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ANALYTICAL TECHNIQUES{*TC "*ANALYTICAL TECHNIQUES*"}*

Quantitative analyses of trace elements in garnet were obtained at the University of Huelva using a Hewlett Packard HP-4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with a CETAC LSX-100 laser ablation microprobe (LAM). Operational conditions for the ICP-MS instrument were the following: power: 1,350 kW; plasma argon flow rate, 14.0 L/min; auxiliar flow rate: 1.0 L/min; carrier gas flow rate: 1.20 L/min. The ablation was performed on Q-switched mode with a Nd YAG LASER, working at 254 nm wavelength. Calibration was performed using NIST SRM 612 (silicate glass with 40 ppm each element) analyzed four times before and two times after each run of sixteen samples. The laser was optimized to make a crater size smaller than 50 :m on the NIST SRM 612 standard. Internal standardization using ^{29}Si was employed to correct ablation differences resulting from differing ablation conditions between sample and reference materials. Data were acquired on selected isotopes using the instrument's time-resolved analysis (TRA) data acquisition software of the HP-4500. The TRA protocol permits observation of the signal for every element as a function of time and aids in detection of inclusions and chemical zonation (Longerich et al., 1996; Taylor et al., 1997). Analytical procedures and data reduction are after Longerich et al. (1996). Lower detection limits (L.D.L.) were calculated for each element using the formula derived by Longerich et al. (1996), and are lower than –0.4 ppm for REE. The precision and accuracy were determined on NIST SARM 612 by repeated analyses in every run (Table 1).

Major element compositions of all the studied garnets were determined with a LINK-ISIS energy-dispersive spectrometer mounted on a JEOL-JSM5410 scanning electron microscope (SEM-EDS) at the University of Huelva, Spain, and with the JEOL JXA 8600 Superprobe at the University of Georgia, USA.

TABLE 1. PRECISION AND ACCURACY OF LAM-ICP-MS ANALYSES OF STANDARD NIST 612

	NIST612 (this study n = 4)			NIST612		
	Mean	S	C.V.	Recommended	%diff.	L.D.L. (ppm)
Sc	42.77	4.04	9.45	41.05	4.20	0.33
V	39.65	0.93	2.34	39.22	1.10	0.12
Cr	38.16	1.89	4.95	39.88	4.30	1.09
Y	37.48	1.44	3.84	38.25	2.01	0.04
La	36.93	2.28	6.18	35.77	3.24	0.05
Ce	39.63	2.72	6.86	38.35	3.35	0.04
Pr	38.54	2.41	6.27	37.16	3.71	0.04
Nd	36.74	4.01	10.90	35.24	4.26	0.22
Sm	38.33	1.42	3.70	36.72	4.40	0.23
Eu	36.15	3.27	9.04	34.44	4.97	0.09
Gd	37.21	1.40	3.76	36.95	0.70	0.36
Dy	36.54	3.48	9.53	35.97	1.59	0.18
Er	38.67	2.53	6.54	37.43	3.30	0.21
Yb	41.23	2.03	4.93	39.95	3.21	0.40
Lu	40.52	3.35	8.28	37.71	7.45	0.06

Note: n: number of analyses; S: the sample standard deviation; C.V.= coefficient of variation; % diff.: the relative difference between the recommended values for NIST 612 (prefered values of Pearce et al. 1997) and those determined in this study; L.D.L.: Lower Detection Limit. Concentrations in ppm.

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Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Near C.R., and Chenery S.P., 1997, A compilation of New and Published Major and Trace Element Data for NIST SRM 610 AND NIST SRM 612 Glass Reference Materials: Geostandards Newsletter 21, p.115-144.

Taylor, R.P., Jackson, S.E., Longerich, P.H., and Webster, J.D., 1997, In situ trace-element analysis of individual silicate melt inclusions by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS): Geochim. Cosmochim. Acta 61 p.2559-2567.

