

Rare-metal enriched peraluminous rhyolites in a continental arc, Sierra Blanca area, Trans-Pecos Texas; Chemical modification by vapor-phase crystallization

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ABSTRACT

Peraluminous rhyolites that are chemically somewhat similar to topaz rhyolites and anorogenic granites occur in an orogenic setting near Sierra Blanca in the Tertiary Trans-Pecos magmatic province. The Sierra Blanca rhyolites are even more enriched in most incompatible trace elements than are topaz rhyolites. Some of the extreme enrichments may in part be the result of chemical modification by crystallization from an F-rich vapor phase.

The rhyolites were intruded as laccoliths at 36 Ma, during the main phase of Trans-Pecos igneous activity, which is characterized by ash-flow eruptions from numerous calderas and widespread mafic, intermediate, and silicic intrusions. A dominant east-northeast orientation of dikes and veins throughout the region indicates mild compression that was residual from Laramide deformation. This compressive tectonic setting, coupled with concurrent volcanism in Mexico and the east-northeast change in magma chemistry from calc-alkalic in western Mexico through alkali-calcic to alkalic in Texas, suggests that the rhyolites were emplaced in a continental arc. Extension did not begin in Trans-Pecos Texas until after 32 Ma; 31- to 17-Ma dikes are dominantly oriented north-northwest, perpendicular to the direction of extension during early Basin and Range deformation. Thus, the tectonic setting of the Sierra Blanca rhyolites contrasts with that of typical topaz rhyolites, most of which were emplaced during periods of crustal extension.

The Sierra Blanca rhyolites are chemical and mineralogic oddities for the region, where most rhyolites are peralkaline or metaluminous. The rhyolites are depleted in the same elements as topaz rhyolites (Mg, Ca, Ti, Sr, Ba) but are more highly evolved than topaz rhyolites. Extreme trace-element enrichments (Li, F, Zn, Rb, Y, Zr, Nb, Sn, Ta, Pb, HREE, Th, U) are accommodated in Li-rich white mica, Zn-rich biotite, Rb-rich feldspars, and numerous trace minerals, including cassiterite, changbaiite, columbite, thorite, xenotime, yttrium- and REE-rich fluorides, and zircon. The rhyolites are large-tonnage, low-grade resources of several rare metals. Also enriched in Be (as much as 180 ppm), the rhyolites are the sources of Be and F in beryllium deposits in fluoritized

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limestones along the contacts with the laccoliths. Interaction with the limestones probably locally elevated the Ca, Mg, and Sr contents of the rhyolites.

Vapor-phase crystallization has modified the original magmatic chemistry of the rocks. Evidence of vapor-phase crystallization includes the presence of minerals typical of pegmatites: cryolite (from 0 to 3 volume percent), alkali feldspars with nearly end-member compositions, polyolithionite-zinnwaldite mica, and rutilated quartz, plus fluid inclusions defining quartz overgrowths on magmatic grains. Extreme HREE enrichments (Yb to 72 ppm; chondrite-normalized REE patterns with positive slopes) may also be the result of vapor-phase crystallization.

INTRODUCTION

The intrusions at Sierra Blanca Peaks in the Trans-Pecos magmatic province of far western Texas (Fig. 1) are highly evolved rhyolites with chemical and mineralogic characteristics that are unusual not only for the province but also for the world. They are also the source of fluorine and beryllium in high-grade beryllium deposits in fluoritized limestones along the contacts with the rhyolites. These shallow rhyolite laccoliths have certain chemical similarities to topaz rhyolites and anorogenic granites but are more extremely enriched in many incompatible elements and are markedly depleted in many compatible elements.

The Sierra Blanca rhyolites are anomalous for the Trans-Pecos magmatic province in that they are peraluminous; that is, they contain two micas (biotite and a lithium-rich trioctahedral mica) and are generally corundum normative (Barker, 1980; Rubin and others, 1987). Other rhyolites in the region tend to be metaluminous or peralkaline. Peralkaline rhyolites occur most commonly in the eastern alkalic belt of the Trans-Pecos magmatic province (Fig. 1), but also in the western alkali-calcic belt, in which the Sierra Blanca peraluminous rhyolites are located.

This work expands on our earlier work on the Sierra Blanca intrusions (Rubin and others, 1987) by providing detailed chemical and mineralogic data on a more representative sampling of unweathered rocks from the Round Top laccolith (Fig. 2). Samples were collected from diamond drill core, rotary drill cuttings, and bulldozer cuts. Our earlier conclusion, that the original magmatic compositions of the rocks were modified by vapor-phase crystallization, still stands (Rubin and others, 1987). The link between magmatic and vapor-phase conditions must, however, have been intimate because the chemical composition of the Round Top intrusion is surprisingly homogeneous.

TECTONIC SETTING

The tectonic setting during emplacement of the Sierra Blanca rhyolites contrasts with that for topaz rhyolites. Whereas most topaz rhyolites were emplaced during periods of crustal extension (Christiansen and others, 1986), the Sierra Blanca rhyolites are contemporaneous with regional subduction-related magmatism in a mildly compressive tectonic setting (Price and Henry, 1984; Price and others, 1986, 1987).

The Cenozoic tectonic history of the Trans-Pecos region is highlighted by three main episodes (Price and others, 1986,

1987): (1) Laramide thrusting and folding, (2) voluminous magmatism caused by subduction, and (3) Basin and Range crustal extension.

Laramide compression in Texas began in the Late Cretaceous, peaked in the late Paleocene, and essentially ended in the early Eocene (Wilson, 1971). Apparently no igneous activity was associated with Laramide folding and thrusting in Trans-Pecos Texas. Laramide deformation is most intense in Chihuahua and dies out to the east and northeast. The dominantly NNW-trending folds and thrusts developed in response to east-northeast compression. The Sierra Blanca intrusions lie near the frontal thrust of the Chihuahua tectonic belt (Fig. 1). Cretaceous sedimentary rocks beneath Sierra Blanca are thrust, and tilted Cretaceous rocks occur below the floors of the other four laccoliths. Cretaceous rocks a few kilometers to the north are horizontal or only gently tilted.

Widespread magmatism occurred during middle Eocene to early Oligocene time from approximately 48 to 32 Ma (Henry and McDowell, 1986). The region was under a state of weak compression that was probably residual from Laramide stress (Price and Henry, 1984; Price and others, 1987). The regional dominance of ENE-striking dikes and veins during this time indicates a direction of maximum principal compressive stress parallel to that during Laramide deformation.

Igneous rocks of this episode can be divided into a western alkali-calcic belt and an eastern alkalic belt (Barker, 1977; Henry and Price, 1984). The Sierra Blanca intrusions lie within the alkali-calcic belt. The Trans-Pecos rocks were the most inland expression of subduction-related volcanism. Igneous activity spread eastward from near the present Pacific coast about 100 Ma to Trans-Pecos Texas about 40 Ma, and then about 30 Ma either swept back to the coast or flared up nearly simultaneously across almost all of western Mexico (Coney and Reynolds, 1977; Keith, 1978; Damon and others, 1981; Henry and McDowell, 1982). There is an apparent gradation from Laramide-age calc-alkaline rocks in Mexico eastward into middle Tertiary alkaline rocks in Texas. The eastward sweep of magmatism from western Mexico inland to Texas was probably the result of progressive shallowing of the subducting slab with time.

The compressive tectonic setting during Trans-Pecos magmatism, the coincidence with volcanism in Mexico, and the progressive east-northeastward change from calc-alkalic to alkali-

calcic to alkalic magma chemistry indicate that the 48- to 32-Ma igneous rocks were emplaced in a continental arc. Subduction-related magmatism during this time can be divided into two phases (Henry and McDowell, 1986). In the Trans-Pecos region an early phase of magmatism (48 to 38 Ma) consisted of abundant, small, mafic to silicic intrusions and mafic lava flows plus two small calderas (Henry and others, 1989). The main phase (38 to 32 Ma) included voluminous volcanic rocks erupted from calderas (Henry and Price, 1984) and numerous mafic, intermediate, and silicic intrusions.

Basin and Range extension, which began with region-wide normal faulting about 24 Ma and continues today, was preceded by a shift in stress orientations about 31 Ma (Henry and Price, 1986). This extension and related, volumetrically minor volcanism postdate intrusion of the Sierra Blanca laccoliths.

The Sierra Blanca laccoliths and the intrusive and extrusive rocks of the Quitman Mountains caldera to the south (Fig. 2) were emplaced about 36 Ma during the main phase of Trans-Pecos magmatism (Henry and others, 1986). Whereas several samples of biotite from the Quitman Mountains have been dated

