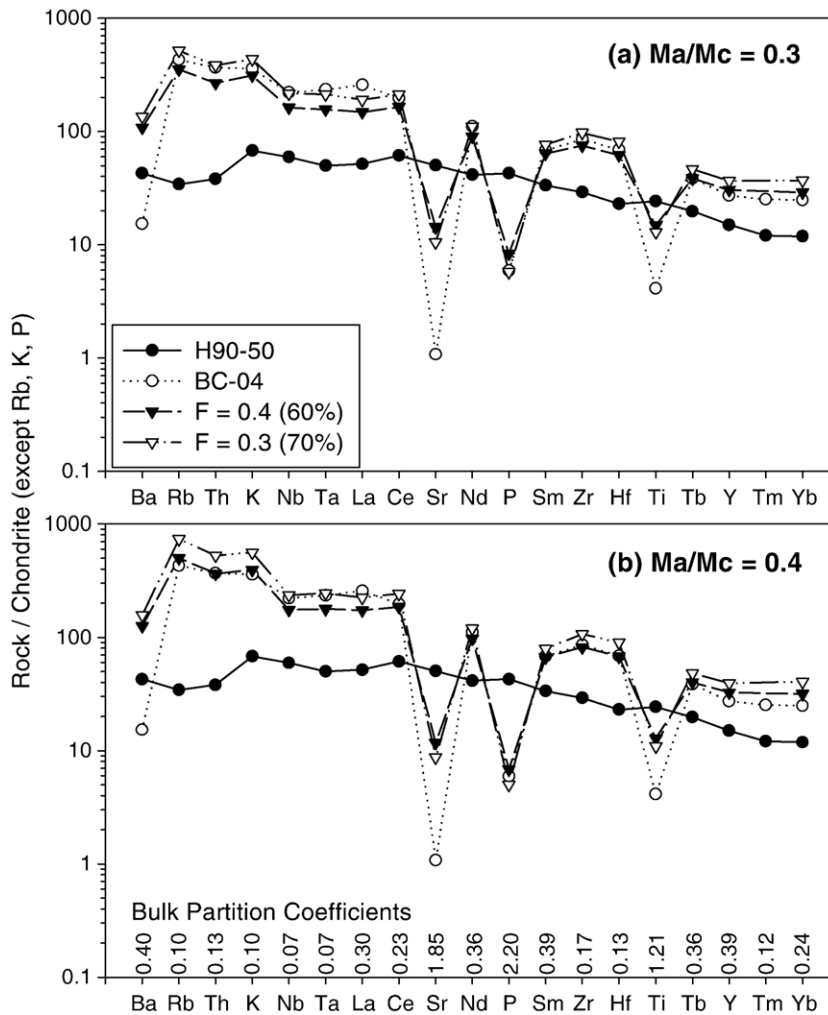


Fig. 7. Results of assimilation–fractional crystallization (AFC) modelling (DePaolo, 1981) of the origin of quartz trachyte (BC-04, ~64 wt.% SiO<sub>2</sub>) from alkali basalt (H90-50, ~48 wt.% SiO<sub>2</sub>) with mass assimilated / mass crystallized ( $M_a/M_c$ ) ratios of (a) 0.3 or (b) 0.4. Model results are plotted on a spider diagram arranged and normalized following Thompson (1982). The model assimilant is average Phanerozoic shale (Condie, 1993). Bulk partition coefficients were calculated using mineral proportions calculated by major-element mass balance modelling (see Table 1, Stage 1) and mineral/melt partition coefficients from Paster et al. (1974), Pearce and Norry (1979), Villemant et al. (1981), and McKenzie and O’Nions (1991).

equation describing bulk  $D(\text{Eu})$  as a function of  $F$  is calculated:

$$D(\text{Eu}) = 0.5266 + 0.8193(F).$$

Greenland (1970) derived an equation for Rayleigh fractional crystallization for a bulk partition coefficient that varies linearly with  $F$ , expressed as  $D=a+bF$ :

$$\ln C_L/C_O = (a-1)\ln F + b(F-1),$$

and this equation is used to model the behavior of Eu.

