Zr-rich garnet and Zr- and Th-rich perovskite from the Polino carbonatite, Italy

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Abstract

Th- and Zr-bearing perovskite and Zr-rich Ti garnet are described from the Polino calcite carbonatite, Italy. The garnets contain 6.05–7.50 wt.% ZrO_2 in cores and up to 15.80 wt.% in rims. Silicon is low in these garnets and substantial Al and Fe^{3+} has been assigned to the tetrahedral sites. A strong correlation of Si with Zr from published data suggests the possibility that some Zr may also be tetrahedrally coordinated. However, the chemistry alone does not constrain the site distribution of Fe, Ti, Zr and Mg unambiguously. The perovskites are very unusual in containing 2.81–3.27 wt.% ZrO_2 and 1.48–1.71 wt.% ThO_2. For comparison, new analyses are presented of the zirconium garnet kimzeyite and coexisting perovskite from the type locality at Magnet Cove.

KEYWORDS: garnet, perovskite, zirconium, thorium, carbonatite, Italy.

Introduction

THE recently discovered Polino carbonatite is located near Terni, Umbria, central Italy. It is part of the Umbria–Latium ultra-alkaline district, which includes leucite–olivine, kalsilite and leucite–wollastonite melilitites and carbonatitic melilitites (Lupini and Stoppa, 1990; Stoppa *et al.*, 1991; Stoppa and Lavecchia, in press). Polino is a small (40 m diameter) diatreme filled with a breccia of massive carbonatite and Liassic sedimentary limestone blocks, ranging from a few millimetres to less than one metre in diameter, set in a carbonatitic lapilli matrix (Lupini and Stoppa, 1991).

The massive carbonatite blocks are light grey, of an even, fine-grained texture and contain micro-xenocrysts of forsteritic olivine and phlogopite, and crystals of Zr-rich garnet and Th-rich perovskite, both less than 2% modally, as well as Fe–Ti oxides in a cryptocrystalline groundmass of calcite and amoeboid blebs of coarser calcite. The olivine (Fo_{93-94}) is rimmed by monticellite, which also forms small subhedral crystals and is plentiful in the matrix; the phlogopite generally forms discrete crystals but may occur in micro-nodules with olivine. The matrix calcite contains significant Sr and Ba (SrO = 0.88%, BaO = 0.37%), but in the amoeboid calcite, which is probably a vesicle filling, these elements were not detected.

Polino zirconian garnet

The garnets are equidimensional, subhedral and often have slightly curved margins. They are generally inclusion-free, 10–25 μm in diameter and are reddish brown in transmitted light. From backscattered electron images the cores of the crystals appear to be unzoned, but thin (2–3 μm) discontinuous, chemically distinct rims are present on some crystals.

Analyses were performed using a Cambridge Instruments Microscan 9 wavelength-dispersive electron microprobe at the Natural History Museum, London, and with a JEOL JXA 8600 microprobe at the University of Bristol.

Sixteen separate crystal cores were analysed, for which the mean and standard deviations are presented in Table 1, together with separate analyses of three rims and two associated cores. The ZrO_2 range in the cores is 6.05–7.50 wt.%, but is significantly larger in the rims (8.28–15.80 wt.%). The TiO_2 values range from 14.21 to 15.61 wt.% in cores, and from 10.19 to 13.65 wt.% in

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TABLE 1. ANALYSES OF ZR-RICH GARNETS FROM POLINO AND KIMZEYITE FROM MAGNET COVE