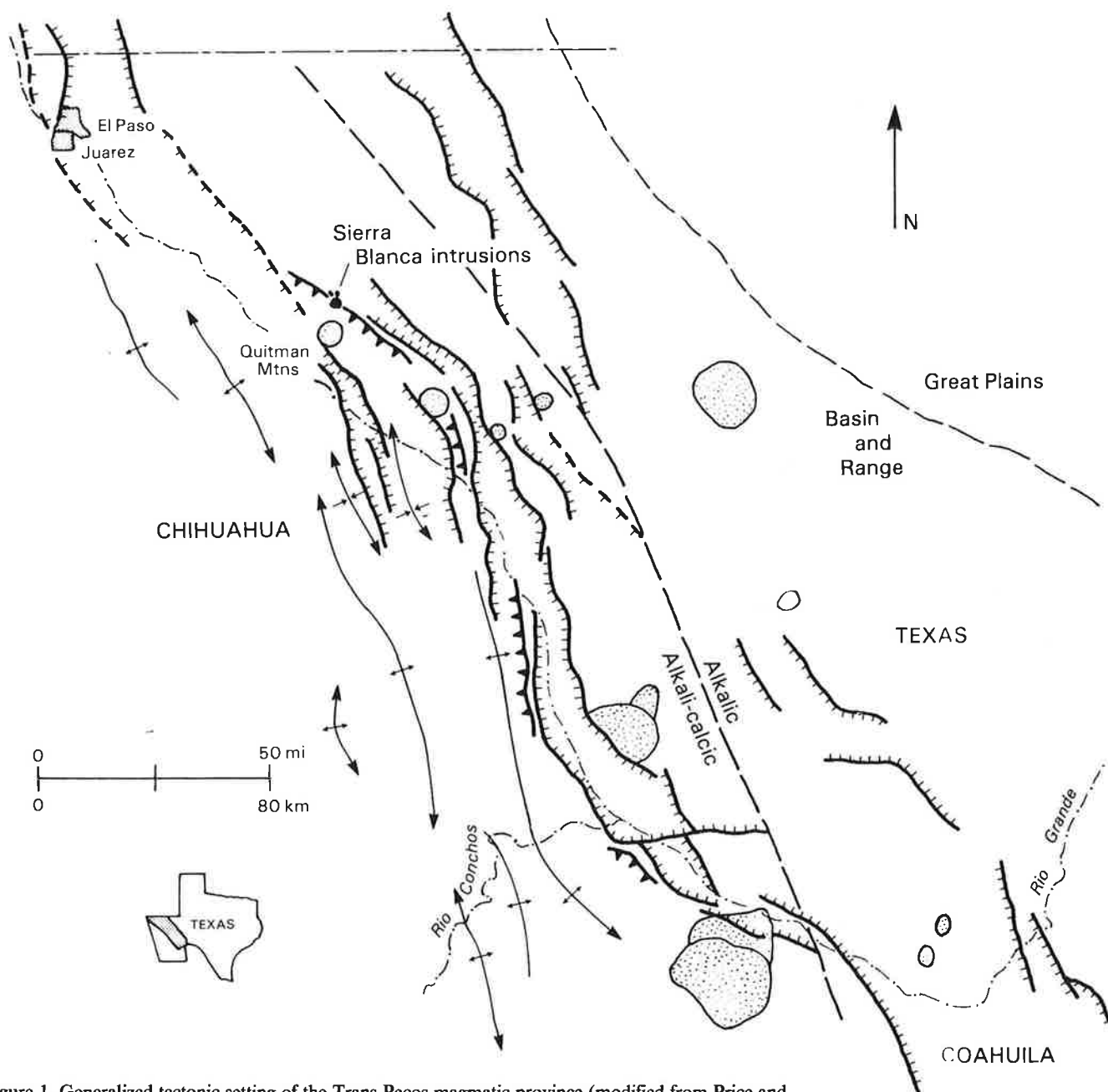


Figure 1. Generalized tectonic setting of the Trans-Pecos magmatic province (modified from Price and others, 1986). Fold and thrust symbols indicate structures of the Laramide Chihuahua tectonic belt. Normal fault symbols are major Basin and Range faults. Dashed line separates belts of middle Tertiary igneous rocks: alkali-calcic to west and alkalic to east (Barker, 1977; Henry and Price, 1984).

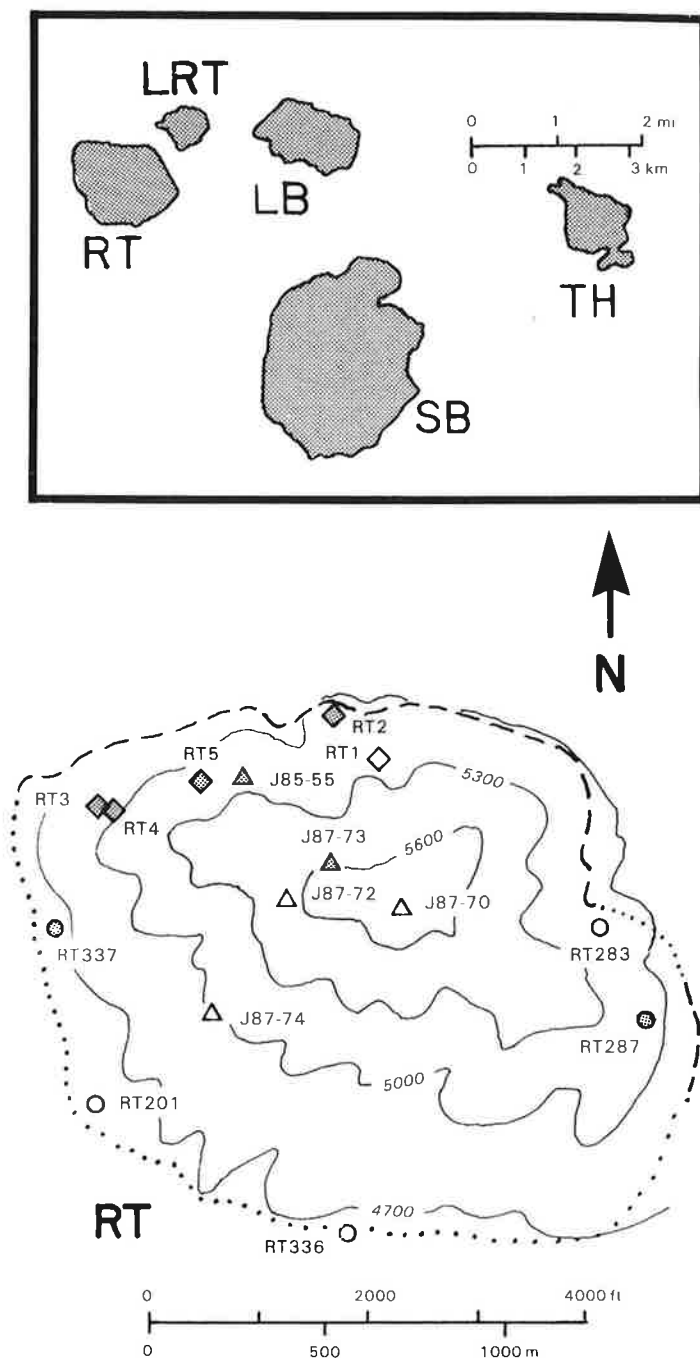


Figure 2. Map showing locations of samples collected from the Round Top intrusion. Diamonds = diamond drill core; circles = rotary cuttings; triangles = outcrop and bulldozer cuts. Filled symbols indicate the presence of optically identifiable cryolite grains. Topographic contours are indicated in feet. Heavy dashed line = contact between rhyolite laccolith and Cretaceous sedimentary rocks; dotted line = contact between rhyolite and Quaternary colluvium. SB = Sierra Blanca; RT = Round Top; LRT = Little Round Top; LB = Little Blanca; TH = Triple Hill. Modified from Rubin and others (1987).

(Henry and others, 1986), the Sierra Blanca laccoliths are represented by only one K-Ar date on an annite-rich biotite. Because the diffusion coefficient of argon in biotite increases with increasing iron content (Harrison and others, 1985), it is possible that the Sierra Blanca rhyolites are older than 36 Ma. However, they are not as old as distinctive titaniferous hornblende porphyry dikes, sills, and small plugs in the Finlay Mountains and in the Sierra Blanca area, which are about 48 m.y. old (K-Ar dates on hornblendes) and predate the main phase of magmatism (Henry and others, 1986). Unambiguous contact relations at Round Top show that the rhyolite intruded and altered a hornblende porphyry sill within the Cretaceous country rock.

Sedimentary cover is eroded from the top of the Sierra Blanca laccoliths. Whereas no evidence is preserved to indicate that the intrusions broke through the surface, they were clearly shallow. Stratigraphic reconstructions (cumulative thickness of strata above the horizon at which the laccoliths were intruded) suggest less than 1,000 m of cover at the time of intrusion (Albritton and Smith, 1965), although outflow-facies volcanic rocks from the Quitman Mountains or other calderas could have added somewhat to this figure. Shallow intrusion is also indicated by the ubiquitous fine grain size and the presence of vesicles, found locally on the upper surface of the Round Top laccolith.

Feeders for the Sierra Blanca laccoliths have not been found by surface mapping or by drilling for fluorite and beryllium deposits (McAnulty, 1980). The slight topographic elongation of Round Top (Fig. 2) may be an expression of a northwest-striking feeder dike. This orientation would be an exception to most middle Tertiary dikes in the Trans-Pecos region, which strike east-northeast. However, northwest-trending structures in the region have been repeatedly activated since Precambrian time (Albritton and Smith, 1957; Muehlberger, 1980). Parallel structures in the Sierra Blanca area include Laramide thrusts and Basin and Range faults.

The Sierra Blanca rhyolites geographically fall within the broad belt of chemically similar topaz rhyolites occupying the interior portion of the western Cordillera in the United States and Mexico (Christiansen and others, 1983). Melting of old continental crust, evidence of which is found only in this interior region, appears to be crucial to the origin of topaz rhyolites (Christiansen and others, 1986). Most, but not all, topaz rhyolites were emplaced in an extensional tectonic setting after 30 Ma (Christiansen and others, 1986). A back-arc setting is typical of topaz rhyolites older than 30 Ma (D. M. Burt, written communication, 1988). In contrast to most topaz rhyolites, the Sierra Blanca laccoliths were emplaced in a compressive, subduction-related tectonic setting at least 36 Ma. Whether their origin requires the melting of continental crust is uncertain.

CHEMICAL AND MINERALOGIC ODDITIES

Several investigators have recognized that the Sierra Blanca rhyolites are chemically anomalous (Barker, 1980; Shannon, 1986; Shannon and Goodell, 1983, 1986; Matthews and Adams,

1986; Rubin and others, 1987). The Round Top cryolite rhyolite, described by Rubin and others (1987), is certainly mineralogically atypical as well. There are, however, many similarities between the Sierra Blanca rhyolites and both topaz rhyolites and peraluminous, anorogenic granites.