Model results and calculated bulk partition coefficients are presented in Fig. 8 for representative trace elements (Rb, Sr, Zr, Ba, Ce, Eu, Yb, and Th) plotted

versus Nb. Trace element models predict that the model daughter (PC-01) would be produced after ~75% crystallization of the model parent (BC-04), which is similar to the amount predicted (~70%) by major-element modelling. These results are combined with the results of AFC modelling of the origin of the quartz trachyte from alkali basalt in Fig. 9, a plot of K/Rb versus Rb. It is very probable that fractional crystallization of the observed assemblage (alkali feldspar, clinopyroxene, fayalite, ilmenite, apatite, and zircon) following protracted AFC of alkali basalt is the petrogenetic mechanism responsible for the chemical variation in the Boot Rock and Pine Canyon Rhyolite Members. These model results for the petrogenesis of

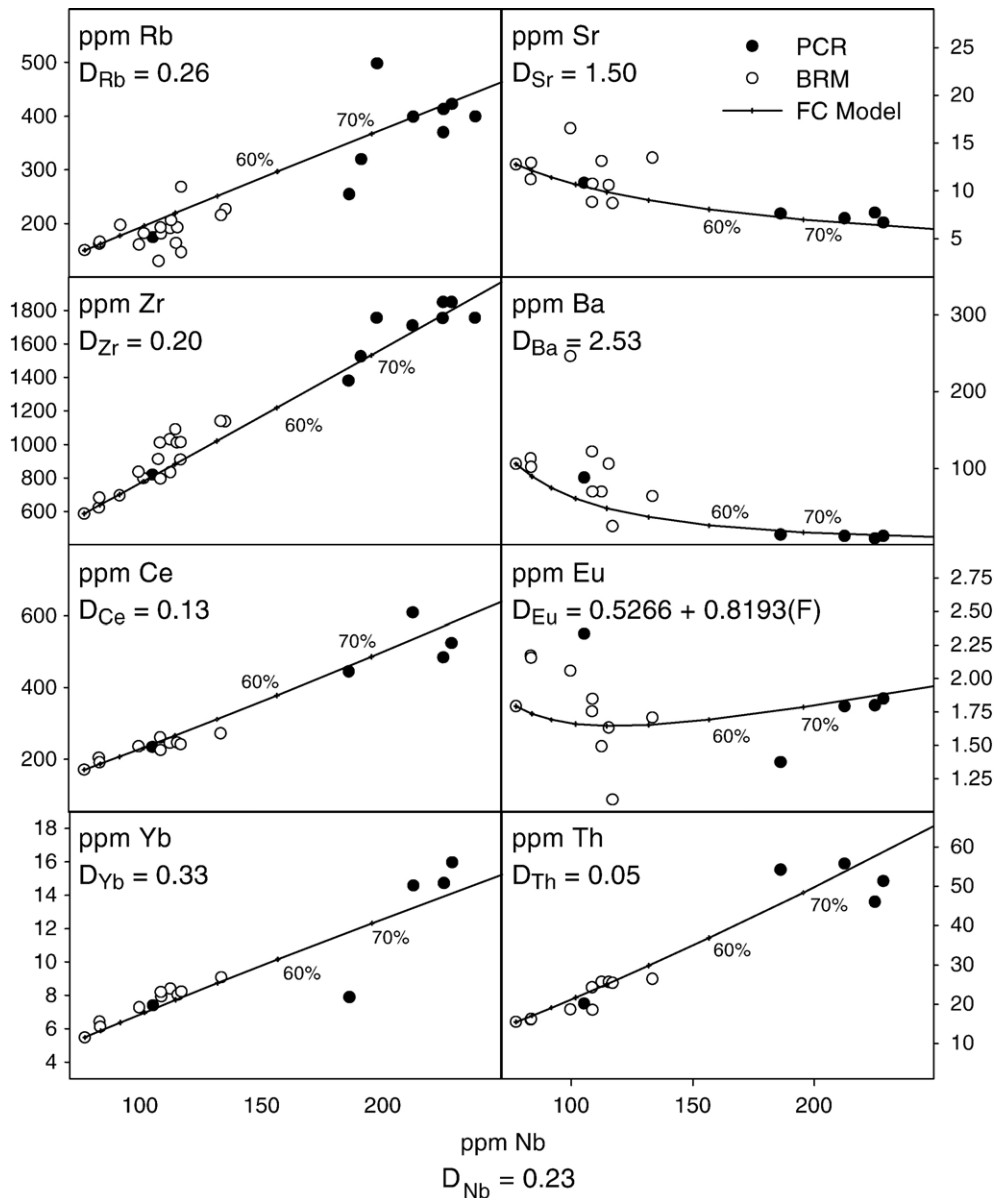


Fig. 8. Results of fractional crystallization (FC) modelling of the origin of rhyolite (PC-01, ~72 wt.% SiO<sub>2</sub>) from quartz trachyte (BC-04, ~64 wt.% SiO<sub>2</sub>) for representative trace elements. Bulk partition coefficients were calculated using mineral proportions calculated by major-element mass balance modelling (Table 1, Stage 2) and mineral/melt partition coefficients from Paster et al. (1974), Pearce and Norry (1979), Fujimaki (1986), Villemant (1988), White (2003), and White et al. (2003). Symbols are the same as in Fig. 3.