					POLINO			MAGNET COVE KIMZEYITE	
	MEAN(16)[1] CORE	STD.DEV. (σ_{n-1})	CORE 1	RIM 1	CORE 2	RIM 2	RIM	MEAN(5)[2]	*
SiO_2	24.53	0.37	24.11	23.80	25.00	23.72	21.29	11.08	9.60
TiO_2	15.12	0.32	15.11	13.65	14.21	11.45	10.19	5.80	5.00
ZrO_2	6.78	0.43	6.26	8.28	6.75	11.21	15.80	29.24	29.90
HfO_2	<.2	-	<.2	<.2	<.2	0.32	-	<.2	-
Nb_2O_5	<.1	-	<.1	<.1	<.1	<.1	<.1	<.1	0.75
Al_2O_3	4.21	0.12	4.21	4.47	4.24	4.37	3.82	7.07	11.00
Y_2O_3	0.09	0.05	0.08	0.16	0.13	0.15	<.05	0.13	-
Ce_2O_3	0.33	0.07	0.33	0.19	0.31	0.17	0.19	0.10	-
Nd_2O_3	0.24	0.06	0.23	0.23	0.24	0.24	-	<.1	-
Fe_2O_3	15.21	0.51	15.59	15.11	15.54	15.00	14.75	14.70	13.40
FeO	-	-	-	-	-	-	-	-	0.8
MnO	<.05	-	<.05	0.05	0.05	<.05	<.05	0.09	0.10
MgO	2.59	0.12	2.41	2.60	2.59	2.29	1.97	0.35	0.50
CaO	31.61	0.43	31.27	31.65	31.20	31.00	30.76	30.92	29.80
ThO_2	0.41	0.07	0.40	0.00	0.45	0.15	-	<.1	-
TOTAL	101.13		100.00	100.19	100.71	100.07	98.77	99.48	100.85
				CATIONS TO 24 OXYGENS					
Si+4	4.171	0.052	4.137	4.095	4.255	4.139	3.850	2.170	1.860
Al+3	0.837	0.027	0.852	0.907	0.850	0.898	0.814	1.632	2.512
Fe+3(TET)	0.992	0.062	1.011	0.998	0.895	0.963	1.336	2.166	1.628
TETRAHEDRAL	6.000		6.000	6.000	6.000	6.000	6.000	5.968	6.000
Fe+3(OCT)	0.953	0.078	1.002	0.959	1.095	1.006	0.671	0.000	0.325
Fe+2	-	-	-	-	-	-	-	-	0.130
Ti+4	1.933	0.039	1.950	1.766	1.818	1.502	1.386	0.854	0.728
Zr+4	0.562	0.035	0.524	0.695	0.560	0.954	1.393	2.792	2.825
Hf+4	0.000	0.000	0.000	0.000	0.000	0.017	0.000	0.000	0.000
Nb+5	-	-	-	-	-	-	-	-	0.069
Mg+2	0.452	0.028	0.427	0.552	0.417	0.438	0.504	0.102	0.144
OCTAHEDEDRAL	3.901		3.903	3.972	3.890	3.917	3.954	3.748	4.222
Ca+2	5.758	0.081	5.750	5.835	5.689	5.794	5.960	6.487	6.186
Mg+2	0.181	-	0.190	0.115	0.240	0.158	0.027	0.000	0.000
Mn+2	0.000	0.000	0.000	0.008	0.008	0.000	0.000	0.015	0.016
Y+3	0.009	0.005	0.008	0.015	0.012	0.015	0.000	0.014	0.000
Ce+3	0.021	0.004	0.022	0.012	0.019	0.011	0.013	0.007	0.000
Nd+3	0.015	0.004	0.015	0.015	0.015	0.016	0.000	0.006	0.000
Th+4	0.016	0.002	0.016	0.000	0.017	0.006	0.000	0.000	0.000
DODECAHEDRAL	6.000		6.000	6.000	6.000	6.000	6.000	6.529	6.202
TOTAL	15.901		15.903	15.972	15.890	15.916	15.954	16.245	16.424

All Fe as Fe_2O_3
Ba, La, Pr, Sm, Gd, Dy, U below detection limit
* from Milton et al., 1961
1 = mean of 16 spot analyses of crystal cores
2 = mean of 5 spot analyses, kimzeyite, sample BM1963,392

the rims. The garnets are thus zirconian schorlomites.

The structural formulae have been calculated on the basis of 24 oxygens. The low Si content of these garnets indicates that the tetrahedral sites contain only just over 4 Si atoms. Complete occupancy of tetrahedral sites can be achieved by assigning all the available Al and about half of the Fe (calculated as Fe^{3+}), to tetrahedral coordination. The correct assignment of Mg (and Fe) into the remaining octahedral and dodecahedral sites poses a problem for the Zr-rich garnets. Assigning the balance of the Fe, Ti and Zr, plus Mg to the octahedral sites gives totals in excess of 6 atoms. Placing all the Ca, Mn and Mg in the dodecahedral site, also leads to totals which are too high. A better balance is achieved if the Mg is distributed between the dodecahedral and octahedral sites, as was done for Stromboli kimzeyite by Munno *et al.* (1980), who justified this on the basis of microprobe analyses, site occupancy refinement and known spectral data, and this procedure has been followed in Table 1 for the Polino analyses.

