A preliminary geochemical study of zircons and monazites from Deccan felsic dikes, Rajula, Gujarat, India: Implications for crustal melting

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Zircons of 10–100 μm size and monazites of up to 10 μm size are present in rhyolite and trachyte dikes associated with Deccan basalts around Rajula in the southern Saurashtra Peninsula of Gujarat. On the basis of structural conformity of the felsic and basaltic dikes, K-Ar ages and trace element considerations, a previous study concluded that the felsic rocks are coeval with the Deccan Volcanics and originated by crustal anatexis. The felsic rocks contain two populations of zircons and monazites, one that crystallized from the felsic melt and the other that contains inherited crustal material. Trace element variations in the rhyolites and trachytes indicate that zircons and monazites crystallized from the felsic melts, but compositional analysis of a zircon indicates the presence of a small core possibly inherited from the crust. Hf compositional zoning profile of this zircon indicates that it grew from the host rhyolitic melt while the melt differentiated, and Y and LREE contents suggest that this zircon crystallized from the host melt. Pb contents of some monazites also suggest the presence of inherited crustal cores. Hence, any age determination by the U-Th-Pb isotopic method should be interpreted with due consideration to crustal inheritance. Temperatures estimated from zircon and monazite saturation thermometry indicate that the crust around Rajula may have been heated to a maximum of approximately 900°C by the intruding Deccan magma. Crustal melting models of other workers indicate that a 1–2 million year emplacement time for the Deccan Traps may be appropriate for crustal melting characteristics observed in the Rajula area through the felsic dikes.

1. Introduction

Zircon and monazite are known for their stability under diverse physical and chemical conditions. Their chemical compositions and bulk composition of their host can provide temperature constraints for the melts in which they dissolved or crystallized (Watson and Harrison 1983; Montel 1993). High elemental closure-temperatures and occurrence of only radiogenic Pb also make zircon and monazite ideal minerals for U-Th-Pb radioisotope dating of rocks. It is important, however, to

establish the origin of zircons and monazites in a rock to correctly interpret the U-Th-Pb analysis results. In igneous rocks that have assimilated older continental crust, inheritance of zircons and monazites from the crust leads to discordant ages with a higher intercept in Pb-isotope evolution diagrams corresponding to the age of the assimilated crust.

Zircons and monazites are rare in the Deccan Volcanics. Zircons have been reported from felsic rocks spatially and temporally associated with Deccan basalts in the Rajula area of

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Figure 1. (A) Location of Rajula on the Saurashtra Peninsula, Gujarat, India, the extent of the Deccan flood basalts, major rift zones and gravity anomaly over Rajula-Palitana-Sihor. (B) Details of the Rajula area showing location of major dikes and flows.

Saurashtra, Gujarat, India (Chatterjee and Bhattacharji 2001, 2002). In this preliminary study we also report the occurrence of monazite in the Rajula felsic rocks, present chemical composition and petrological significance of the zircons and the monazites and explore crustal melting behavior in the Rajula area of the Deccan volcanic province.

2. Geological setting

The Deccan Traps of India are associated with two prominent rift zones: the north-south western continental margin rift and the east-west intraplate Narmada-Tapti Rift (figure 1). The intersection of these two rifts is a region of high heat flow and

a +70 mGal gravity high (Kaila 1988), which can be explained by plume-related mantle upwelling (Bhattacharji *et al* 1996). The northward extension of the western continental margin rift is known as the Cambay Rift. The westward extension of the Narmada-Tapti rift is marked by ENE-WSW to NE-SW trending doleritic dike swarms outcropping as prominent ridges in the southern Saurashtra Peninsula of Gujarat, India (Auden 1949; Fedden 1884). The doleritic dikes are interspersed with clusters of rhyolite, trachyte and dacite dikes trending approximately NE-SW to NNE-SSW near Rajula (Misra 1981). The Rajula-Hindorna-Loingdi rhyolite dikes occur on the southwestern flank of a +40 mGal gravity high (Kaila 1988). Several N-S trending dolerite and granophyre (trachyte) dikes occur at Chamardi-Chogat, about

5 km northeast of Rajula (Misra 1981). These granophyre dikes are located on the western flank of the Cambay Rift and are parallel to it. At places, they cross-cut the NE-SW dikes showing offsets in some cases (figure 1) implying their relatively younger age.