the Pine Canyon quartz trachyte–rhyolite suite are similar to those described by Peccerillo et al. (2003) for the peralkaline rocks from the Quaternary Gedemsa volcano in the Central Ethiopian Rift: they showed that trachyte could evolve from basalt following ~70% fractional crystallization plus moderate assimilation, and that peralkaline rhyolite could evolve from trachyte following ~50–60% fractional crystallization with small rates of assimilation.

### 5.3. Origin of high-silica rhyolite by crustal melting, volatile enrichment, and fractional crystallization

There is strong evidence that indicates that the EPR high-silica rhyolite is not related to the BRM and PCR quartz trachyte–rhyolite suite by fractional crystallization processes: (1) PER diagrams suggest that the high-silica rhyolite forms a liquid line of descent distinct from the quartz trachyte–rhyolite suite, (2) high-silica

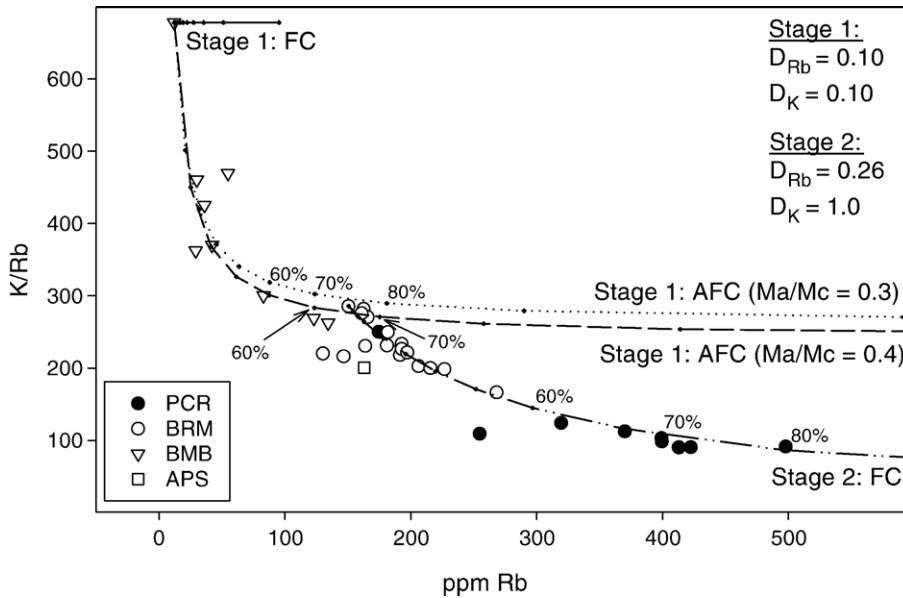


Fig. 9. Plot of K/Rb versus Rb showing the combined results of Stage 1 (AFC) and Stage 2 (FC) modelling. Symbols are the same as in Fig. 3, plus APS, average Phanerozoic shale (Condie, 1993).

rhyolite is depleted in incompatible elements (including Be, Zn, Ga, Rb, Y, Zr, Th, and REE) with respect to quartz trachyte and low-silica rhyolite; and (3) high-silica rhyolite has lower Zr/Hf and Zr/Nb ratios than the quartz trachyte–rhyolite suite. Since quartz trachyte and rhyolite must be excluded as possible parental magmas, models of crustal anatexis for the origin of the Emory Peak suite are evaluated.

