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Hydrothermal zircons and zircon overgrowths, Sierra Blanca Peaks, Texas*

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ABSTRACT

Zircons from the Sierra Blanca Peaks, a group of mildly peraluminous, rare-element–enriched rhyolite laccoliths in Trans-Pecos Texas, display textures that indicate formation and/or alteration in a hydrothermal environment. These zircons can be categorized into three types according to host rock, texture, and mineral chemistry: (1) magmatic zircons hosted by intrusive igneous rocks; (2) hydrothermal (or late magmatic) zircon overgrowths on magmatic zircons; and (3) hydrothermal zircons hosted by replacement bodies of fluorite in limestone. Rims of magmatic zircons from the Round Top intrusion generally are enriched in Y, Hf, Th, and U relative to cores. Magmatic zircons from the Sierra Blanca intrusion show a negative correlation between Y and U contents. Overgrowths from the Round Top intrusion have generally higher Hf contents (5.1 to 7.6 wt% HfO_2) than do their magmatic substrates (3.9 to 6.3 wt%). Hydrothermal zircons in replacement bodies contain much less Hf (1.1 to 2.2 wt% HfO_2). Compositions of magmatic zircons vary between intrusions.

Magmatic zircons in most of the intrusions display amoeboid texture and, in samples from the more Th-rich intrusions, host numerous thorite inclusions. Some magmatic zircon grains from Round Top have conspicuously inclusion-free zircon overgrowths. Round Top also has zircon veinlets and tiny "stringers" that connect to the overgrowths. Zircon overgrowths also occur in the Triple Hill intrusion, where the magmatic zircons tend to be less corroded. Hydrothermal fluorspar replacement bodies in limestone that are associated with intrusion of the Sierra Blanca laccoliths contain subhedral to anhedral, commonly corroded, inclusion-free zircon grains.

INTRODUCTION

Zircon is a common accessory mineral in felsic igneous rocks, where it generally forms as a magmatic phase. It also occurs as a detrital mineral in sediments derived from felsic igneous rocks. Trace elements within zircon (P, Ca, Y, Nb, REE, Hf, U, Th; Speer, 1982) make it useful for isotopic and fission-track geochronology and for geochemical tracer studies.

Zircon is highly stable in most nonmagmatic environments (e.g., Speer, 1982). In igneous geochemistry studies, Zr is generally considered to be an immobile element (e.g., Finlow-Bates and Stumpfl, 1981). Nevertheless, hydrothermal zircons or zircon overgrowths have been described in contact metamorphic and metasomatic environments (Taubeneck, 1957; Davis et al., 1968), hydrothermal veins (Johnson and McIntyre, 1983, 1986), hydrothermally altered intrusive and extrusive igneous rocks (Ludington et al., 1980; Dziedzic, 1984; Jackson et al., 1985), and mineralized shear zones (Gates, 1987). Saxena (1966) discussed authigenic zircons formed from remobilization of Zr derived from metamorphic source rocks. Magmatic corrosion of zircons was noted by Murthy (1958). Gulson and Krogh (1975) determined that zircon overgrowths, related to posttectonic intrusions in igneous and high-grade metamorphic rocks, could be distinguished from their zircon substrates by trace-element contents. Despite the observed occurrences of hydrothermal zircons, no detailed mineralogic examination of them has been published. This paper focuses on textures and trace-element contents of magmatic and hydrothermal zircons and zircon overgrowths from the Sierra Blanca Peaks, Trans-Pecos (Texas) magmatic province.

HOST ROCKS

The Sierra Blanca Peaks are located approximately 120 km southeast of El Paso, just north of Interstate Highway 10, and at the west edge of the town of Sierra Blanca (see Rubin et al., 1987, for map). The peaks are mildly peraluminous rhyolite laccoliths, 36.2 m.y. old (Henry et al., 1986), that are highly enriched in Li, Be, F, Zn, Rb, Y, Zr, Nb, Sn, REEs, and Th (Rubin et al., 1987). All the laccoliths contain zircon as the most abundant trace mineral. The Round Top intrusion has the highest concentrations of incompatible elements among the group, including the highest Zr content (maximum of 1200 ppm Zr) and the greatest abundance of zircon (approximately