The tetrahedral site preference in Fe- and Ti-rich garnets is Al > Fe > Ti (Huggins *et al.*, 1977*a*) and it has been demonstrated (Huggins *et al.*, 1977*b*) that no single substitution is responsible for the introduction of all the Ti into the garnet structure. One of the five coupled substitutions defined by them involves the substitution of Ti^{4+} for Si^{4+}, concomitant with Al, Fe and Ti exchange reactions between the octahedral and tetrahedral sites. It is certainly this substitution that leads to the inverse correlation between Si and Ti in the Ti-rich garnets illustrated by Howie and Woolley (1968, Fig. 3). A similar phenomenon for Zr appears to take place in the Zr-rich garnets. Fig. 1 is a plot of Zr against Si for the Polino garnets together with data for Zr garnets from eight other localities (of which five are from carbonatites). The correlation is apparent. Although it is clearly necessary for other techniques to be applied to resolve the exact role of Zr in these garnets, the Si–Zr correlation demonstrated by Fig. 1 may be indicating that Zr, just like Ti, plays a complex role in these garnets and that a proportion of the Zr may be located in the tetrahedral sites. It is noteworthy that the plot of Ti against Si for the Zr-rich garnets (Fig. 2) does not show the inverse correlation reported for the Ti-rich garnets (cf. Fig. 2 with Howie and Woolley, 1968, Fig. 3). It is suggested that these

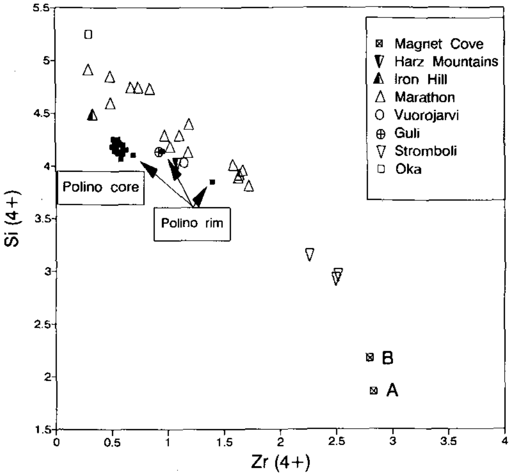

FIG. 1. Plot of Si against Zr (atoms per 24 oxygens) for Zr-bearing garnets. Filled squares, Polino garnets, this paper. Magnet Cove plot A = original analysis of Milton *et al.* (1961); B = new data this paper; Oka (Nickel, 1960); Harz (Koritnig *et al.*, 1978); Marathon dykes (Platt and Mitchell, 1979); Guli and Vuorijarvi (Borodin and Bykova, 1963); Stromboli (Munno *et al.*, 1980); Iron Hill (Dowty, 1971).

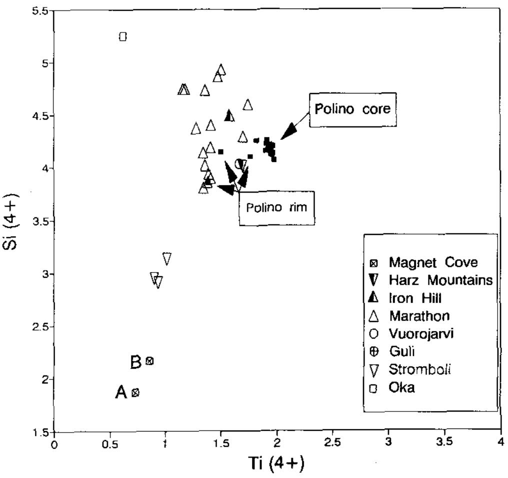

FIG. 2. Plot of Si against Ti (atoms per 24 oxygens) for Zr-bearing garnets to show that, unlike the titanium garnets containing little or no Zr, there is no inverse correlation.

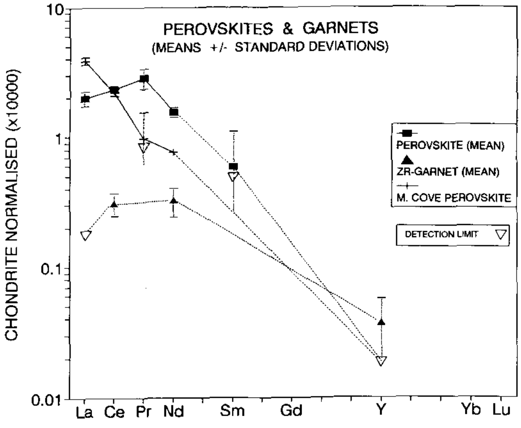

FIG. 3. Chondrite-normalised *REE* plots of means and standard deviations (error bars) in Polino garnets and perovskites, and perovskite from Magnet Cove.

TABLE 2. ANALYSES OF PEROVSKITES FROM POLINO AND MAGNET COVE.