The Sierra Blanca rhyolites are anomalous in major- and trace-element contents. Although numerous analyses of these rocks have been reported (Barker, 1980; Shannon, 1986; Shannon and Goodell, 1986; Matthews and Adams, 1986; Rubin and others, 1987), reliable comparisons between data sets are difficult to make because of uncertainty concerning the extent of alteration or weathering of samples employed in previous studies and because of analytical biases. With the exception of one sample reported by Rubin and others (1987), all previous studies involved outcrop samples that may have been substantially weathered. In Tables 1 and 2 we report analyses of 13 unweathered "fresh" samples, which are gray and contain relatively abundant magnetite and little hematite. As is demonstrated below, the "fresh" samples are all to some extent chemically disturbed from their original magmatic composition by magmatic vapor-phase crystallization and, for at least 7 samples, by minor contamination from country rocks.

In addition to the "fresh" samples, we report analyses of two outcrop samples (J87-70 and -74 in Tables 1 and 2) that have been exposed to weathering for probably thousands of years. The weathered samples contain more hematite and less magnetite, and they lack cryolite as discrete grains. We also report analyses of standard reference materials that were co-analyzed with the study samples (Table 3).

Major minerals and vapor-phase crystallization

The samples from the Round Top laccolith are composed dominantly of K-feldspar, plagioclase, and quartz; micas and iron oxides are minor phases. Closer inspection reveals minerals characteristic of granitic pegmatites: nearly end-member albite and microcline, rutilated quartz, polyolithionite-zinnwaldite mica, and cryolite (Rubin and others, 1987). Another feature suggestive of a pegmatitic fluid is ubiquitous fluid inclusions defining overgrowths on magmatic quartz grains. Alternating centimeter-scale dark and light gray bands, similar to liesegang rings, and centimeter-scale amoeba-shaped patches of dark and light gray rhyolite in some "fresh" samples probably indicate penetration of the rock by a pegmatitic or hydrothermal fluid. The dark bands and patches contain slightly more magnetite than the light bands.

Application of the two-feldspar geothermometer of Price (1985) to the most potassic albite ($\text{Ab}_{92}\text{Or}_{08}$) and the most sodic K-feldspar ($\text{Ab}_{67}\text{Or}_{33}$) analyzed by Rubin and others (1987) from the Round Top laccolith yields temperatures of approximately 560°C at low pressures (less than 1 kbar). This temperature may have been above the solidus for these F-rich magmas; Webster and others (1987) indicated solidus temperatures less than 525°C for F-rich vitrophyre of somewhat similar composition (topaz rhyolite) from Spor Mountain, Utah. Thus, some of

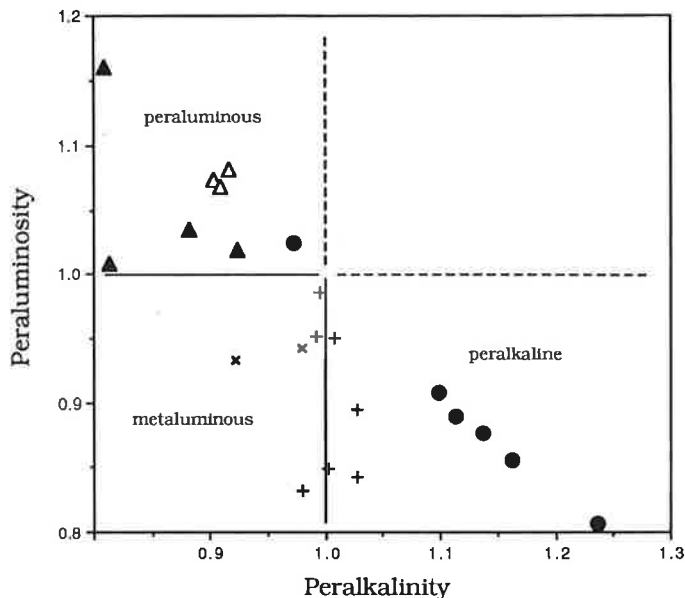


Figure 3. Peraluminosity vs. peralkalinity in samples of the Sierra Blanca laccoliths. Peraluminosity, molar $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, is a measure of Al content relative to what would be accommodated by feldspars. Peralkalinity, molar $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$, is a measure of the Na and K content relative to what would be accommodated by alkali feldspars. Some Round Top samples appear to be peralkaline due to their high cryolite contents. Samples with little or no cryolite are peraluminous or metaluminous. Round Top samples: ● = gray, relatively unaltered, low Sr; ○ = gray, high Sr; x = weathered. Samples of other laccoliths: Δ = unweathered Little Round Top and Little Blanca; ▲ = unweathered Sierra Blanca and Triple Hill.

the Round Top feldspar compositions appear to be magmatic, consistent with porphyritic textures, which indicate original magmatic crystallization. These magmatic feldspars contain almost no Ca and suggest that the magmas themselves were very low in Ca. Other alkali feldspars analyzed by Rubin and others (1987) have nearly end-member compositions and most likely formed below the solidus.

Cryolite occurs as both discrete grains intergrown with groundmass quartz (nearly 3 vol % groundmass cryolite in some samples) and as inclusions in overgrowths on quartz phenocrysts. Rutilated quartz is commonly intergrown with cryolite (see Fig. 4 of Rubin and others, 1987). A third, much less common mode of cryolite (clear, cubiform, striated crystals as much as 2 mm wide as fracture coatings and locally cementing broken fragments of rhyolite along the fracture surfaces) indicates that some, if not all, cryolite formed at subsolidus temperatures.

Samples containing relatively abundant cryolite also have anomalously high amounts of Na (first five samples in Table 2) and appear to be peralkaline (Fig. 3). However, the "fresh" rhyolite sample with lowest F content (RT1-230.5 in Table 2) and the other Sierra Blanca laccoliths are peraluminous (Fig. 3). Relative to other rhyolites of the Trans-Pecos magmatic province, the Sierra Blanca rhyolites are unusually peraluminous. The high Na

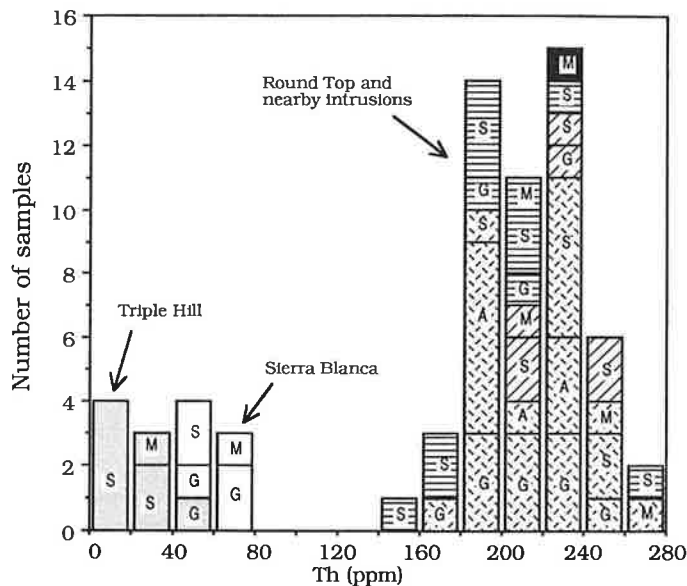


Figure 4. Histogram of Th concentrations in Sierra Blanca intrusions. Stippled pattern = Triple Hill; blank = Sierra Blanca; horizontal = Little Blanca; thatch = Round Top; black = Four Hills, a small outcrop 2 km north of Round Top; diagonal = Little Round Top; G = gray, relatively unaltered samples with both low and high Sr (this study, analyses by ICP-MS, see Tables 1 and 2); A = weathered and hydrothermally altered samples (this study, ICP-MS); S = analyses reported by Shannon (1986, INAA); M = analyses reported by Matthews and Adams (1986, XRF).

content and presence of cryolite, rather than topaz, in the Round Top rhyolite, suggests that they are akin to the more typically peralkaline rhyolites of the province. In fact, cryolite, with a molar Na:Al ratio of 3:1, can be considered a peralkaline mineral, and several high Na, high F Round Top samples are peralkaline (Fig. 3).

Compatible elements

Relative to typical rhyolites and to topaz rhyolites (Christiansen and others, 1984, 1986), most compatible elements in unaltered rhyolite samples from the Round Top laccolith are depleted (Table 4). The elements Mg, P, Ca, Ti, V, Sr, and Ba are especially low (Table 2). Some samples, however, have considerably higher contents of Mg, Ca, and Sr, which we attribute to interaction between the Cretaceous limestone country rock and the rhyolites. Although we only report analyses of relatively fresh samples in Tables 1 and 2, we have also analyzed other rhyolite samples with varying degrees of hydrothermal alteration. Alteration occurs chiefly near the contacts between the rhyolite and sedimentary country rock, the Cretaceous Buda Limestone and underlying Del Rio Shale. Intense bleaching (apparent total destruction of mafic minerals, yielding a pale cream color) commonly occurs closest to the contact; hematitic alteration (with destruction of magnetite, yielding a pink color) commonly occurs farther into the laccolith (W. T. Miller, personal commu-

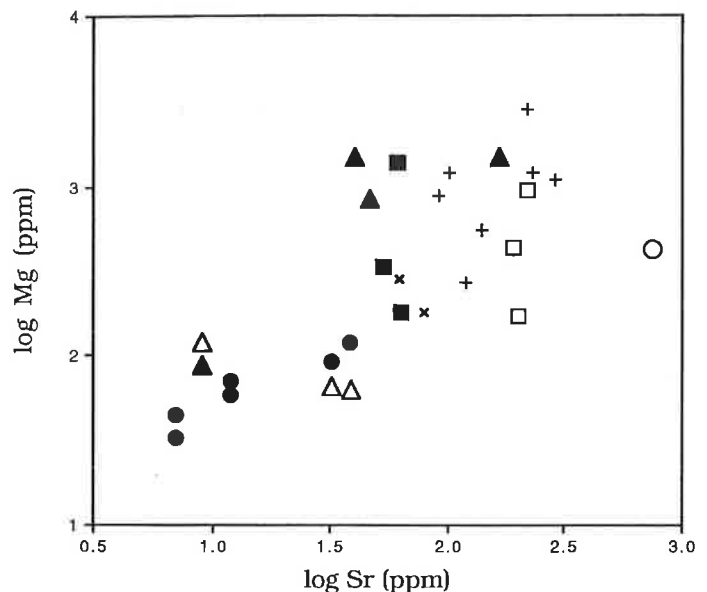


Figure 5. Plot of Mg vs. Sr for unaltered and altered rhyolite samples. Round Top samples: ● = gray, relatively unaltered, low Sr; + = gray, high Sr; x = weathered; altered samples (unreported data, ■ = hematitic; □ = bleached; ○ = fluoritized). Samples of other laccoliths: Δ = unweathered Little Round Top and Little Blanca; ▲ = unweathered Sierra Blanca and Triple Hill.

nication, 1987). Although these alterations do not have marked effects on some elemental concentrations, such as Th (Fig. 4), they do cause increases in Mg, Ca, and Sr (Fig. 5). Fluoritized rhyolite, sampled from the contact with the Del Rio Shale, also has elevated values of Mg, Ca, and Sr (Fig. 5).