3. Geochemistry and petrography

There is a prominent compositional gap in SiO_2 (between 59 wt% and 67 wt%), MgO and La contents between the basalts and the felsic rocks near Rajula precluding a fractional crystallization relation between the two rock types, although preliminary K-Ar dating indicates they are possibly coeval with both rock types straddling the ~ 65 Ma Cretaceous-Tertiary boundary (Chatterjee and Bhattacharji 2001). Trace element modeling indicates that the felsic rocks, with the exception of the trachytes of Chamardi-Chogat, originated by very high degrees of melting of the Proterozoic granitic crust into which the Deccan basaltic magma intruded (Chatterjee and Bhattacharji 2001). The heat for crustal melting was presumably supplied by the Deccan magma. The Chamardi-Chogat trachytes possibly originated by partial melting of previously emplaced basalts (Chatterjee and Bhattacharji 2001), with crustal contamination playing a secondary role.

The rhyolites are pink to grey with a glassy to hypocrySTALLINE, porphyritic texture. Phenocrysts of sanidine, anorthoclase, orthoclase, plagioclase, quartz and opaques, and occasionally augite have been reported in these rocks. The granophyres (trachytes) are fine grained and consist of quartz-feldspar $\pm$ amphibole. Zircons and monazites are present in both rhyolites and trachytes. Other accessory phases include allanite and REE rich Ca-carbonates in the trachytes. In the rhyolites, the zircons are about $100\text{ }\mu\text{m}$ in the longest dimension, subhedral to euhedral, and have oscillatory zoning, as seen in backscattered electron and cathodoluminescence images (figure 2A–D). In the trachytic granophyres, the zircons are irregular, $10\text{--}20\text{ }\mu\text{m}$ in size, and occur as clusters (figure 2E and F). They are sometimes associated with ilmenite and apatite. Monazite occurs in clusters of small grains up to $10\text{ }\mu\text{m}$ in size.

4. Analytical methods

Backscattered electron and cathodoluminescence images of zircons were obtained with a JEOL-733 Superprobe at the Massachusetts Institute of Technology. Chemical composition of the zircons and monazites were also obtained with the same

instrument with a beam energy of 15 keV, a probe current of 300 nA and typical counting times of 240 sec per element. In zircons, the standard deviation (1σ) of counts were 1–6% for Y, 0.1% for Zr, 0.4% for Hf, 60% for La, 4–20% for Ce, 6–60% for Nd, 2–11% for Th and 3–20% for U. In monazites, the 1σ standard deviations of counts were 1–2% for Y, 0.1% for La, Ce and Nd, 19% for Pb, 0.2–2% for Th and 18% for U. $\text{UM}\beta$ was used for U measurement and the counts were corrected for Th interference. The Pb counts were corrected for La, Y and Th interferences. The background positions were carefully chosen to avoid secondary peak interferences and the detectors were optimally set for pulse-height-analysis. These analytical methods are similar to those described in Pyle *et al* (2002). The data were reduced with the CITZAF program (Armstrong 1995) using the atomic number correction of Duncumb and Reed, Heinrich's tabulation of mass absorption coefficients and the fluorescence correction of Reed.

5. Results

Results of the electron microprobe analysis are presented in tables 1 and 2. The HfO_2 values in zircons range 0.56–0.88 wt% with the zircon from the trachyte showing the lowest value. These values fall at the lower end of the published range of values for zircons in terrestrial felsic igneous rocks (Belousova *et al* 2002; Hoskin and Schaltegger 2003), which can contain up to 12.3 wt% HfO_2 (Uher *et al* 1998). Analysis of points along a core-to-rim traverse in a single zircon from a Hindorna rhyolite dike indicates a decrease in U and Th (except at the rim) and an increase in Hf from core to rim, whereas, Ce and Nd possibly show oscillatory behavior (figure 3). Y is low in the core, but increases and then decreases toward the rim. The Th/U ratio decreases from 1.2 in the core to 0.4 in the rim (table 1). Except for one analysis, the U, Th and Th/U values of the zircons in this study (table 1) are typical of zircons found in granitoid rocks (Belousova *et al* 2002). In a C1 chondrite-normalized plot, Ce shows a positive anomaly in the zircon from trachyte (figure 4A), and the Ce/Nd ratios are greater than 1 with a range of 1.7–5.6 (table 1). The REE results are thus in agreement with previous studies on zircons of granitoid and pegmatitic rocks, which indicate a characteristic positive Ce-anomaly in *in situ* zircon analyses related to the replacement of Zr^{4+} by large ionic radius- Ce^{4+} ion in the zircon structure (Belousova *et al* 2002; Hoskin and Schaltegger 2003). The zircons from rhyolite in this study are enriched in Y and light rare earth elements (LREE)