TABLE 2. CHEMICAL DATA FOR ANALYZED GARNET CRYSTALS

Sample	RSR31B crystal 1						
Analysis	C3	C4	C5	C6	C7	C8	C9
	Rim						Rim
Distance (µm)	0	397	850	1392	1782	2256	2867
	Major elements (%wt)						
SiO_2	37.75	38.40	38.29	38.23	38.40	38.38	38.51
Al_2O_3	21.91	22.63	22.34	22.22	22.30	21.97	22.22
FeO	30.60	29.44	30.00	29.92	29.26	30.16	30.53
MgO	7.22	7.90	7.63	7.92	7.75	7.71	7.46
MnO	1.29	0.93	1.02	0.99	0.80	0.98	1.00
CaO	0.84	0.84	0.94	0.98	1.60	1.37	0.95
Total	99.61	100.14	100.22	100.26	100.11	100.57	100.67
	Trace elements (ppm)						
Sc	427.34	397.49	399.59	412.35	377.37	364.76	316.16
V	199.67	242.73	198.62	171.38	200.05	251.70	193.07
Cr	508.08	503.29	373.80	349.12	307.86	257.21	326.23
Y	485.94	489.03	487.19	917.08	5411.14	4352.00	755.11
La	0.00	0.37	0.01	0.16	0.63	1.09	0.11
Ce	0.09	0.85	0.09	0.53	2.73	2.45	0.15
Pr	0.17	0.14	<0.06	<0.06	0.65	0.48	<0.07
Nd	0.18	1.26	0.65	0.17	11.64	3.90	1.73
Sm	1.84	4.65	3.53	3.63	12.08	4.31	4.29
Eu	0.75	0.29	0.26	0.58	3.72	1.95	0.56
Gd	39.45	38.23	12.54	14.27	108.91	53.68	22.47
Dy	131.45	110.71	70.29	110.21	694.84	494.87	113.23
Er	36.77	37.44	35.25	107.95	811.87	736.85	81.75
Yb	11.37	21.57	17.00	71.62	840.55	811.40	54.49
Lu	2.46	3.74	1.97	6.67	125.99	118.04	8.15

Sample	RSR31B crystal 2					
Analysis	C10	C11	C12	C13	C14	C15
	Rim					Rim
Distance (µm)	0	316	679	954	1274	1563
	Major elements (%wt)					
SiO2	37.99	38.18	38.22	38.11	38.21	37.81
Al2O3	21.73	22.04	21.98	21.95	22.15	21.99
FeO	31.1	30.02	29.69	30.36	30.31	30.8
MgO	7.4	7.66	8.18	7.71	7.49	7.35
MnO	0.95	1.06	1.02	0.95	0.93	0.99
CaO	1.16	0.95	0.92	1.03	1.06	0.8
Total	100.33	99.91	100.01	100.11	100.15	99.74
	Trace elements (ppm)					
Sc	439.76	372.03	384.90	373.45	358.03	434.62
V	189.28	162.45	175.76	161.46	169.29	196.25
Cr	339.04	299.60	315.10	340.16	305.63	376.49
Y	489.83	529.09	577.58	601.94	520.34	507
La	<0.06	0.22	<0.06	0.14	0.52	0.13
Ce	0.30	0.02	0.21	<0.03	0.30	<0.03
Pr	<0.03	0.17	0.16	<0.03	0.28	0.04
Nd	<1.5	0.64	3.21	0.54	<0.06	<0.06
Sm	5.18	1.71	<0.08	3.07	0.78	0.17
Eu	<0.03	0.13	0.11	1.21	<0.03	0.45
Gd	21.78	12.80	15.22	20.41	9.15	19.51
Dy	94.50	77.30	74.49	79.43	70.34	70.26
Er	33.02	32.78	52.14	52.89	30.54	37.63
Yb	15.19	26.67	18.53	20.42	13.15	16.00
Lu	2.62	2.36	2.88	3.42	1.94	1.53