Presumably the source of Mg, Ca, and Sr in these altered intrusive rocks near the contacts with Cretaceous limestone was the calcareous rock itself. We therefore suspect that the seven apparently unaltered, gray rhyolite samples with relatively high Mg, Ca, and Sr (the plus signs in Fig. 5) owe at least part of their composition to interaction with the limestones. Because the rhyolites apparently were neither hot enough to melt nor hydrous enough to dissolve the carbonate country rock, this interaction was not traditional assimilation. Reaction with ground waters in the carbonate country rock was probably sufficient to introduce the necessary small amounts of Mg, Ca, and Sr.

Four of the seven high-Sr samples were collected from locations within the laccolith that would have been near the limestone country rock at the time of intrusion. The morphology of Round Top suggests that postintrusion erosion has not significantly affected the rhyolite body. Therefore, at the time of cooling three samples (J87-73 and -72 from outcrop, plus RT2-34 from a shallow drillhole; Tables 1 and 2) may have been close to the upper surface of the laccolith before subsequent erosion stripped away the sedimentary cover. Sample RT283-182.5 was collected less than a meter above the floor of the laccolith. The other three

TABLE 1. MINERALOGIC VARIABILITY IN RHYOLITE SAMPLES*

Sample†	Cy	Rt	Xe	Yc	Yf	X	Y	Z	Bf	Cf	Ur	Ks	Tm	Ep	Fu	Fl	Zu	Ka	Ba	Cr
RT4-96	x	-	x	x	x	-	-	-	-	-	-	-	-	x	-	-	-	-	-	-
RT3-130	x	-	x	-	x	-	-	-	-	-	-	x	-	-	-	-	-	-	-	-
RT337-310	x	-	x	x	x	x	-	-	-	-	-	-	-	-	-	-	-	-	-	-
J85-55	x	x	x	x	x	x	-	-	-	x	-	-	-	-	-	-	-	-	-	-
RT287-200	x	-	-	-	x	x	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RT1-230.5	-	-	-	x	x	-	-	-	-	-	-	-	-	-	-	-	x	-	-	-
J87-73	x	x	-	x	x	x	-	-	-	x	-	-	x	-	-	-	-	-	-	-
J87-72	-	x	-	x	x	-	-	x	-	-	x	-	-	-	-	x	x	x	-	-
RT336-200	-	-	-	x	x	x	-	-	x	-	-	-	-	-	-	-	x	-	-	-
RT283-182.5	-	-	-	x	x	x	-	-	-	-	-	-	-	-	-	-	-	x	-	-
RT5-169	x	-	-	-	x	x	-	-	-	-	-	x	x	-	-	-	x	-	-	-
RT2-34	x	-	-	x	x	-	-	-	-	-	-	-	x	-	x	-	-	-	-	-
RT201-355	-	-	-	x	x	-	-	-	-	-	-	-	x	-	-	-	-	-	-	-
J87-70	-	-	-	x	x	x	x	-	-	-	-	-	-	-	-	-	-	-	x	x
J87-74	-	-	-	-	-	x	-	-	-	-	-	-	-	-	-	-	x	-	x	-

Note: Abbreviations: x = present; - = absent; Ba = barite, BaSO_4 ; Bf = betafite, $(\text{Ca}, \text{Na}, \text{U})_2(\text{Nb}, \text{Ti}, \text{Ta})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$; Cf = coffinite, $\text{U}(\text{SiO}_4)_2 \cdot x(\text{OH})_4$; Cr = cerussite, PbCO_3 ; Cy = cryolite as discrete grains; Ep = elpasolite, K_2NaAlF_6 ; Fl = fluorite, CaF_2 ; Fu = fluellite, $\text{AlF}_3 \cdot 4\text{H}_2\text{O}$; Ka = kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; Ks = kasolite(?), $\text{Pb}(\text{UO}_2) \cdot \text{H}_2\text{O}$; Rt = Nb-rich rutile as needles in quartz; Tm = thomsenolite, $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$, with variable Mg; Ur = uraninite, UO_2 ; Xe = xenotime, $(\text{Y}, \text{HREE})(\text{PO}_4)$; Yc = yttrocerite, $(\text{Y}, \text{HREE}, \text{LREE}, \text{Ca})\text{F}_{3-x}$; Yf = yttriofluorite, $(\text{Y}, \text{HREE}, \text{Ca})\text{F}_{3-x}$; Zu = zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH}, \text{F})_{18}\text{Cl}$; X = Ca-Th-Pb-REE fluoride(?); Y = Ca-Th phosphate-silicate; Z = Pb-rich Mn oxide.

*All samples contain albitic plagioclase, K-feldspar, quartz, Zn-, Mn-, Fe-rich biotite, trioctahedral Li-rich mica, magnetite, hematite (as an alteration product of magnetite), cryolite (Na_3AlF_6 , as inclusions in quartz, but not necessarily as discrete grains), cassiterite (SnO_2), cerfluorite (Ce, LREE, CaF_{3-x}) and/or bastnaesite (CeCO_3F), changbaiite (PbNb_2O_6), columbite (FeNb_2O_6), thorite (ThSiO_4), and zircon (ZrSiO_4).

†Samples are grouped into three categories (see also Table 2):

- (1) Gray, relatively unaltered, containing low Sr: RT4-96, RT3-130, and RT1-230.5 from diamond drill core; RT337-310 and RT287-200 from rotary cuttings; J85-55 from bulldozer cut.
- (2) Gray, apparently unaltered, containing high Sr: RT5-169 and RT2-34 from core; RT336-200, RT283-182.5, and RT201-355 from cuttings; J87-73 and J87-72 from bulldozer cut.
- (3) Pink, weathered, from outcrop.

high-Sr samples were collected well within the rhyolite mass, such that no direct relation to the contact is evident. Ground waters carrying Ca, Sr, and Mg may have penetrated the intrusion along fractures, such as along northwest-striking fractures that were prospected for fluorite along the southwest flank of Round Top (McAnulty, 1980).

The samples with lower Ca, Sr, and Mg content therefore appear to be closer to the magmatic composition than those with higher Ca, Sr, and Mg. An alternative but less likely explanation for the extremely low Ca, Sr, and Mg in some samples (see Table 2 and the black circles in Fig. 5) is hydrothermal alteration involving the introduction of cryolite and leaching of Ca and Sr from feldspars and Mg from biotite. All 13 "fresh" rhyolite samples (with both low and high Sr) contain largely unaltered feldspars and micas (only small amounts of kaolinite were found, Table 1), but these minerals have unusual chemical compositions

that are probably the result of subsolidus alteration or vapor-phase crystallization. In a well-characterized sample of the Round Top intrusion, alkali feldspars have nearly end-member compositions, and micas include a Mg-poor biotite and a Li-rich trioctahedral white mica (Rubin and others, 1987).

Five of the six relatively unaltered, low-Sr samples from Round Top contain abundant groundmass cryolite, indicative of substantial late-stage crystallization (Table 1). As expected, these five samples (the first five in Table 2) also contain relatively high Na and F. The sixth low-Sr sample (RT1-230.5) is, however, lower in Na and F, contains no groundmass cryolite, and is perhaps more representative of magmatic conditions than the cryolite-rich samples. We suggest that late-stage crystallization, possibly from a vapor phase, has modified the chemical composition of many of the rhyolite samples, notably by increasing Na and F. The fact that several of the gray, relatively unaltered

TABLE 2. CHEMICAL ANALYSES OF MAJOR AND TRACE ELEMENTS IN THE ROUND TOP LACCOLITH

	Gray, unaltered, low Sr				
	RT4-96	RT3-130	RT337-310	J85-55	RT287-200
(wt.%)					
SiO ₂	70.48	70.50	70.56	72.47	72.53
TiO ₂	0.02	0.02	0.03	0.02	0.03
Al ₂ O ₃	13.43	13.73	13.52	13.68	13.49
FeO (total)	2.97	2.91	2.95	1.34	2.57
MnO	0.08	0.08	0.08	0.08	0.08
MgO	0.01	0.01	0.04	0.01	0.01
CaO	0.02	0.03	0.06	0.08	0.02
Na ₂ O	7.42	6.72	6.89	6.48	6.29
K ₂ O	4.07	4.20	4.04	4.22	4.12
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	<0.01
CO ₂	<0.04	<0.04	<0.04	0.00	<0.04
H ₂ O ⁺	0.20	0.12	0.25	0.13	0.14
F	1.68	1.69	1.97	1.94	1.38
-O for F	-0.71	-0.71	-0.83	-0.82	-0.58
Total	99.72	99.35	99.61	99.64	100.13
(ppm)					
Li	480	470	520	460	500
Be	58	31	45	180	14
V	7	6	<5	<5	<5
Ni	32	29	42	<5	21
Cu	68	51	89	13	45
Zn	590	580	630	610	620
Rb	1700	2000	1600	2000	2000
Sr	14	12	40	32	7
Y	200	200	240	200	230
Zr	1000	1100	1200	1000	1100
Nb	350	400	420	340	410
Mo	3	4	2	2	<1
Cs	62	75	53	83	51
Ba	8	8	6	5	12
La	20	21	25	22	21
Ce	73	84	96	80	73
Pr	9.6	10	13	10	11
Nd	25	28	34	25	28
Sm	9.5	10	13	9.7	10
Eu	0.1	0.1	0.1	0.1	0.1
Gd	17	12	15	11	12
Tb	3.2	3.7	4.6	3.5	4.0
Dy	29	32	39	30	33
Ho	6.9	7.6	9.7	7.4	8.0
Er	26	29	37	30	30
Tm	5.3	6.0	7.8	6.0	6.0
Yb	41	44	58	48	44
Lu	5.8	6.3	8.2	7.1	6.1
Ta	40	39	42	35	38
Pb	280	320	300	320	300
Th	200	200	220	230	210
U	38	66	54	54	35