Figure 2. (A, C, E) Backscattered electron, and (B, D, F) cathodoluminescence images of zircons and surrounding phases in rhyolites (A, B: sample R-Hi-2 from Hindorna; C, D: sample Ra-4 from Rajula) and trachytes (E, F: granophyre sample CH-9 from Chamardi-Chogat) from the Rajula area of the Deccan Traps (see figure 1 for locations). In (B), points analyzed by electron microprobe from core to rim are visible. In (C), the phase in contact with zircon is ilmenite. (F) shows a cluster of small zircons among larger grains of other phases.

Table 1. *Electron microprobe analysis of zircons in felsic rocks of Rajula area.*

	R-Hi-2			R-Hi-2 zircon 3						CH-9
	zircon 1	zircon 2	zircon 3 avg	core					rim	zircon 1
Weight per cent										
SiO ₂	32.62	31.56	32.08	31.92	31.95	32.16	32.02	31.97	32.46	30.33
Al ₂ O ₃	0.011	0.005	0.006	bdl	bdl	bdl	0.003	0.006	0.025	0.076
FeO	0.449	0.410	0.132	0.105	0.114	0.108	0.115	0.130	0.218	0.231
CaO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.136
P ₂ O ₅	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.203
Y ₂ O ₃	0.212	1.330	0.522	0.625	0.992	0.435	0.331	0.351	0.400	3.920
ZrO ₂	65.63	64.32	65.20	64.68	64.14	65.40	65.68	65.72	65.60	58.15
La ₂ O ₃	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.008
Ce ₂ O ₃	0.018	0.036	0.032	0.034	0.036	0.032	0.044	0.030	0.014	0.162
Nd ₂ O ₃	0.005	0.017	0.010	0.006	0.010	0.008	0.026	0.007	0.003	0.071
HfO ₂	0.761	0.660	0.751	0.694	0.691	0.744	0.759	0.736	0.882	0.560
ThO ₂	bdl	0.210	0.078	0.166	0.108	0.034	0.034	0.029	0.094	1.287
UO ₂	0.011	0.155	0.104	0.137	0.106	0.062	0.053	0.046	0.220	0.170
Total	99.72	98.70	98.92	98.37	98.15	98.98	99.07	99.02	99.91	96.30
Parts per million										
Th	bdl	1842	682	1458	952	299	297	255	830	11314
U	97	1362	919	1211	938	548	470	403	1942	1496
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	5252
Hf	6455	5600	6368	5883	5859	6312	6436	6238	7478	4749
Zr	485850	476200	482683	478800	474800	484200	486200	486500	485600	430450
Y	1670	10471	4113	4919	7812	3425	2603	2766	3153	30870
La	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	64
Ce	154	307	272	293	311	274	379	256	118	1383
Nd	39	147	85	52	82	72	221	57	29	613
ΣLREE	193	454	357	345	393	346	600	313	147	2060
Ratio										
Th/U		1.4	0.7	1.2	1.0	0.5	0.6	0.6	0.4	7.6
Zr/Hf	75.3	85.0	75.8	81.4	81.0	76.7	75.5	78.0	64.9	90.6
Ce/Nd	4.0	2.1	3.2	5.6	3.8	3.8	1.7	4.5	4.1	2.3

1σ Analytical uncertainties are Y: 1–6%, Zr: 0.1%, Hf: 0.4%, La: 60%, Ce: 4–20%, Nd: 6–60%, Th: 2–11% and U: 3–20%; bdl: Below detection limit.