BBNP is underlain by Phanerozoic crust accreted during the late Paleozoic Marathon–Oucachita orogeny (James and Henry, 1993). This crust consists primarily of allochthonous, Cambrian to Pennsylvanian clastic sedimentary rocks that have undergone low-grade regional metamorphism, and have been locally modified by middle Tertiary magmatism. Evidence from xenoliths at La Olivina, Chihuahua, México, show that deep crust in this terrane consists of paragneisses, interpreted to represent metamorphic Carboniferous flysch deposits; intermediate- to silicic-orthogneisses, interpreted to represent fragments of accreted Precambrian continental crust; and mafic granulites, interpreted to represent middle Tertiary olivine-rich gabbroic cumulates (Cameron et al., 1992).

It is unlikely that the peralkaline Emory Peak Rhyolite was generated by partial melting of alkali-poor and alumina-rich sedimentary or metasedimentary rocks; therefore, the most likely source rock would be either igneous or metaigneous. Equilibrium batch melting (EBM) is tested first with major element mass balance modelling (Table 2, Stage 3); the model source

rock is a trace-element depleted deep crustal (<25 km) mafic granulite (MN32) adopted from Cameron et al. (1992). Major-element modelling suggests that the most primitive high-silica rhyolite melt (SR-08) can be produced with 4.1% partial melting of mafic granulite with a residual assemblage of approximately 50% plagioclase, 21% clinopyroxene, 12% orthopyroxene, 16% magnetite, and 1% apatite. This model has an acceptable  $\Sigma r^2$  of 0.370.

The EBM hypothesis is further tested with trace-element modelling (e.g., Minster and Allègre, 1978) (Fig. 10). Mineral proportions used to calculate bulk partition coefficients for the mafic granulite were adopted from Cameron et al. (1992): 42% plagioclase, 23% clinopyroxene, 28% orthopyroxene, and 7% Fe–Ti oxide. Mineral/melt partition coefficients were adopted from Schnetzler and Philpotts (1970), Paster et al. (1974), McKenzie and O’Nions (1991), and Sobolev et al. (1996). These results suggest that it may be possible to produce the least silicic sample of EPR (SR-08) with ~5% partial melting of mafic granulite. However, the predicted negative anomaly at Eu is not deep enough; this may be due to either residual plagioclase in the source during melting, a source rock with lower Eu, or a need for larger plagioclase/melt partition coefficients.

Model concentrations of other incompatible elements show an interesting decoupling: for a 5% partial melt of mafic granulite, predicted values for Nb (127 ppm), Y (156 ppm), and Zr (882 ppm) are close to SR-08 (135 ppm Nb, 123 ppm Y, and 829 ppm Zr), but