TABLE 2. CHEMICAL ANALYSES OF MAJOR AND TRACE ELEMENTS IN THE ROUND TOP LACCOLITH
(continued)

	Low Sr	Gray, high Sr			
	RT1-230.5	J87-73	J87-72	RT336-200	RT283-182.5
(wt.%)					
SiO ₂	73.15	69.34	70.10	70.90	71.55
TiO ₂	0.02	0.03	0.03	0.02	0.04
Al ₂ O ₃	13.71	13.43	13.62	13.19	13.26
FeO (total)	1.72	3.58	3.43	3.08	2.19
MnO	0.08	0.10	0.09	0.08	0.08
MgO	0.01	0.17	0.22	0.05	0.12
CaO	0.03	0.67	1.32	1.62	1.16
Na ₂ O	5.34	5.74	5.51	5.29	5.44
K ₂ O	4.20	4.02	4.23	3.90	4.32
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	<0.01
CO ₂	<0.04	<0.04	<0.04	0.04	0.04
H ₂ O ⁺	0.39	0.59	0.82	0.43	0.31
F	0.31	1.72	1.63	1.33	1.18
-O for F	-0.13	-0.72	-0.69	-0.56	-0.50
Total	98.88	98.72	100.36	99.38	99.20
(ppm)					
Li	490	470	470	470	510
Be	19	57	46	26	18
V	<5	<5	<5	5	5
Ni	16	29	26	27	22
Cu	37	49	46	40	62
Zn	590	590	620	580	630
Rb	2200	1800	1900	1500	1800
Sr	7	290	230	120	140
Y	200	280	310	250	240
Zr	1100	1100	1200	1000	1100
Nb	370	380	370	380	400
Mo	2	5	4	3	1
Cs	49	93	86	67	58
Ba	8	10	19	15	22
La	21	27	31	29	28
Ce	77	110	120	110	110
Pr	10	13	15	14	13
Nd	26	36	41	38	36
Sm	10	13	15	13	13
Eu	0.1	0.2	0.2	0.2	0.2
Gd	11	15	17	15	14
Tb	3.2	4.7	5.5	4.7	4.4
Dy	28	40	46	38	37
Ho	6.7	9.7	11	8.9	8.9
Er	26	39	45	34	34
Tm	5.4	8.1	9.1	6.9	6.9
Yb	40	64	72	54	51
Lu	5.8	9.7	11	7.8	7.4
Ta	38	47	43	26	31
Pb	250	320	290	210	290
Th	170	250	210	190	230
U	36	51	21	46	56

TABLE 2. CHEMICAL ANALYSES OF MAJOR AND TRACE ELEMENTS IN THE ROUND TOP LACCOLITH
(continued)

	Gray, high Sr			Weathered	
	RT5-169	RT2-34	RT201-355	J87-70	J87-74
(wt.%)					
SiO ₂	71.94	71.97	72.72	72.65	73.15
TiO ₂	0.02	0.02	0.02	0.03	0.02
Al ₂ O ₃	13.55	13.99	13.69	13.42	13.82
FeO (total)	2.80	2.50	2.58	2.07	1.52
MnO	0.08	0.08	0.07	0.06	0.06
MgO	0.14	0.45	0.20	0.06	0.03
CaO	0.33	0.15	0.44	0.60	1.14
Na ₂ O	5.61	5.74	5.56	5.27	5.33
K ₂ O	4.09	4.13	4.09	4.13	3.66
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	<0.01
CO ₂	<0.04	0.04	<0.04	<0.04	<0.04
H ₂ O ⁺	0.41	0.41	0.55	1.01	0.59
F	1.24	1.57	1.32	0.42	1.06
-O for F	-0.52	-0.66	-0.56	-0.18	-0.45
Total	99.74	100.40	100.73	99.59	99.98
(ppm)					
Li	510	520	480	380	590
Be	14	13	100	24	13
V	<5	<5	6	11	7
Ni	25	23	23	23	14
Cu	52	45	56	49	40
Zn	600	580	550	570	510
Rb	1700	2000	2000	1700	1600
Sr	90	220	100	62	79
Y	280	230	220	220	240
Zr	1100	1100	1100	1100	1200
Nb	410	390	380	380	370
Mo	3	3	2	3	2
Cs	56	48	49	69	66
Ba	14	14	7	210	17
La	31	26	27	27	24
Ce	110	88	97	99	85
Pr	16	12	12	13	10
Nd	40	31	29	34	26
Sm	14	11	12	13	9.4
Eu	0.2	0.1	0.1	0.2	0.1
Gd	17	12	12	13	11
Tb	5.3	3.8	4.1	4.0	3.7
Dy	42	33	32	31	31
Ho	10	7.9	8.1	7.9	7.3
Er	41	30	32	30	31
Tm	8.1	5.9	5.7	5.9	6.7
Yb	61	44	47	46	54
Lu	8.9	6.0	7.1	6.9	8.2
Ta	36	37	42	41	51
Pb	250	240	260	250	200
Th	210	180	190	190	220
U	40	28	33	23	44

TABLE 3. ANALYSES OF STANDARD REFERENCE MATERIALS*

	NIM-G (granite)		BHVO-1 (basalt)		BE-N (ultramafic)	
	Found	Accepted	Found	Accepted	Found	Accepted
(wt. %)						
SiO ₂	76.10	75.70	48.67	49.90	37.43	38.20
TiO ₂	0.11	0.09	2.83	2.69	2.72	2.61
Al ₂ O ₃	12.37	12.08	13.77	13.85	10.12	10.07
FeO (total)	1.78	1.82	11.18	11.01	11.70	11.55
MnO	0.02	0.02	0.18	0.17	0.21	0.20
MgO	0.10	0.06	7.22	7.31	13.44	13.15
CaO	0.78	0.78	11.29	11.33	13.86	13.87
Na ₂ O	3.55	3.36	2.32	2.29	3.25	3.18
K ₂ O	5.15	4.99	0.56	0.54	1.54	1.39
P ₂ O ₅	0.01	0.01	0.26	0.28	1.09	1.05
CO ₂	0.04	0.10	0.04	0.79	0.74
H ₂ O ⁺	0.45	0.49	0.19	0.20	2.05	2.24
F	0.41	0.42
-O for F	-0.17	0.18
Total	100.70	100.10	98.47	99.61	98.20	98.25
(ppm)						
Li	14	12	<2	5.3	12
Be	8.0	7.0	2.0	4.0
V	<5	2	310	300	230	235
Ni	<5	8	130	140	291	267
Cu	14	12	146	74	72
Zn	54	50	100	100	113	120
Rb	323	320	12	10	60	47
Sr	14	10	440	420	1340	1370
Y	130	143	22	27	31	30
Zr	360	300	150	180	150	265
Nb	60	53	23	19	93	100
Mo	3	3	1	1	3
Cs	1	1	<1	<1	1	0.8
Ba	140	120	180	135	1070	1025
La	117	109	12	17	77	82
Ce	190	195	27	39	140	152
Pr	23	4.1	16
Nd	70	72	32	24	58	70
Sm	15	15.8	7.2	6.1	13.	12
Eu	0.33	0.35	2.1	2.0	3.4	3.6
Gd	18	14	7.7	6.0	11	9.0
Tb	3.1	3	1.0	1.0	1.4	1.3
Dy	19	17	5.5	5.0	8.7
Ho	4.3	1.0	1.4
Er	14	2.6	3.5
Tm	2.1	2.0	0.4	0.3	0.4
Yb	14	14.2	2.2	1.9	2.0	1.8
Lu	2.0	2.0	0.3	0.26	0.24
Ta	4	4.5	1	1.1	7	5.5
Pb	38	40	3	5	4
Th	61	51	2	1	11	11
U	24	15	0.7	0.4	3	2.4

*Analyses at Mineral Studies Laboratory, Bureau of Economic Geology: most major oxides and Zr by ICP-AES after lithium tetraborate fusion; H₂O⁺ by conversion to CO₂ and coulometric determination; CO₂ by coulometry; all reported on H₂O-free basis; Li, Be, V, Ni, P, some Mg, Cu, and Zn by ICP-Aes using multiple acid digestion; F by ISE after pyrohydrolytic evolution; all other elements by ICP-MS using multiple acid digestion. With the exception of sample J85-55, Fe is erroneously high in all Round Top samples due to contamination by steel during crushing.