with Y ranging 1670–10471 ppm and total LREE (ΣLREE) ranging 193–600 ppm. Highest Y content previously analyzed in zircons from granitoid rocks is 6.8 wt% (Belousova *et al* 2002). The zircon from trachyte contains an order of magnitude higher Y and ΣLREE. Although the Y and ΣLREE contents of the zircons in this study are within the range found in zircons of granitoid rocks (Belousova *et al* 2002), the possibility of tiny xenotime or monazite inclusions within the zircon from trachyte cannot be excluded given its high Ca, P and Th contents (table 1). In a Y versus U discriminant plot (Belousova *et al* 2002), the zircons of this study fall in the granitoid or syenite pegmatite field.

The monazites analyzed in this study contain 0.24–0.3 La, 0.49–0.52 Ce and 0.14–0.18 Nd atoms for four atoms of oxygen (table 2). The La and

Ce values are higher than average values of these elements in metamorphic monazites (Spear and Pyle 2002). Consequently, the monazites of this study have high Ce/Nd ratios (2.8–3.6, table 2). The Y (except in monazite3), Th and U values are near the lower end of ranges given in Spear and Pyle (2002). Th and U show positive anomalies in a C1 chondrite-normalized plot except in one analysis (figure 4B). The high Y content of monazite3 (figure 4B, table 2) may be due to xenotime substitution in the monazite structure. In addition, this monazite shows no Th positive anomaly and Pb and U are below detection limit. Since Pb in monazite is mostly of radiogenic origin, the low Pb content of monazite3 is possibly a consequence of its low U and Th content.

Table 2. *Electron microprobe analysis of monazites in a trachyte of Rajula area.*

	monazite 1	monazite 2	monazite 3
Weight per cent			
SiO ₂	0.502	0.448	0.289
Al ₂ O ₃	0.914	bdl	0.531
CaO	0.068	0.119	0.170
P ₂ O ₅	31.10	30.94	29.74
Y ₂ O ₃	0.269	0.327	0.827
La ₂ O ₃	19.72	16.49	20.77
Ce ₂ O ₃	35.49	34.87	36.32
Nd ₂ O ₃	11.10	12.61	10.14
PbO ₂	0.013	0.014	bdl
ThO ₂	1.145	2.111	0.167
UO ₂	bdl	0.006	bdl
Total	100.32	97.94	98.95
Formula			
Si	0.0190	0.0174	0.0113
Al	0.0408		0.0245
Ca	0.0028	0.0049	0.0071
P	0.9972	1.0196	0.9850
Y	0.0054	0.0068	0.0172
La	0.2755	0.2367	0.2996
Ce	0.4922	0.4969	0.5201
Nd	0.1502	0.1753	0.1416
Pb	0.0001	0.0001	
Th	0.0099	0.0187	0.0015
U		0.0001	
O	4	4	4
ΣCation	1.9930	1.9760	2.0080
Parts per million			
Th	10062	18549	1471
U	bdl	51	bdl
Pb	113	122	bdl
P	135729	135031	129794
Y	2115	2577	6515
La	168200	140600	177100
Ce	303000	297700	310100
Nd	95200	108100	86900
ΣLREE	566400	546400	574100
Ratio			
Th/U		363.7	
Th/Pb	89.0	152.0	
Ce/Nd	3.2	2.8	3.6

All analyses are from sample CH-9;
1σ Analytical uncertainties are Y: 1–2%, La,Ce,Nd: 0.1%,
Pb: 19%, Th: 0.2–2% and U: 18%;
bdl: Below delection limit.

6. Discussion

Field relations such as coexistence and structural conformity of the rhyolite dikes with Deccan basaltic dikes, rare presence of dacite and andesite that resulted from crustal assimilation by Deccan basalt and K-Ar age determinations indicate that the rhyolites near Rajula are coeval with the Deccan basalts. Here we evaluate whether the zircons and monazites in the felsic rocks near Rajula can be used for precise U-Th-Pb dating.