Table 2  
High-silica rhyolite major-element mass balance models

	Source	Melt						Source	
<i>Stage 3 EBM</i>	MN32	SR-08	Pl	Cpx	En	Mgt	Ap	Calc.	Residuals
SiO <sub>2</sub>	46.60	74.87	54.52	51.81	58.48	0.00	0.00	46.62	-0.02
TiO <sub>2</sub>	3.72	0.22	0.00	1.01	0.00	26.49	0.00	4.25	-0.53
Al <sub>2</sub> O <sub>3</sub>	15.00	12.25	28.26	1.65	0.88	2.31	0.00	14.99	0.01
FeO <sup>T</sup>	13.12	2.99	0.00	9.02	4.73	68.46	0.22	12.92	0.20
MnO	—	—	—	—	—	—	—	—	—
MgO	7.00	0.01	0.00	13.37	34.71	2.74	0.57	6.99	0.01
CaO	11.10	0.29	12.63	21.85	0.50	0.00	55.67	11.12	-0.02
Na <sub>2</sub> O	2.70	4.26	4.41	0.68	0.23	0.00	0.00	2.48	0.22
K <sub>2</sub> O	0.29	5.04	0.18	0.00	0.08	0.00	0.00	0.31	-0.02
P <sub>2</sub> O <sub>5</sub>	0.37	0.02	0.00	0.00	0.00	0.00	43.54	0.34	0.03
		<i>F</i>						100.01	0.370
Results:		0.041	0.484	0.206	0.110	0.152	0.008		= $\sum r^2$
Normalized:			0.504	0.214	0.115	0.158	0.008		
	Parent	Daughter						Parent	
<i>Stage 4 FC</i>	SR-08	EP-01	Kfs	Qtz	Bt	Mgt		Calc.	Residuals
SiO <sub>2</sub>	74.87	78.29	66.07	100.00	35.51	0.17		74.87	0.00
TiO <sub>2</sub>	0.22	0.16	0.00	0.00	3.66	15.27		0.25	-0.03
Al <sub>2</sub> O <sub>3</sub>	12.25	10.60	18.84	0.00	5.55	0.06		12.22	0.04
FeO <sup>T</sup>	2.99	2.53	0.26	0.00	38.40	74.03		2.99	0.01
MnO	0.03	0.03	0.00	0.00	0.54	0.43		0.03	0.00
MgO	0.01	0.01	0.00	0.00	0.02	0.00		0.01	0.00
CaO	0.29	0.07	0.01	0.00	0.13	0.04		0.05	0.24
Na <sub>2</sub> O	4.26	3.87	6.61	0.00	0.12	0.03		4.33	-0.06
K <sub>2</sub> O	5.04	4.42	7.17	0.00	8.61	0.01		5.08	-0.04
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.00	0.00	0.00	0.00		0.01	0.01
		<i>F</i>						99.84	0.067
Results:		0.638	0.281	0.053	0.029	0.003			= $\sum r^2$
Normalized:			0.769	0.146	0.079	0.007			

Analysis MN32 (mafic granulite) adopted from Cameron et al. (1992).

Key to minerals: Pl, plagioclase feldspar; Kfs, alkali feldspar; Ol, olivine; Cpx, clinopyroxene; Mgt, magnetite; En, Enstatite; Bt, biotite; Qtz, quartz; Ap, apatite. Stage 3 mineral analyses adopted from Schucker (1986), Nelson et al. (1987), and Deer et al. (1966); all others are from this report. Other symbols: *F*=liquid fraction;  $\sum r^2$ =sum of squares of residuals.

predicted values for Rb (34 ppm) are much lower than SR-08 (292 ppm Rb). The inconsistency of Rb concentrations with a mineral–melt differentiation model such as EBM may suggest a role for volatile enrichment in the origin of the high-silica rhyolite. Several previous workers have suggested that metal cations may form complexes with specific halogens: Bailey and Macdonald (1975) described strong linear correlations for Cl–Nb–Y and F–Zr–Rb, although others (e.g., Hildreth, 1981) have suggested that Zr complexes with Cl. The presence of high-F biotite and vapor-phase arfvedsonite in the EPR shows this component was present in the magma, and may be responsible for Rb-enrichment of the EPR. If this interpretation is valid, then it is likely that the high-silica rhyolite formed by a small degree (~4–5%) of partial melting of a mafic granulite under the fluxing influence of fluorine. In the Rio Grande rift in southern New

Mexico, young (<10 Ma) hydrothermal deposits closely related to asthenosphere-derived basalts have characteristically high concentrations of fluorine, probably derived from these basalts (Lueth et al., 2005). The origin of alkaline rocks via crustal anatexis was proposed by Bailey (1974), and has also been used to explain the origin of peralkaline magmas in the Kenya rift, including high-silica rhyolite at the Naivasha complex (Macdonald et al., 1987; Davies and Macdonald, 1987) and plateau-type flood phonolites (Hay and Wendlandt, 1995; Hay et al., 1995a,b). Unfortunately, at this time it is not possible to qualitatively test models of volatile enrichment; likewise, experimental evidence for the generation of peralkaline magmas from crustal anatexis is lacking (Scaillet and Macdonald, 2003).