TABLE 4. COMPARISON OF ROUND TOP RHYOLITE WITH TRIPPLE HILL AND SIERRA BLANCA RHYOLITES AND WITH TOPAZ RHYOLITES FROM UTAH*

	SM-35†	Topaz rhyolites SM-61a†	SM-29-206†	Triple Hill§	Sierra Blanca§	Round Top**	
(wt. %)							
SiO ₂	73.9	75.0	76.2	71.9	74.4	72.5	-
TiO ₂	0.06	0.28	0.07	0.27	0.02	0.03	-
Al ₂ O ₃	13.1	13.1	12.7	14.8	14.1	13.7	
FeO (total)	1.29	1.13	0.89	1.38	0.79	1.34	
MnO	0.06	0.04	0.07	0.03	0.05	0.08	
MgO	0.08	0.19	0.05	0.22	0.01	0.01	-
CaO	1.27	0.82	0.72	1.03	0.45	0.08	-
Na ₂ O	4.33	3.48	3.74	4.17	5.06	6.48	+
K ₂ O	3.65	5.51	4.80	4.69	4.30	4.22	
P ₂ O ₅	0.00	0.02	0.00	0.08	<0.01	<0.01	
LOI	3.55	2.97	2.84	0.69	0.33	0.13	
F	1.10	0.19	0.32	0.19	0.65	1.94	+
-O for F	-0.46	-0.08	-0.13	-0.08	-0.27	-0.82	
Total	101.9	102.6	102.3	99.4	99.9	99.7	
(ppm)							
Li	80	20	60	28	170	490	+
Be	52	2	7	7	4	58	
Rb	1060	186	433	n.a.	1090	1900	+
Sr	5	83	5	160	9	19	
Y	135	35	75	54	200	210	+
Zr	120	190	100	290	100	1100	+
Nb	120	40	47	n.a.	72	380	+
Cs	58	2.5	9.7	n.a.	30	62	
Ba‡	(63)	(41)	(41)	860	16	8	-
La	59	73	18	87	20	22	
Ce	137	132	53.1	130	54	80	
Nd	51	63	31	64	26	28	
Sm	17.8	8.8	7.5	13	9.2	10	
Eu	0.04	1.2	0.065	1.9	0.1	0.1	
Tb	3.4	1.3	1.9	1.7	2.4	3.7	+
Yb	15.7	4.0	9.6	31	24	46	+
Lu	2.6	0.53	1.7	0.6	3.6	6.6	+
Ta	25	2.3	5.4	n.a.	14	39	+
Pb‡	(56)	(31)	(31)	40	70	300	+
Th	69	25	47	40	60	200	+
U	38	5	19	4	14	47	

*from Christiansen and others (1984).

†SM-35 = vitrophyre from Spor Mountain; SM-61a and SM-29-206 = vitrophyres from Thomas Range.

§Data from Rubin and others (1987) and new analyses of Triple Hill sample J88-14 and Sierra Blanca sample 81-60.

**Major oxides for sample J85-55; trace elements are averages of first six samples in Table 2 (presumably the least weathered and least altered by interaction with limestones). + = Round Top enriched relative to topaz rhyolites; - = Round Top depleted.

‡Values in parentheses are averages from Christiansen and others (1986).

samples containing high Mg, Ca, and Sr also contain groundmass cryolite (Table 1) indicates that this modification did not selectively leach Mg, Ca, and Sr. The most likely source of these elements in relatively high-Sr (but otherwise apparently unaltered) samples is therefore the limestone country rock and its contained ground water. Oxygen and strontium isotopic studies are needed to substantiate this hypothesis.

If our hypothesis is correct that the Ca, Mg, and Sr contents of the gray, apparently unaltered rhyolites containing high Sr (Table 2 and the plus signs in Fig. 5) are largely the result of interaction with the country rock, then an interesting corollary is that apparently "fresh" samples of the Sierra Blanca rhyolites will not necessarily yield Sr isotopic data that relate entirely to magmatic processes. It would have been extremely difficult to recognize the addition of nonmagmatic Ca, Mg, and Sr had not the magma been so unusually depleted in these elements.

Incompatible trace elements and trace minerals

Some of the highly enriched trace elements substitute in the major silicate phases: Li in white to pale green mica, Zn in Mn-rich annite and in the Li-rich mica, and Rb in feldspars and micas (Rubin and others, 1987; plus new data from wavelength dispersive spectrometer scans). Other highly enriched incompatible trace elements form discrete minerals (Table 1).

Thorium is one of several particularly enriched incompatible elements. Concentrations of Th, unlike most other trace elements, are similar in all published work on the Sierra Blanca rhyolites (Shannon, 1986; Matthews and Adams, 1986; and this study); weathering probably did not significantly mobilize Th (Fig. 4). Thorium contents indicate significant differences between the superficially similar intrusions. The Round Top, Little Round Top, and Little Blanca rhyolites are much more enriched in Th than the Sierra Blanca rhyolite, which in turn, is more enriched than the Triple Hill rhyolite. Shannon (1986) and Shannon and Goodell (1986) used REE data to show that the Triple Hill rhyolite is the least evolved of the five laccoliths. The Triple Hill rhyolite is also petrographically least evolved; it contains more plagioclase and biotite and fewer quartz phenocrysts than the other rhyolites.

Many of the enriched trace elements form discrete minerals rather than trace substitutions in solid solutions. For example, thorite is ubiquitous in the Round Top and Little Blanca intrusions. It commonly forms small ($<5\ \mu\text{m}$) grains in zircon crystals but also forms relatively large (as much as $200\ \mu\text{m}$ long) euhedral crystals intergrown with anhedral zircon (Fig. 6). Rubin and others (1989) described magmatic and hydrothermal zircons from the Sierra Blanca intrusions. In the less Th-rich Sierra Blanca rhyolite, however, thorite has not been identified, but Th occurs in solid solution in zircon (Rubin and others, 1987). Other ubiquitous trace minerals include cassiterite, cerfluorite, bastnaesite(?), changbaiite, columbite, and zircon (Table 1). Tourmaline, which might be expected from the anomalously high amounts of B in the Sierra Blanca rhyolites (as much as 100 ppm; W. P.

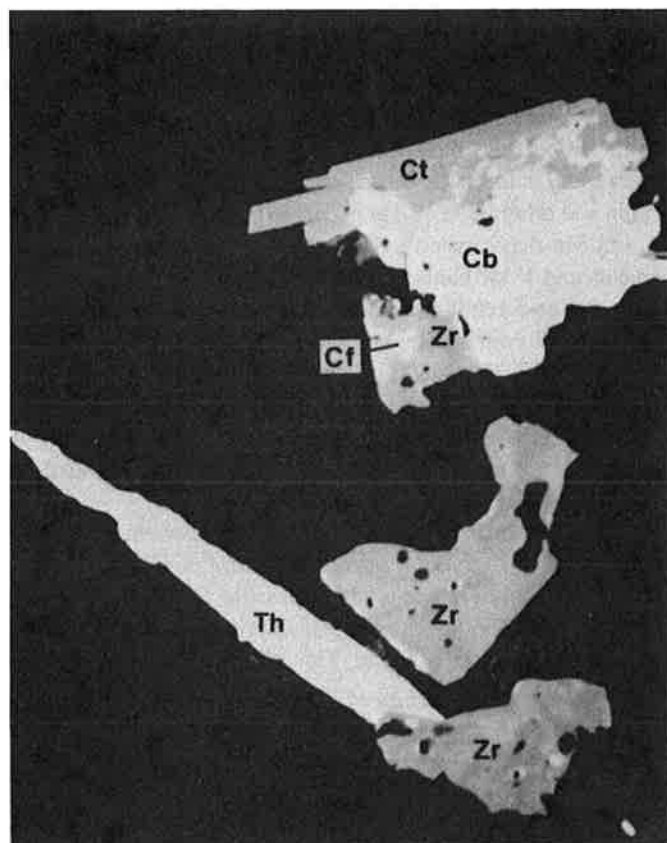


Figure 6. Backscattered electron image of thorite (Th), zircon (Zr), columbite (Cb), Mn- and Fe-rich cassiterite (Ct), and coffinite (Cf) in sample J87-73. The thorite grain is 110 μm long.

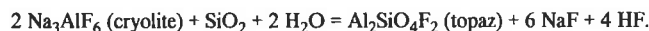
Leeman, personal communication, 1987), occurs locally on fractures at Little Blanca and Sierra Blanca.

Identification of trace minerals and of solid solutions is facilitated by the use of backscattered electron imaging on the electron microprobe coupled with energy and wavelength dispersive analysis. A wealth of unusual trace minerals in the Round Top rhyolite has been identified with this technique (Table 1). Because our microprobe lacks the capability to detect light elements, including C, O, B, Li, and Be, some of the identifications (e.g., bastnaesite) are at this time tentative. Small grain size (trace minerals commonly $<10\ \mu\text{m}$ long) makes unambiguous identification with conventional optical microscopy impossible.

Several REE-bearing fluorides are tentatively identified by their energy dispersive spectra. Yttrocerite, or cerian fluorite, has discrete Y, HREE, LREE, F, and minor Ca peaks. Yttrofluorite, or fluocerite-(Y), has Y, HREE, F, and minor Ca peaks, but lacks LREE. Cerfluorite, or fluocerite-(Ce), has Ce, LREE, and minor Ca peaks, but lacks HREE. Bastnaesite (?) has an F peak less pronounced than cerfluorite. More definitive identification of these phases awaits quantitative chemical analysis and diffraction studies.

Trace minerals detected by backscattered electron imaging and identified by energy dispersive spectra account for many of the enriched trace elements in the rhyolites (Tables 1 and 2). For example, Nb occurs in columbite, changbaiite, and to a lesser extent, Nb-bearing rutile. Tantalum substitutes for Nb in these minerals and in the Little Blanca intrusion, also occurs as tantalite (Rubin and others, 1987). Tin occurs in pure cassiterite and in an Fe- and Mn-rich cassiterite or other tin oxide. Heavy rare earth elements and Y are contained in the trace minerals yttrifluorite, yttrocerite, and xenotime. Light rare earth elements are dominantly in cerfluorite, bastnaesite(?), yttrocerite, and an unnamed Ca-Th-Pb-REE fluoride(?). Several phases account for Pb: changbaiite, kasolite(?), Ca-Th-Pb-REE fluoride(?), Pb-rich Mn oxide, and, in a weathered sample, cerussite. Additional Pb is probably incorporated in K-feldspar but has not been detected on scans using wavelength-dispersive spectrometers.