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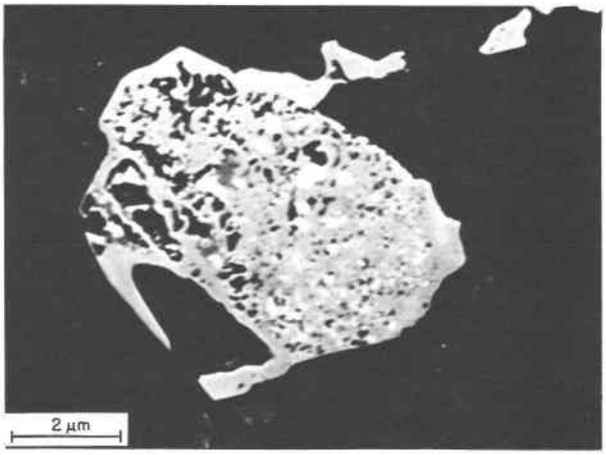

Fig. 1. **Backscattered-electron image of vacuolized magmatic** zircon (inclusion-rich) from Round Top with hydrothermal(?) overgrowths (inclusion-free). Inclusions are thorite.

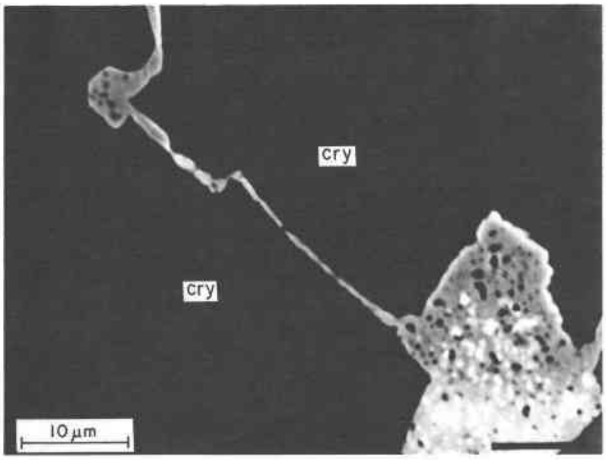

Fig. 2. Backscattered-electron image of thorite-rich magmatic zircon from Round Top and hydrothermal "stringer." "Stringer" cuts cryolite (cry).

0.2 vol%). Round Top contains groundmass cryolite, a likely vapor-phase precipitate, as well as numerous trace minerals that contain most of the incompatible lithophile elements in the intrusion (Rubin et al., 1987; Price et al., 1989). The other Sierra Blanca Peaks are, in decreasing order of incompatible-element enrichment, Little Round Top, Little Blanca, Sierra Blanca, and Triple Hill (Rubin et al., 1987; Price et al., 1989).

Fluorspar replacement deposits, highly enriched in Be, occur at the contacts between the laccoliths and Cretaceous limestone. Zircon is the most abundant trace mineral in these hydrothermal replacement bodies, occurring in fluorite (Rubin et al., 1988).

ZIRCON TYPES

We recognize three distinct zircon types on the basis of host rock and texture: (1) magmatic zircons, hosted by intrusive igneous rocks; (2) hydrothermal (or late magmatic) overgrowths of zircon, associated with magmatic types; and (3) hydrothermal zircon, hosted by replacement bodies. All three types have been observed in samples from Round Top. The other four intrusions contain magmatic zircon, and Triple Hill also displays overgrowths. All zircons in this study were observed by backscattered-electron imaging on an electron microprobe, and their identity was confirmed using energy-dispersive spectrometry.

Magmatic zircons in the Sierra Blanca intrusions range from <10 μm to >100 μm in longest dimension and have amoeboid shapes (Figs. 1–3), except those on Triple Hill. Triple Hill zircons are generally subhedral to euhedral and do not display the degree of vacuolization present in zircons in the other four peaks. Vacuoles are irregular in shape and generally less than 5 μm in longest dimension. They may represent more soluble areas within the zircons; they are not a result of plucking during thin-section preparation. Zircons in the more Th-rich intrusions (i.e., Round Top, Little Round Top, and Little Blanca) contain abundant thorite inclusions as much as 10 μm long (Figs. 1–3). Thorite does not occur in the less Th-rich intrusions (Sierra Blanca proper and Triple Hill). Iron oxide inclusions in the zircons are common; coffinite inclusions are rare. Other phases occurring with or within zircon (Fig. 3) include bastnäsite(?) [$(Ce,La)CO_3F$], cerfluorite [$(LREE)F_3$], changbaiite ($PbNb_2O_6$), columbite [$(Fe,Mn)Nb_2O_6$], xenotime [$(Y,HREE)PO_4$], and yttrofluorite (YF_3).