A major-element mass balance model of fractional crystallization for variation within the EPR is presented in Table 2 (Stage 4). Variation within the high-silica

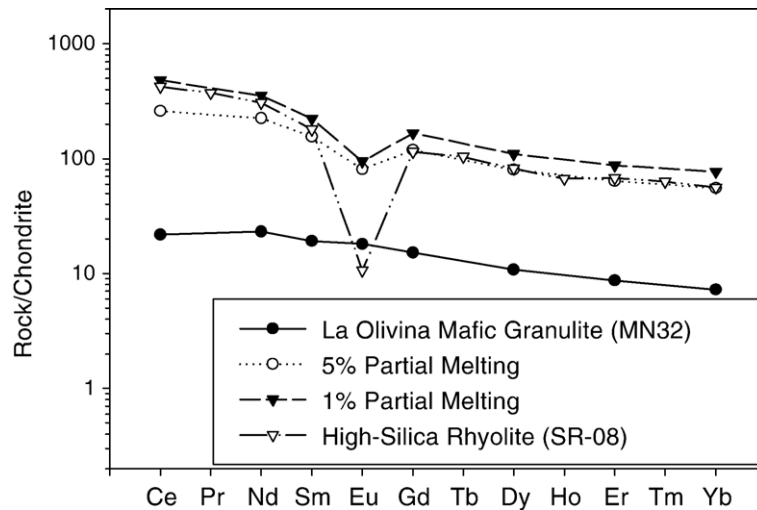


Fig. 10. Results of modal equilibrium batch melting (EBM) modelling of the origin of high-silica rhyolite (SR-08, ~74% SiO<sub>2</sub>) from mafic granulite (MN32, Cameron et al., 1992).

rhyolite suite from 74.8 to 78.3 wt.% SiO<sub>2</sub> (SR-08 to EP-01) can be explained by 36% fractional crystallization ( $F=0.64$ ) of an assemblage dominated by alkali feldspar (77%) and quartz (15%) with subordinate biotite and magnetite; this is consistent with petrography, mineralogy, and PER diagram analysis. The  $\Sigma r^2$  for this model is 0.067. Minor- and trace-element data suggest that, in addition to alkali feldspar and quartz, accessory minerals (monazite and zircon) have a dominant role in differentiation of this suite. From SR-08 to EP-01, P<sub>2</sub>O<sub>5</sub> stays constant (~0.02 wt.%), Ce<sub>N</sub>/Yb<sub>N</sub> falls from 7.5 to 1.0 (see Fig. 6), Th/U drops from 3.2 to 2.3 due to the near-steady state behavior of Th (32 to 28 ppm), and both Zr (828 to 739 ppm) and Hf (25 to 22 ppm) also demonstrate near-steady state behavior. Monazite fractionation is evidenced by petrography and a progressive “flattening” of the REE pattern (Wark and Miller, 1993; Bea et al., 1994). Steady state behavior of P and Th, both of which are essential structural constituents (ESC) of monazite, suggest that the melt was saturated with respect to monazite throughout differentiation; similarly, steady state behavior of Zr and Hf (ESCs for zircon) in the suite suggest that the high-silica rhyolite was saturated with respect to zircon (Evans and Hanson, 1993).

## 6. Tectonic setting

Barker (1977) interpreted the TPMP to be the result of intraplate extension analogous with the Kenya Rift based primarily on petrology (voluminous outcrops of metaluminous to peralkaline quartz trachyte and

rhyolite) and structural setting (normal faulting). Other workers suggested TPMP magmatism prior to 31 Ma was the result of subduction-related, continental arc volcanism instead of intraplate extension, based on the age of normal faults (<24 Ma) in the Trans-Pecos (Henry and Price, 1986); paleostress analysis of orientations of dikes and veins, which were interpreted to suggest a compressional stress regime until 31 Ma (Henry et al., 1991); and the different trace element ratios of basalts erupted before and after 31 Ma (James and Henry, 1991). This interpretation of the tectonic history of the TPMP is also consistent with space-time patterns of continental arc migration in the western USA and México (e.g., Coney and Reynolds, 1977).