Since the Rajula rhyolites originated by crustal anatexis (Chatterjee and Bhattacharji 2001), it is important to determine whether the zircons and monazites within them are inherited from the crust or crystallized from the rhyolitic melt. Relative variation of trace elements in the felsic rocks near Rajula indicates that zircon, monazite, apatite and ilmenite were involved in the differentiation of the felsic rocks (figure 5). A positive correlation of Zr with Y and Ce (in each sub-area) is possibly related to zircon fractionation, whereas, a positive correlation of P₂O₅ with CaO and Ce may be due to apatite and monazite fractionation. Both Zr and P₂O₅ are also positively correlated with TiO₂ possibly indicating ilmenite co-crystallization. A negative correlation of Zr with Th and P₂O₅ perhaps indicates a lesser role of monazite/apatite compared to zircon in the differentiation of these rocks.

6.1 Zircon

Zircon plays an important role in fractionation of rhyolites (Evans and Hanson 1993). Hf concentration in zircon increases with magmatic differentiation (Wark and Miller 1993). In a zircon from Hindorna (figure 2), Hf increases from core to rim (figure 3) perhaps indicating fractional crystallization of this zircon during the differentiation of the host liquid. For Ce, Nd and Y concentrations measured at the core and rim of this zircon (figure 3), distribution coefficients (^{zircon/melt}D_M, where M is Ce, Nd or Y) of 0.9–2.3 for Ce, 0.5–1.1 for Nd and 43–87 for Y are required to reproduce the Ce, Nd and Y concentrations of the Hindorna rhyolites (as in Chatterjee and Bhattacharji 2001). These values compare favorably with the ^{zircon/melt}D_M determined by Thomas *et al* (2002, 2003) on quartz-diorites and rhyolites. Hence, it is possible that the zircon of figure 2 crystallized from a Hindorna rhyolitic melt. However, the relatively low Y in the center compared to the other parts of the zircon in figure 2 may imply a small, inherited core from the crust. Preliminary U-Pb isotopic analyses (unpublished data) also yield concordant

Figure 3. Core-to-rim traverse showing elemental concentrations in a zircon from Hindorna rhyolite R-Hi-2 (figure 2A, B). Error bars represent the highest observed analytical uncertainties in terms of 1σ standard deviation of counts (see section on analytical methods).

Figure 4. C1 chondrite-normalized (McDonough and Sun 1995) incompatible element contents of (A) zircons and (B) monazites from felsic rocks of the Rajula area. For analytical uncertainties, see section on analytical methods.

as well as discordant ages in a Pb-isotope evolution diagram, possibly due to the older inherited crustal cores.

The experimental study of Watson and Harrison (1983) suggests that Zr-saturated rhyolitic melts contain approximately 500–1500 ppm Zr at 930°C, and 1200–3500 ppm Zr at 1020°C. Zr content of

the Rajula rhyolites range 308–517 ppm (Chatterjee and Bhattacharji 2001). The zircon saturation equation of Watson and Harrison (1983) predicts that zircon with Zr-contents as in table 2 will be dissolved in Rajula (Hindorna) rhyolitic and trachytic melts above approximately 890°C and 868°C, respectively. Since inherited crustal cores

Figure 5. Trace element variations as a function of P_2O_5 (A–D) and Zr (E–H) concentrations in felsic rocks of the Rajula area (data from Chatterjee and Bhattacharji 2001). Elemental concentrations are in ppm and oxides are in wt%.

are probably present in the zircons, these calculated temperatures on the basis of Zr-contents might represent approximate maximum temperatures attained by the crustal country rocks of this region. However, kinetics also played a role on the survival of zircon cores during dissolution and slightly higher temperatures cannot be ruled out.

6.2 Monazite

Monazite solubility depends on temperature, composition and H_2O -content of the liquid (Rapp and Watson 1986; Montel 1986). The monazite saturation equation of Montel (1993) predicts that the Rajula rhyolitic and trachytic melts (bulk REE

contents from Chatterjee and Bhattacharji 2001) will dissolve monazite above 855–915°C and 805–818°C, respectively, under anhydrous conditions. If loss-on-ignition values (0.8–2.9 wt%, Chatterjee and Bhattacharji 2001) of the rhyolites and trachytes are assumed to be the H₂O contents of the melts, the saturation temperatures will be lower by about 50°C. These temperatures are in good agreement with the zircon saturation temperatures predicted with the equation of Watson and Harrison (1983). Monazite stability, however, depends on complex REE interactions among all different REE-bearing phases that can occur in the crust (Bea 1996).