	POLINO								MAGNET COVE BM1963,392	
	1	2	3	4	5	6	MEAN (6)	STD.DEV. (σ_{n-1})	MEAN	STD.DEV.
SiO_2	2.92	2.11	3.46	1.78	2.20	1.71	2.36	0.69	<.05	-
ThO_2	1.63	1.50	1.71	1.51	1.63	1.48	1.58	0.09	<.1	-
UO_2	<0.1	<0.1	<0.1	0.37	0.13	0.13	0.11	0.14	<.1	-
TiO_2	39.87	43.42	42.57	43.80	41.30	41.88	42.14	1.45	42.35	0.27
ZrO_2	3.25	3.11	3.27	3.22	2.94	2.81	3.10	0.19	0.62	0.12
HfO_2	0.31	<.2	<.2	0.26	<.2	<.2	<.2	-	<.25	-
Nb_2O_5	0.17	0.27	0.17	0.15	0.32	0.24	0.22	0.07	8.58	0.19
Al_2O_3	1.49	1.20	0.75	0.95	0.88	1.27	1.09	0.28	0.72	0.07
Fe_2O_3	6.10	5.41	6.10	5.48	5.49	5.52	5.67	0.31	5.42	0.15
Y_2O_3	<.05	<.05	<.05	0.06	<.05	<.05	<.05	-	<.05	-
La_2O_3	0.63	0.81	0.80	0.74	0.81	0.95	0.79	0.10	1.53	0.05
Ce_2O_3	2.25	2.47	2.49	2.65	2.56	2.46	2.48	0.13	2.34	0.08
Pr_2O_3	0.42	0.39	0.44	0.40	0.48	0.27	0.40	0.07	0.14	0.13
Nd_2O_3	0.95	1.23	1.19	1.19	1.17	1.20	1.16	0.10	0.57	0.03
Sm_2O_3	0.14	0.22	<.12	0.15	<.12	0.29	0.13	0.12	<.12	-
MgO	0.27	0.23	0.73	0.15	0.23	0.25	0.31	0.21	<.05	-
CaO	37.51	36.73	37.47	37.63	37.38	36.80	37.25	0.39	37.08	0.16
SrO	0.29	0.25	0.21	0.22	0.26	0.25	0.25	0.03	0.17	0.05
BaO	0.25	0.27	0.09	0.13	0.13	0.07	0.16	0.06	<.1	-
Na_2O	0.12	0.14	0.12	0.32	0.02	0.02	0.12	0.11	0.16	0.11
TOTAL	98.57	99.76	101.57	101.16	97.93	97.60	99.32		99.67	

CATIONS TO 24 OXYGENS

	1	2	3	4	5	6	MEAN (6)	STD.DEV. (σ_{n-1})	MEAN	STD.DEV.
Si+4	0.570	0.405	0.650	0.341	0.433	0.338	0.457	0.116	0.004	0.003
Al+3	0.343	0.272	0.166	0.214	0.204	0.296	0.249	0.060	0.163	0.016
Fe+3	0.851	0.782	0.862	0.789	0.813	0.805	0.817	0.030	0.789	0.021
Mg+2	0.079	0.066	0.204	0.043	0.068	0.074	0.089	0.053	0.013	0.009
Ti+4	5.856	6.273	6.012	6.301	6.116	6.218	6.131	0.156	6.158	0.032
Zr+4	0.310	0.291	0.299	0.300	0.282	0.271	0.292	0.013	0.058	0.011
Hf+4	0.017	0.000	0.000	0.014	0.000	0.000	0.000	0.008	0.000	0.000
Nb+5	0.015	0.023	0.014	0.013	0.028	0.021	0.019	0.006	0.750	0.016
SUM	8.040	8.113	8.208	8.015	7.945	8.022	8.054	-	7.936	-
Y+3	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.002	0.005	0.003
Na+1	0.045	0.052	0.044	0.119	0.008	0.008	0.045	0.037	0.061	0.042
Ca+2	7.849	7.560	7.540	7.713	7.886	7.785	7.721	0.133	7.681	0.042
Th+4	0.072	0.066	0.073	0.016	0.073	0.066	0.070	0.021	0.000	0.000
U+4	0.004	0.004	0.004	0.000	0.006	0.006	0.007	0.002	0.000	0.000
Sr+2	0.033	0.028	0.023	0.024	0.030	0.029	0.028	0.003	0.020	0.006
Ba+2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
La+3	0.045	0.057	0.055	0.052	0.059	0.069	0.056	0.007	0.109	0.003
Ce+3	0.161	0.174	0.171	0.186	0.185	0.178	0.176	0.008	0.165	0.006
Pr+3	0.030	0.027	0.030	0.028	0.034	0.019	0.028	0.005	0.010	0.009
Nd+3	0.066	0.084	0.080	0.081	0.082	0.085	0.080	0.006	0.039	0.002
Sm+3	0.009	0.015	0.000	0.010	0.000	0.020	0.009	0.007	0.000	0.000
SUM	8.316	8.067	8.020	8.235	8.362	8.264	8.220	-	8.090	-
TOTAL	16.418	16.246	16.279	16.384	16.362	16.337	16.330	-	16.025	-