However, the onset of magmatism prior to faulting by a few million years does not preclude an extensional origin for the magmas: in the southern Ethiopian segment of the East African Rift system, volcanism preceded faulting by ~20 Ma, and in northern Kenya volcanism began about 33 Ma and faulting began about 25 Ma (Ebinger et al., 2000). It is worth noting that volcanism at Pine Canyon began about 33 Ma while faulting in the Big Bend began between 28 and 23 Ma (Dickerson and Muehlberger, 1994). Additionally, paleostress analysis of dikes and veins does not provide a unique solution; although Henry et al. (1991) interpreted the orientation of maximum principal stress ( $\sigma_1$ ) in pre-31 Ma structures to be east-northeast and thus perpendicular to the late Cretaceous–early Tertiary paleotrench, they note (p. 13, 551) that  $\sigma_1$  could range between east-northeast and vertical, which would be



consistent with north-northwest extension. They also note (p. 13, 552) that there is considerable scatter in the orientation of dikes and veins, which indicates a small difference in magnitude between  $\sigma_1$  and the minimum principal stress ( $\sigma_3$ ) typical of tectonically inactive regions. Thus, it may be valid to characterize pre-31 Ma stresses in the TPMP as near-neutral, which is how Chapin et al. (2004) characterize the regional stress field between 45 and 36 Ma in New Mexico and Colorado. Finally, metasomatism of the mantle by slab-derived fluids during earlier an earlier phase of subduction could result in arc-like trace-element signatures in basalts that are clearly erupted in a continental rift (e.g., the Pliocene Taos Plateau Volcanic Field, northern Rio Grande rift, New Mexico: Dungan et al., 1986).

Structural and petrologic evidence from New Mexico and central Colorado suggest that a weakly compressional, near-neutral stress field persisted from 45 to 36 Ma, and that extension began in the region by 36 Ma (Lawton and McMillan, 1999; McMillan et al., 2000; Chapin et al., 2004; McIntosh and Chapin, 2004). These ages are consistent with plate motion evidence for a decrease in the rate of subduction at 43 Ma, and the onset of transtensional extension related to the formation of the Sierra Madre Occidental in northern México at 36–34 Ma (Ward, 1991). The petrology and petrogenesis of the Pine Canyon caldera is also consistent with development in a neutral or extensional, rather than compressional, stress field: the petrogenetic mechanisms described for the origin of the South Rim Formation are more consistent with those operating in extensional environments, such as the East African Rift system (e.g., Macdonald et al., 1987; Peccerillo et al., 2003), rather than compressional environments (cf. Eichelberger, 1978); these are A-type magmas with major- and trace-element signatures consistent with continental rifting (Martin, 2006-this volume); and ascent of viscous high-silica rhyolite from deep crust would be facilitated in an extensional regime and inhibited in a compressional one.

We suggest that the model for post-collisional and post-orogenic magmatism summarized by Bonin (2004) might be the best to use to describe the tectonic history of the TPMP:

- (1) Collision (“Normal Subducton” phase of Lawton and McMillan, 1999). Flat-slab subduction of the Laramide plate from 100 to 45 Ma resulted in lithosphere stacking and orogenic growth, and was less favorable for magma ascent, as evidenced by a paucity of pre-45 Ma volcanic rocks in Trans-Pecos Texas (Henry and McDowell, 1986) and southern New Mexico (Chapin et al., 2004).
- (2) Post-collision or late orogenic (“Early Slab Retreat” phase of Lawton and McMillan, 1999). A “relaxation” phase followed roll-back or break-off of the subducting slab from 45 to 36–34 Ma, which resulted in asthenospheric upwelling, partial melting of the (slab fluid-metasomatized) lithospheric mantle, partial melting of the crust due to the intrusion of basaltic magmas, and widespread and voluminous volcanism (Bonin et al., 1998). Most of the silicic volcanism in the TPMP, and especially the Davis Mountains volcanic field, occurred between 39 and 36 Ma (Henry and McDowell, 1986; Henry et al., 1994). In the southern Rio Grande rift, New Mexico, this phase is represented by the eruption of the arc-like Rubio Peak Formation (McMillan et al., 2000).
- (3) Post-orogenic (early “Asthenospheric Magmatism” phase of Lawton and McMillan, 1999). This phase, which represents the early stage of continental rifting, is characterized by uplift and an increase in bimodal and peralkaline volcanism, and is the result of delamination of the lithosphere and sinking of the detached lithosphere from 36–34 to ~27 Ma. The stress field shifted from weakly compressional or neutral to extensional and magma sources shifted from more lithospheric to more asthenospheric. The lack of development of normal fault-bounded sedimentary basins during early continental rifting could be due to decoupled behavior between the upper crust and the lower crust and upper mantle: Wilson et al. (2005) have shown that in the Rio Grande rift, extension in the lower crust is distributed over a region four times as wide as the crustal expression of extension. Thus, in the early stage of continental rifting, continental extension may have triggered magmatism in the upper mantle/lower crust long before that extension was manifested at the surface. During the post-orogenic phase, the majority of volcanism in the TPMP is concentrated in the Big Bend area in both alkali-calcic (e.g., the 32 Ma Chinati Mountains caldera) and alkalic volcanic centers (Pine Canyon caldera) (Henry and McDowell, 1986). In the southern Rio Grande rift, this phase is represented by eruption of the bimodal basalt–rhyolite Bell Top Formation (McMillan et al., 2000). In the northern Rio Grande rift (San Juan Mountains, Colorado), lavas and tuffs of the Conejos Formation erupted between 35–33 Ma;