Whether or not crustal monazite was completely consumed during melting can be evaluated from the measured monazite compositions (table 2). Pb was detected and analyzed in two of the monazites. Assuming this Pb is fully of radiogenic origin, the Pb-evolution equation (e.g., Montel *et al* 1996) yields chemical ages of 252 and 147 Ma for these two monazites. Even though these ages are highly uncertain because of only two analyses and high uncertainties in Pb and U measurements, they prove that these monazites predate the Deccan event and must have been inherited from the crust by the felsic melt. Monazite crystallization as overgrowths, however, cannot be ruled out because of a positive correlation between Ce and P₂O₅ in the bulk composition of the samples of Rajula area (figure 5B). For cooling rates of 10–1000°C/Ma, Pb is essentially immobile in 10 µm-sized monazites up to temperatures of 925–1050°C (Cherniak *et al* 2004). For isothermal heating, however, a 10 µm-sized monazite grain would lose approximately 15% of its Pb by volume diffusion if heated at 900°C for 1–2 million years (Cherniak *et al* 2004), which is the approximate duration of Deccan eruptions. Since the melt temperature could have been up to 915°C (see above) and most of the monazites in these rocks are less than 10 µm in size, it is plausible that some Pb has been lost from the monazites. These monazites may thus be older than their calculated chemical ages.

6.3 Crustal melting around Rajula

Composition of primitive picrites of Gujarat yields potential temperatures of 1430–1468°C for the intruding Deccan magma (Melluso *et al* 1995). Yet, zircon and monazite saturation thermometry indicates that the maximum temperatures attained by the crust near Rajula were probably not much higher than 900°C. Annen and Sparks (2002) parameterized experimental data on crustal melting to predict melt fraction and temperature of crust due to repetitive emplacement of basalts at different time intervals. These authors predict that

a fertile upper crust can be heated to 900°C and melted 65% at 20 km depth by dry basalt at 1300°C intruding at the rate of 50 m every 10 000 years for 1.6 million years. Deccan magma production rates are uncertain, but rates of 26–40 m per 10 000 years (Sen 1995, assuming an aerial extent of 1 million km²) were possible. If the Deccan Traps were emplaced over 1–2 million years, it is possible that picritic magma at ~1450°C heated granitic crust to ~900°C and produced high fractions of melt. We have shown through trace element considerations that high fractions of melting occurred in the crust around Rajula (Chatterjee and Bhattacharji 2001), and through zircon and monazite saturation thermometry that the crust was heated to about 900°C. It must be noted, however, that only minor volumes of felsic volcanic rocks are exposed among the Deccan Volcanics. Hence, melting was probably localized and aided by local crustal heterogeneities. A 1–2 million year emplacement time for the Deccan basalts seems appropriate since faster emplacement rates would heat and melt the crust quickly (Annen and Sparks 2002) and produce a more extensive felsic province.

7. Conclusion

The felsic dikes associated with Deccan Volcanics near Rajula, Gujarat, India contain zircons that crystallized from anatectic felsic melts, although small cores inherited from the crust are possibly present. Hf zoning profile of a zircon suggests that it grew from the host melt during melt-differentiation, and Y and LREE contents indicate that this zircon may have crystallized from the host melt. Pb-content of monazites in trachytes indicates that inherited crustal cores are most likely present. Monazite overgrowth rims may have crystallized from the felsic melts. Zircons and monazites of the felsic rocks around Rajula thus may be analyzed for U-Th-Pb isotopes for age determination with due consideration to crustal inheritance. Temperature estimates from zircon and monazite saturation thermometry indicate that the crust around Rajula may have been heated to a maximum of approximately 900°C by the intruding Deccan magma. Crustal melting models indicate that a 1–2 million year emplacement time for the Deccan Traps may be appropriate for crustal melting characteristics observed in the Rajula area through the study of the felsic intrusive rocks.

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