Zircon overgrowths in the Round Top rhyolite appear as rims on earlier magmatic zircons. These overgrowths are texturally distinct from the magmatic grains. Whereas the magmatic zircons commonly contain thorite inclusions, the overgrowths are conspicuously inclusion free. The overgrowths are less corroded and vacuolized than their hosts (Figs. 1 and 3). In some cases, the inclusion-free overgrowths connect to tiny "stringers" of zircon (Fig. 2). Some Triple Hill zircons display a different type of overgrowth, distinguished from its substrate only by its greater brightness (due to a greater mean atomic weight) in a backscattered-electron image.

Hydrothermal zircons in the fluorspar replacement bodies at Round Top are rarely greater than 15 μm in longest dimension; they are commonly less than 5 μm wide. Unlike some of the larger magmatic zircons in the Sierra Blanca Peaks, the hydrothermal zircons are too small for conventional petrographic observation. The hydrothermal zircons are, however, irregular in shape and grain boundaries (Fig. 4). All occur in fluorite, and those near the rhyolite contact commonly occur with hydrothermal garnet. With the exception of some iron oxide inclusions, the hydrothermal zircons are generally inclusion free.

ZIRCON CHEMISTRY

Zircons from the Sierra Blanca intrusions and the fluorspar replacement bodies at Round Top were analyzed

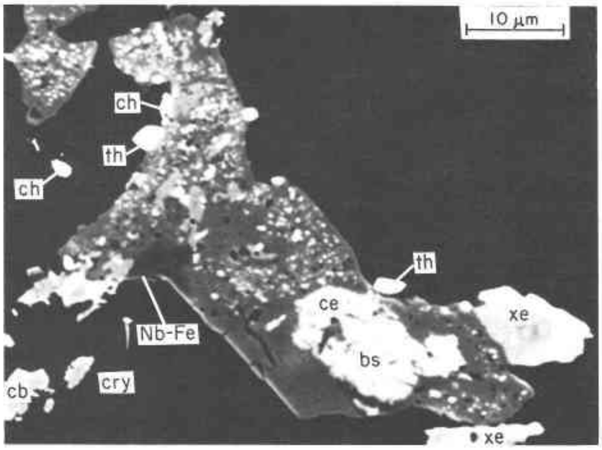

Fig. 3. Backscattered-electron image of zircon from Round Top hosting several phases. Note inclusion-free (hydrothermal overgrowth?) areas. bs = bastnäsite(?); cb = columbite; ce = cerfluorite; ch = changbaiite; cry = cryolite; Nb-Fe = niobium-rich iron oxide; th = thorite; xe = xenotime.

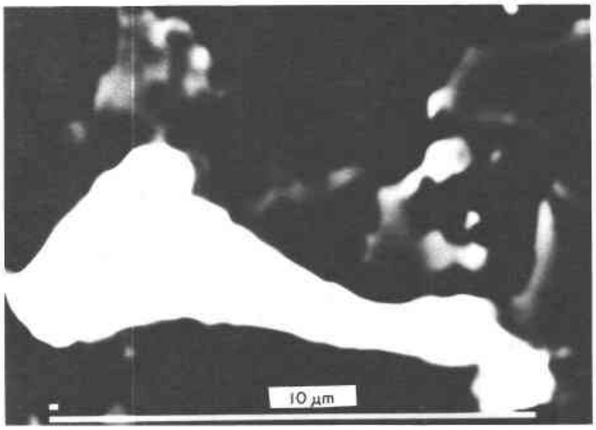

Fig. 4. Backscattered-electron image of hydrothermal zircon from Be-bearing fluorspar replacement body, Round Top.