this high-K basalt–andesite–rhyolite suite evolved via fractional crystallization, assimilation, and partial melting processes (Parker et al., 2005). Silicic volcanism ended between 28.5 and 27 Ma in both southern New Mexico (McMillan et al., 2000) and in the TPMP (Leyva Canyon volcano: White and Urbanczyk, 2001), which also marked the end of the post-orogenic phase.

- (4) Relaxation. In the final phase, a clearly extensional, intraplate regime characterized by normal faulting was established, and magma geochemistries reflected a greater influence from the asthenosphere and a smaller influence from the crust. Magmatism in the TPMP from 27 to 16 Ma was primarily mafic, more sporadic, and after 24 Ma was coeval with normal faulting (Henry and McDowell, 1986).

## 7. Summary

Two different petrogenetic mechanisms for generating peralkaline rocks operating nearly simultaneously have been identified as responsible for the origin of the South Rim Formation at the Pine Canyon caldera in Trans-Pecos Texas. Ultimately, both mechanisms begin with the intrusion of mantle-derived alkali basaltic magmas into the crust. Heat from the intrusion of basalt, coupled with metasomatism from a F-rich volatile phase, resulted in partial melting of deep (<25 km) crust mafic granulite. Approximately 5% partial melting of mafic granulite produced peralkaline high-silica rhyolite (Emory Peak Rhyolite Member), which differentiated via fractional crystallization of alkali feldspar, quartz, biotite, magnetite, zircon, and monazite. Alkali basalt evolved via ~70% fractional crystallization coupled with assimilation ( $M_a/M_c \approx 0.4$ ) of shale wall-rock to produce peralkaline quartz trachyte (Boot Rock Member). Closed-system fractional crystallization (~70–75%) of the Boot Rock Member quartz trachyte at low  $fO_2$  produced the more strongly peralkaline (A.I. = 1.21) rhyolite (Pine Canyon Rhyolite Member). The eruption of ash-flow tuffs of the Pine Canyon Rhyolite Member produced the Pine Canyon caldera (Ogley, 1978; Barker et al., 1986). Lavas and tuffs of the Boot Rock Member erupted shortly thereafter from vents both along the margin of the caldera and outside of the caldera (Urbanczyk and White, 2000). The final eruptive event is represented by rheomorphic ash-flow tuffs of the Emory Peak Rhyolite Member from vents both along the margin of the caldera and from an extensive ring dike outside of the caldera (Barker et al., 1986). The geochemical

characteristics and petrogenetic mechanisms responsible for the development of the peralkaline magmas of the South Rim Formation are most consistent with those operating in continental rift environments. On the basis of these results coupled with petrologic, structural, and geophysical results from other workers in the region, these peralkaline rocks are interpreted to represent the earliest evidence for continental extension in the TPMP.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.lithos.2006.03.015](https://doi.org/10.1016/j.lithos.2006.03.015).

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