All Fe as Fe_2O_3
Mn, Gd, Dy below detection limit

observations may indicate that Zr^{4+} is more dominant than Ti^{4+} in controlling cation site locations in these complex substitutions.

Only Ce, Nd and Y of the rare earth elements (*REE*) were above the detection limit of the microprobe. The chondrite-normalised pattern for Zr garnet is presented in Fig. 3. The pattern shows a maximum at Nd which contrasts with reported data for *REE*-bearing garnets which are generally Y dominant (Deer *et al.*, 1982). The rims are enriched in Y and depleted in Ce relative to the cores, see Table 1, indicating fractionation towards heavy-*REE* enrichment during the garnet crystallisation history. The cores also contain detectable levels of Th, which were higher than those measured in the rims.

Polino perovskite

Perovskite is rather less abundant than garnet and forms smaller (5–10 μm), subhedral grains. There is no indication of zoning.

A range of analyses is given in Table 2. Two features are noteworthy: the ZrO_2 values range from 2.81 to 3.27 wt.% and the ThO_2 from 1.48 to 1.71 wt.%, which in combination possibly makes these perovskites unique. Comparable and higher Th values have been reported in the literature, for instance irinite contains 13.00% ThO_2 (Borodin and Kazakova, 1954) and lueshite from Kovdor 3.2% ThO_2 (Kukharenko *et al.*, 1965; Lapin and Kazakova, 1966) but these are both Nb-bearing varieties of perovskite. Usually, only very small amounts of Zr have been recorded in Nb-bearing perovskites, the only perovskite with high Zr being the mineral uhligite which, according to (Hauser, 1909), contains 21.95 wt.% ZrO_2. Vlasov (1966), however, considers that the original analysis may be in error.

The *REE* abundances are higher in the perovskite than in the garnet, but their chondrite-normalised patterns are broadly similar with maxima at Pr and Nd (Fig. 3).

Kimzeyite and perovskite from Magnet Cove

The most Zr-rich garnet plotted on Fig. 1 is the type kimzeyite from Magnet Cove, for which the analysis of Milton *et al.* (1961) (Fig. 1, point A) lies somewhat off the general trend. To check this, new analyses were undertaken of Magnet Cove kimzeyite from the Natural History Museum, London, collection (BM 1963,392). An average of the new analyses is given in Table 1 together with the original analysis of Milton *et al.* (1961). The new analysis shows a significantly higher value for SiO_2, a much lower value for Al_2O_3 and lower values for CaO and Fe_2O_3. Y_2O_3, Ce_2O_3 and Nb_2O_5 were not determined by Milton and are not present in significant amounts. In terms of Si and Zr the new analysis is plotted on Fig. 1 as point B and now lies closer to the projected trend.

In comparison with the Zr-rich garnets from Polino, kimzeyite from Magnet Cove has higher concentrations of Zr, Al and Nb, but is lower in Mg, Si, Ti and the *REE*.

Perovskite co-existing with the kimzeyite was identified and also analysed (Table 2). It is Nb-rich with relatively low Zr and undetectable Th. The total *REE* content is similar to that of perovskite from Polino, but is more light *REE* enriched, La being the maximum chondrite-normalised *REE* (Fig. 3).

The co-existing garnet–perovskite mineral pairs from Magnet Cove and Polino, which are both carbonatites with similar mineral assemblages, show surprisingly different mineral/mineral partition coefficients for Zr; K_D^{Zr} garnet/perovskite = 2.19 for Polino core but 47.2 for Magnet Cove. If in each case the two minerals are in equilibrium with each other, and the textural evidence does not indicate otherwise, such large differences in K_D are difficult to explain, but may reflect fundamental differences in *PT* conditions of crystallisation. The Polino diatreme is small and was probably emplaced very rapidly so that the carbonatite melt was quickly chilled from a high temperature. The Magnet Cove kimzeyite-bearing carbonatite, however, is a coarse vein facies and probably represents crystallisation of either a late, comparatively low temperature liquid, or possibly a late hydrothermal/carbothermal fluid.

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