using a Cameca MBX electron-probe microanalyzer with four wavelength-dispersive spectrometers, employing a ZAF correction program. Operating conditions were as follows: accelerating voltage = 15 kV, beam current = 15 nA (measured on the Faraday cup), beam diameter = 2–3 µm. Primary standards were natural zircon (Zr, Hf, Si), apatite (Ca, P), synthetic garnet (Y), ThO_2 (Th), and U-bearing glass (NBS Standard K-378). Counting times were 15 s for Zr and Si and 30 s for Ca, Y, Hf, Th, U, and P. Standards were checked after a maximum of every 20 unknown points. Many analyses were hindered by small grain size, vacuoles, inclusions, and instability under the electron beam, resulting in low totals. Zircon degradation under the beam is probably indicative of hydration, which would also lead to low totals. Table 1 contains representative analyses of the different zircon types. Although most trace- and minor-element concentrations varied considerably, three patterns were detectable: (1) trace-element zonation within Round Top magmatic grains; (2) zonation of Y and U in zircons from Sierra Blanca proper; and (3) Hf concentration among the different zircon types in Round Top.

Rims of magmatic zircons from Round Top generally are enriched in Y, Hf, Th, and U relative to cores. Y and U concentrations display an antithetic relationship in the Sierra Blanca magmatic zircons; Y is generally enriched in cores relative to rims. Magmatic zircons from the other intrusions are not distinctly zoned. The third pattern was more consistent: Hf showed trimodal distribution depending on zircon type in Round Top. Hydrothermal overgrowths and "stringers" displayed the highest Hf contents, ranging from 5.1 to 7.6 wt% HfO_2; magmatic grains had a range of 3.9 to 6.3 wt%, and fluorite-hosted hydrothermal zircons had 1.1 to 2.2 wt%. Although the Hf content of the overgrowths overlapped with that of the magmatic grains, the overlap was only between zircons in different samples; overgrowths had a consistently higher Hf content than magmatic grains within the same sample.

Trace-element contents of magmatic zircons vary among the different intrusions. Hf contents of magmatic zircons from the other intrusions range as follows (wt% HfO_2): Sierra Blanca; 2.3 to 7.9; Little Blanca; 4.7 to 6.7; Little Round Top; 4.3 to 6.3; Triple Hill; 1.2 to 2.2. Analyses of two overgrowths from Triple Hill are markedly

TABLE 1. Representative microprobe analyses (wt%) of zircons from Sierra Blanca Peaks

	RT283-182.5		J87-96	J88-10	J88-11	J88-12	J88-14	
	RT-M	RT-O	RT-H	SB-M	LB-M	LRT-M	TH-M	TH-O
ZrO_2	60.0	59.2	64.8	50.9	62.9	62.3	66.3	56.5
HfO_2	4.91	6.50	1.61	4.39	5.00	5.63	1.77	2.23
ThO_2	0.19	0.96	0.00	6.99	0.10	0.09	0.00	0.68
UO_2	1.04	0.95	0.00	5.84	0.31	0.28	0.12	0.22
Y_2O_3	0.38	0.84	0.52	1.33	0.36	0.00	0.32	1.97
CaO	0.00	0.00	0.08	0.02	0.02	0.00	0.00	0.56
SiO_2	30.9	30.2	32.9	29.8	31.3	31.9	32.4	34.3
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56
Total	97.4	98.6	99.9	99.3	100.0	100.2	100.9	97.0

Note: RT = Round Top; SB = Sierra Blanca proper; LB = Little Blanca; LRT = Little Round Top; TH = Triple Hill; M = magmatic; O = overgrowth; H = hydrothermal.

different, and both have low totals. One overgrowth (TH-O) was enriched in Hf, Th, and especially Y relative to its substrate (Table 1); the other showed no enrichment in Y or Th and a depletion in Hf. Although magmatic zircons in Sierra Blanca proper did not have discrete thorite inclusions, they did have consistently high Th contents (3.2 to 9.4 wt% ThO_2), as well as high U contents (2.7 to 5.2 wt% UO_2). These high concentrations of Th and U may have metamictized the zircons in Sierra Blanca proper, resulting in the low totals. Low totals in many of the magmatic zircons and overgrowths may also have been caused by water, probably occurring as molecular water rather than as hydroxyl (Mumpton and Roy, 1961; Speer, 1982). Either hydration or metamictization could have caused the observed zircon instability under the electron beam. Such high Th and U contents exceed the limits for these elements in the zircon structure proposed by Mumpton and Roy (1961). It is unlikely that the high values for Th and U are due to inclusions of thorite or coffinite, as such inclusions would be visible down to a diameter of less than 1 μm in a backscattered-electron image, and none was seen. Triple Hill zircons contained neither thorite inclusions nor high Th contents (18-point average of 0.1 wt%). Sierra Blanca and Triple Hill magmatic zircons also had much higher Y contents (1.9 and 0.6 wt% Y_2O_3 averages, respectively) than those from Round Top, Little Round Top, and Little Blanca (approximately 0.2 wt% averages for each). Some zircons from Sierra Blanca contained up to 2.0 and 0.7 wt% CaO and P_2O_5, respectively. All other zircons had low values of Ca and P, mostly below detectability (approximately 170 and 290 ppm oxide, respectively).