Fluorine occurs not only in micas but also in numerous fluoride minerals: cryolite, yttrocerite, yttrifluorite, cerfluorite, bastnaesite(?), and rarely, zunyite, elpasolite, thomsenolite, fluellite, Ca-Th-Pb-REE fluoride(?), and fluorite. Somewhat surprisingly, topaz has not been found. The following reaction, used by Burt and London (1982) to describe the relative stabilities of topaz and cryolite, illustrates some of the possible causes for the lack of topaz:



The vapor or hydrothermal phase that deposited cryolite in the Round Top rhyolite could have been exceptionally rich in Na or F, or it could have been relatively poor in H₂O. Because quartz appears to be a stable phase in the Round Top rhyolite as well as in topaz-bearing rhyolites, it is unlikely that the absence of topaz is due to low activity of silica in the fluid.

Weathering modified the chemical and mineralogic composition of some rhyolite samples. Although the two obviously weathered samples that were collected from outcrops (Tables 1 and 2) are not so highly weathered that all magnetite has been destroyed or that feldspars have been significantly attacked, they do differ significantly from the 13 relatively "fresh" samples in several respects. The weathered sample containing cerussite also contains barite and is an order of magnitude more enriched in Ba than other samples (Tables 1 and 2). The source of Ba and sulfate in this rock may have been the overlying (now eroded) Cretaceous sedimentary rocks, which are regionally gypsiferous. Cryolite that may have been in the groundmass of weathered samples has been destroyed. McNulty (1980) identified greaksutite, ralstonite, and thomsenolite, common alteration products of cryolite, in altered rhyolite breccias near the contacts between Sierra Blanca Peaks rhyolites and the limestone country rock. Thomsenolite and other fluorides occur in some "fresh" samples (Table 1) but not in the two weathered samples that were studied in detail.

Samples with high U contents generally contain discrete U minerals: coffinite and kasolite(?); uraninite has been identified in one sample (Table 1). As would be expected from the high

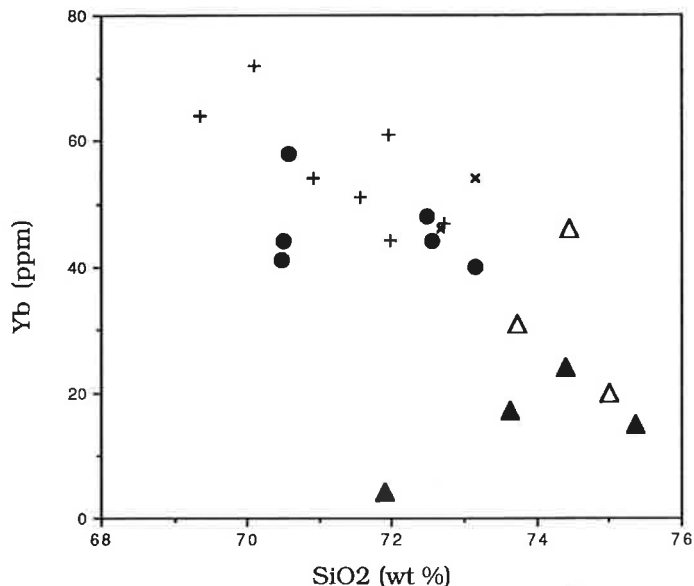


Figure 7. Plot of Yb vs. SiO₂. Symbols as in Figures 3 and 5.

mobility of U in oxidizing waters, the weathered samples have lower U concentrations and do not contain discrete U minerals. Variability in U content among the 13 "fresh" samples (Table 2), coupled with relatively constant Th contents and the ubiquitous presence of secondary hematite rimming magnetite grains, suggests that at least some oxidizing waters penetrated the entire mass of the laccolith.

Petrogenesis—Comparison with topaz rhyolites

Although highly evolved in terms of most trace- and major-element characteristics, the Sierra Blanca rhyolites are not particularly high in silica. In fact, some of the most incompatible element-enriched rocks are low-silica rhyolites (Table 2 and Fig. 7). Quartz occurs as both groundmass grains and as phenocrysts in the rhyolites. Crystal fractionation involving removal of quartz could explain the increasing REE content with decreasing silica concentration. Quartz fractionation may also link the Round Top intrusion to Sierra Blanca, which is relatively enriched in silica and depleted in REE (Figs. 7 and 8), Th (Fig. 4), and other incompatible elements (Shannon, 1986; Rubin and others, 1987; Table 4). As noted by Shannon and Goodell (1986), using the data of Manning (1982) on the effect of F on the crystallization of granitic melts, the bulk compositions of the Sierra Blanca rhyolites project into the quartz liquidus field on an NaAlSi₃O₈-KAlSi₃O₈-SiO₂ diagram at low water pressures and F contents comparable to those analyzed. Christiansen and others (1984) favored quartz fractionation in the geochemical evolution of topaz rhyolites, which have many geochemical similarities to the Sierra Blanca Peaks rhyolites.

Crystal fractionation involving one or more REE-enriched phase, such as those listed in Table 1, is an unlikely alternative explanation for the observed increase in REE concentration with decrease in silica content (Fig. 7). Because essentially all in-

compatible trace elements are more enriched in the low-silica Round Top rhyolite than in the high-silica Sierra Blanca rhyolite (Table 4), many incompatible element-bearing phases would have to be fractionating simultaneously.

The rhyolites of Sierra Blanca Peaks are quite unusual in their rare earth patterns (Fig. 8). They are extremely enriched in HREE, so much so that the chondrite-normalized REE patterns have positive slopes. Conversely, most rhyolites have negative slopes. The ratio of Yb_N to Nd_N is used in Figure 9 as a measure of the slope of the REE pattern. It is clear from this plot that the Round Top, Little Blanca, and Sierra Blanca rhyolites are highly enriched in HREE. Rhyolites elsewhere in the world that are most similar to the Sierra Blanca Peaks are topaz rhyolites and related ongonites, which typically have Yb_N/Nd_N values of approximately 1 (Christiansen and others, 1986). Most other rhyolites, including calc-alkaline and peralkaline varieties and the more typical metaluminous and peralkaline rhyolites of Trans-Pecos Texas (Barker, 1987; Cameron and Cameron, 1986; Cameron and others, 1986) typically have Yb_N/Nd_N values less than 1.

The slope of a chondrite-normalized rare earth pattern generally becomes increasingly more positive with differentiation of rhyolites (Hildreth, 1979; Christiansen and others, 1984, 1986). Similarly, samples of the highly evolved Round Top rhyolite have more positive slopes than the less evolved Sierra Blanca and Triple Hill rhyolites (Figs. 8 and 9).

The rhyolites of Sierra Blanca Peaks are similar to topaz rhyolites (Christiansen and others, 1986) in other geochemical respects. They all have pronounced negative Eu anomalies, are

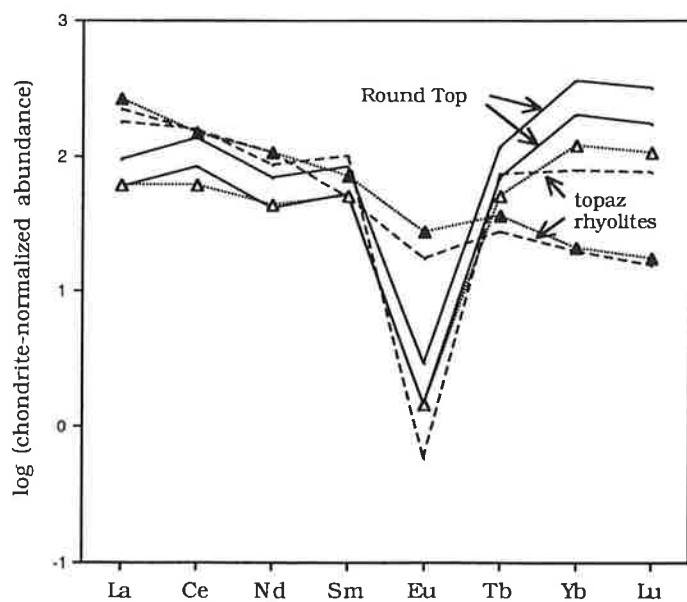


Figure 8. Chondrite-normalized rare earth abundances. The range of 13 gray, unaltered rhyolite samples from Round Top (see Tables 1 and 3) is indicated. Topaz rhyolites are samples SM-35 (73.9 percent SiO_2) and SM-61a (75.0 percent SiO_2) from Christiansen and others (1984). \blacktriangle = Triple Hill; \triangle = Sierra Blanca (Table 4).