DISCUSSION

Textural and geochemical characteristics of the zircons at Round Top clearly indicate a high degree of Zr mobility in a hydrothermal environment, contrary to characterizations of Zr as immobile (e.g., Finlow-Bates and Stumpfl, 1981). Multiple zircon generations at Round Top provide additional evidence in support of late-stage, possibly vapor-phase crystallization (Rubin et al., 1987; Price et al., 1989). The zircon "stringer" shown in Figure 2 is cutting cryolite, which is a likely vapor-phase precipitate; it is clearly not magmatic. Zircons in fluorite are clearly hydrothermal and were probably deposited by the same fluids that deposited fluorite and hydrothermal garnet. The large difference in Hf content between the hydrothermal zircons in the fluorspar replacement bodies and the overgrowths in the rhyolite may indicate different fluid sources for each, or may represent temporal, spatial, or thermal variation in one fluid.

The difference in zircon composition among intrusions largely reflects differences in whole-rock trace-element contents. For example, intrusions most enriched in Th (i.e., Round Top, Little Round Top, and Little Blanca) have zircons bearing abundant thorite inclusions, but the zircons themselves have low Th levels. The thorite inclusions presumably are a product of exsolution from their zircon hosts. The Sierra Blanca intrusion, which has an intermediate Th content, contains Th-rich zircons but no thorite inclusions in zircon. Triple Hill has a low Th concentration, Th-poor zircons, and no thorite.

The question of Zr mobility is important for its implications in igneous petrogenesis and isotopic dating. Two geochemical factors that may influence Zr mobility and require further investigation are F concentration and "aluminosity." Studies by Dietrich (1968) and Ludington et al. (1980) suggest that high F concentrations promote Zr mobility. Watson (1979) and Watson and Harrison (1983) suggested that peralkaline magmas should be able to carry Zr in solution more effectively than peraluminous magmas.

Zr mobility in other areas of the Trans-Pecos magmatic province was probably facilitated by high-F environments. Fluorite deposits associated with peralkaline intrusions in the Christmas Mountains contain as much as 14000 ppm Zr in the form of tiny zircons (Duex and Henry, 1985). A quartz-fluorite vein in metaluminous quartz monzonite in the Infiernito caldera (Price and Henry, 1982) contains zircons and zircon outgrowths. Although more thorough characterization of the samples from the Infiernito caldera and the Christmas Mountains is necessary, preliminary microprobe analysis of samples from the latter suggests considerable Zr concentrations in sodic pyroxenes and amphiboles.

All three examples of Zr mobility and hydrothermal zircons in Trans-Pecos Texas are related to fluorite mineralization and F-rich magmas (as much as 1.30 wt% F in Round Top; Rubin et al., 1987). F is probably significant in Zr mobility. However, the three Texas examples span the range of "aluminosity": the Sierra Blanca Peaks are peraluminous, the intrusive rocks of the Infiernito caldera are metaluminous, and the Zr-rich rocks in the Christmas Mountains are peralkaline. Clearly, the question of relative importance of "aluminosity" still needs to be addressed.

Lack of recognition of Zr remobilization and zircon alteration may lead to confusion in interpreting U-Pb or fission-track dating. Hydrothermal zircons could, however, provide an excellent means for dating alteration of igneous rocks or certain hydrothermal mineral deposits. Given the size of the zircons observed in this study, backscattered imaging seems to be a necessary tool for characterizing the zircon population in a suite of samples, especially when hydrothermal activity is suspected.

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