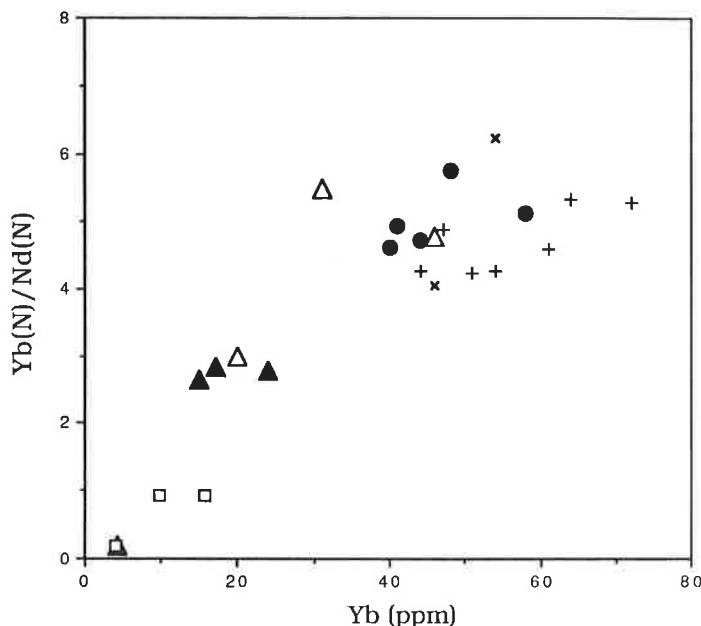


Figure 9. Plot of Yb_N/Nd_N vs. Yb for individual rhyolite samples. Yb_N/Nd_N is a measure of the slope of the chondrite-normalized rare earth plot; a value greater than 1 indicates a positive slope (HREE > LREE), and a value less than 1 indicates a normal, declining rare earth pattern. Round Top samples: \bullet = gray, relatively unaltered, low Sr; $+$ = gray, high Sr; \times = weathered. Samples of other laccoliths: \triangle = unweathered Little Round Top and Little Blanca; \blacktriangle = unweathered Sierra Blanca and Triple Hill; \square = topaz rhyolites from Table 4 (Christiansen and others, 1986).

enriched in F and many incompatible elements (Li, Be, Rb, Nb, Cs, Y, Ta, Th, U), and are depleted in many compatible elements (Sr, Ba, Ti, P). The Round Top rhyolite is, however, extreme in these enrichments and depletions. Relative to topaz rhyolites (Christiansen and others, 1984, 1986), the Round Top rhyolite is more enriched in most incompatible elements and HREE and more depleted in compatible elements and LREE (Table 4 and Fig. 8). Our REE data support the conclusion of Shannon (1986) and Shannon and Goodell (1986) that the Round Top and Little Blanca rhyolites are more highly evolved than the Sierra Blanca rhyolite, which comes close to approaching the values of topaz rhyolites (Fig. 8). The rhyolites at Sierra Blanca Peaks thus appear to be extreme differentiates of magmas similar to topaz rhyolites. Round Top, Little Round Top, and Little Blanca are more highly evolved than Sierra Blanca proper (Figs. 4 and 8). The Triple Hill rhyolite, the least evolved of the laccoliths, has an REE pattern most comparable to topaz rhyolites (Fig. 8 and Table 4).

It is uncertain what roles liquid-state differentiation (Hildreth, 1979) and vapor-phase transport and crystallization have played in the extreme HREE, Th, and other trace-element enrichments of Round Top rhyolite samples. London and others (1987), in experimental studies of the crystallization of peraluminous, F-rich magmas, concluded that HREE are more soluble in

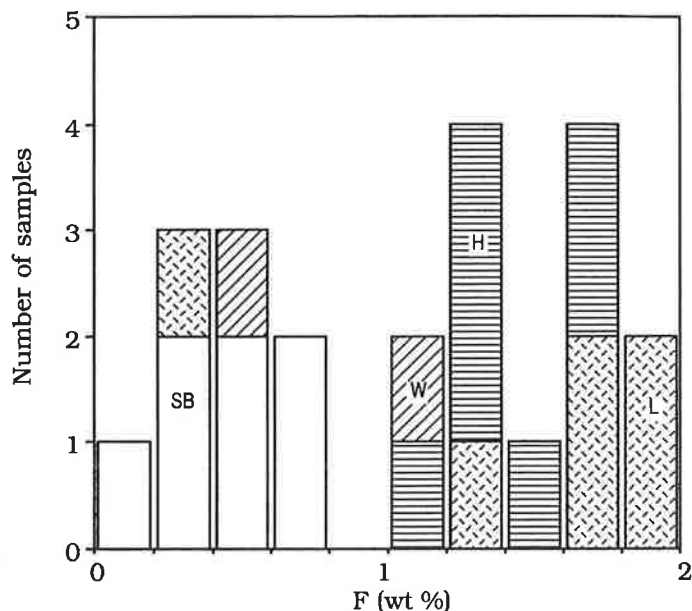


Figure 10. Histogram of F concentrations. Round Top samples (see Table 1): L = gray, relatively unaltered, low Sr; H = gray, high Sr; W = weathered. SB = other Sierra Blanca rhyolites.

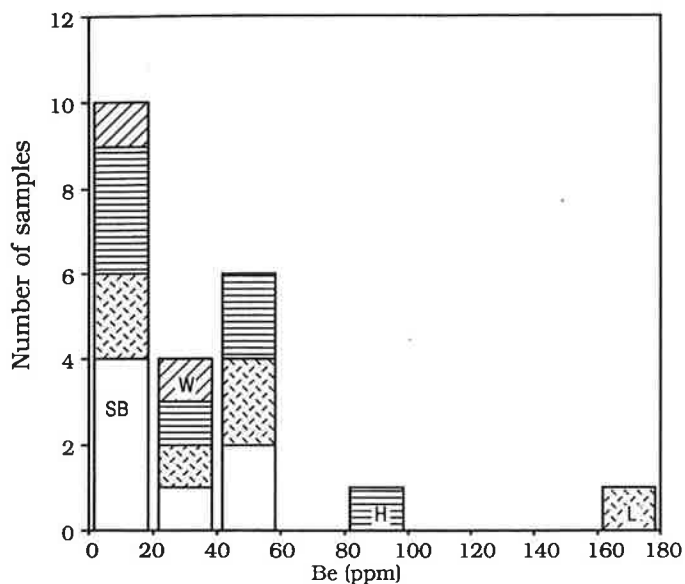


Figure 11. Histogram of Be concentrations. Symbols as in Figure 10.

a vapor phase than are LREE. It is possible that some of the variability in REE contents in the Round Top rocks (Table 2, Figs. 7 and 9) is the result of vapor-phase crystallization. Differences in Na and F contents, expressed by differences in cryolite content, are clear indications of variability in the degree of vapor-phase crystallization. The Round Top rhyolites are, however, broadly homogeneous in their REE and other trace-element contents. Analyzed samples were collected from the top, bottom, and interior of the laccolith. If vapor-phase processes are in part responsible for the extreme HREE enrichments, then these processes have affected the entire mass of the laccolith.

Uncertainties abound regarding the origin of the rhyolites at Sierra Blanca Peaks. Are they simply extreme differentiates of rocks similar to topaz rhyolites, which appear to have developed from melting of granulitic crust (Christiansen and others, 1986)? To what extent were Precambrian cassiterite-topaz-bearing granites, like those exposed in the Franklin Mountains 120 km to the northwest (Harbour, 1960, 1972; Thomann, 1980, 1981), melted to yield "second-cycle" rhyolites? How do the Sierra Blanca rhyolites relate to other Tertiary rhyolitic rocks in the Trans-Pecos region, which largely appear to be differentiates from mantle-derived mafic magmas (Price and others, 1987; Henry and others, 1988) and which are characteristically enriched in many of the same trace elements (Li, Be, F, Nb, REE, Th, U, etc.) found in extreme quantities at Round Top? Isotopic data, especially Nd, Pb, and O isotopes, are needed to resolve these uncertainties. Xenoliths of biotite schist occur in the Triple Hill rhyolite, the least differentiated of the five laccoliths. They are similar to rocks of the Precambrian Carrizo Mountain Group that crop out 30 km

to the east and suggest that crustal melting may have been important in the origin of the Sierra Blanca magmas.

RELATION TO ORE DEPOSITS

The Round Top intrusion is extremely enriched in F and Be (Figs. 10 and 11). Typical rhyolites contain only 0.08 percent F and 3 ppm Be (Rose and others, 1979). Round Top is undoubtedly the source of these elements in high-grade beryllium ores in fluoritized limestones along the contacts with the laccolith. The contact deposits were examined as sources of fluorite by McNulty (1974, 1980) and are currently being evaluated by Cyprus Minerals Company as sources of beryllium. Topaz rhyolites associated with the large-tonnage beryllium deposits at Spor Mountain, Utah, are similarly enriched in F and Be. Details of the mineralogy of the Round Top ores and their relation to the Na-Al-F-rich vapor phase that deposited cryolite in the rhyolites are reported by Rubin and others (1988).

The rhyolites themselves are so enriched in a number of trace elements that they should be considered large-tonnage, low-grade resources of several rare metals, including Y, HREE, Nb, Ta, Li, and Th. For example, the average Th content of the Round Top rhyolite is 3.6 times higher than that of the Conway Granite, New Hampshire, which is considered a large-tonnage resource of Th (Finch and others, 1973). Recent breakthroughs in research on superconducting materials may dramatically increase the long-term demand for certain rare metals, including yttrium and both LREE and HREE (Geballe and Hulm, 1988). The fact that many of the economically interesting trace elements occur in

discrete minerals in the Round Top intrusion (Table 1) is encouraging, and resources are vast: the Round Top laccolith alone has a mass of at least 1,600 Mt.

CONCLUSIONS

The Round Top and other laccoliths at Sierra Blanca Peaks are chemically and mineralogically unusual. Although they are part of the main phase of Tertiary subduction-related magmatism in the Trans-Pecos region, they are chemically unusual in that they are peraluminous, unlike the regionally more typical metaluminous and peralkaline rhyolites. The Sierra Blanca rhyolites are chemically somewhat similar to incompatible element-enriched topaz rhyolites (Christiansen and others, 1986) but are even more enriched in most incompatible trace elements (Table 4). The Sierra Blanca rhyolites, which formed in a mildly compressive tectonic setting, further contrast with topaz rhyolites, most of which were emplaced in an extensional environment. The rhyolites are the sources of Be and F in economically important Be deposits in fluoritized limestones in contact with the Round Top laccolith. The rhyolites are also large-tonnage, low-

grade resources of several rare elements. Vapor-phase crystallization, exemplified by near end-member feldspar compositions, fluid inclusions defining overgrowths on magmatic grains, Li-rich micas, rutiled quartz, and abundant cryolite, has clearly modified the original magmatic chemistry of these rocks.

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