Sample	RSR-18 crystal 3									
Analysis	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12
	Rim					Mnz incl				Rim
Distance (µm)	0	278	578	940	1316	2051	2629	3022	3442	3807
	Major elements (%wt)									
SiO_2	39.24	39.54	38.56	39.05	38.7	39.09	39.13	39.38	38.94	39.11
Al_2O_3	22.45	22.69	22.32	22.6	22.32	22.4	22.66	22.14	22.32	22.16
FeO	26.35	25.99	26.3	26.97	26.08	25.42	25.35	25.61	26.64	26.69
MgO	9.89	10.34	10.31	9.95	10.52	10.36	10.22	10.73	10.56	10.19
MnO	0.75	1.08	1.18	0.85	0.88	1.02	1	0.82	0.95	0.84
CaO	1.63	1.44	1.29	1.3	1.19	1.49	1.5	1.06	1.14	1.14
Total	100.31	101.08	99.96	100.72	99.69	99.78	99.86	99.74	100.55	100.13
	Trace elements (ppm)									
Sc	315.06	386.83	411.93	390.09	509.28	650.41	554.60	590.44	456.17	402.23
V	199.31	196.96	140.39	142.79	104.08	102.82	119.80	103.38	97.73	115.66
Cr	1157.31	507.17	377.57	536.17	348.66	349.53	345.03	391.85	342.61	343.67
Y	1199.64	618.55	783.77	647.76	771.93	2244.52	2333.23	2266.06	1215.47	870.80
La	0.44	3.26	n.a.	1.66	0.34	854.42	12.12	1.57	1.84	0.38
Ce	0.36	5.91	0.63	3.25	0.95	1731.92	30.67	2.84	3.49	0.72
Pr	0.42	0.80	0.19	0.67	0.22	196.69	2.17	0.33	0.41	0.12
Nd	4.71	9.90	2.23	1.32	0.95	707.79	10.30	4.58	2.01	2.67
Sm	10.96	21.68	12.25	7.32	6.14	129.35	7.61	6.23	10.86	17.29
Eu	2.21	4.11	2.53	2.08	0.81	18.42	0.55	1.15	0.79	1.43
Gd	47.60	106.83	68.95	51.33	23.28	129.79	28.13	28.96	48.72	58.89
Dy	152.86	127.13	142.56	121.48	112.41	285.90	264.46	242.94	172.67	154.49
Er	153.14	47.19	68.52	47.70	58.27	381.74	466.02	394.50	124.60	77.17
Yb	151.72	28.46	76.98	35.76	28.01	684.01	795.25	493.28	104.79	67.45
Lu	20.23	3.15	10.33	4.85	3.29	102.32	127.91	70.63	15.32	9.42

TABLE 3. BULK AND TRACE ELEMENTS COMPOSITIONS OF SAMPLES RSR31B AND RSR18

Sample	RSR31B	RSR18		RSR31B	RSR18
	Major elements (% wt)			Trace elements (ppm)	
SiO_2	61.10	57.57	Cr	79	73
TiO_2	1.19	1.66	Ni	46	57
Al_2O_3	17.61	17.35	Co	28	23
FeO_T	8.52	12.94	Sc	14	21
MnO	0.15	0.27	V	126	69
MgO	3.55	6.21	Zn	116	56
CaO	1.26	1.87	Rb	72	6
Na_2O	1.95	0.82	Cs	4	1
K_2O	3.85	0.19	Ba	526	20
P_2O_5	0.07	0.03	Sr	122	36
LOI	0.84	0.78	Y	29	68
Total	100.09	99.69	Th	10	5
			La	25.8	12.7
			Ce	62	23
			Pr	7.6	2.9
			Nd	28	11
			Sm	5.7	2.7
			Eu	1.3	0.5
			Gd	5.2	5.1
			Tb	0.9	1.3
			Dy	5.9	11.2
			Ho	1.2	2.7
			Er	3.7	8.2
			Tm	0.5	1.2
			Yb	3.5	7.2
			Lu	0.5	1.0

TABLA 4. RESULTS OF THE CALCULATION OF GARNET/MATRIX BULK PARTITION COEFFICIENTS

	Initial bulk rock abundance (M^O)*	Concentration in garnet core†		$D^{garnet/matrix}$ §	
		Crystal 1 RSR31B	Crystal 3 RSR18	Crystal 1 RSR31B	Crystal 3 RSR18
Gd	6.3	109	130	< 17	< 21
Dy	5.3	490 – 695	264 – 286	92 - 131	50 - 54
Er	3.2	736 – 812	382 – 466	230 - 254	119 - 146
Yb	3.0	811 – 840	684 – 795	270 – 280	228 – 265
Y	29	4350 – 5411	2244 – 2333	150 – 187	77 – 80

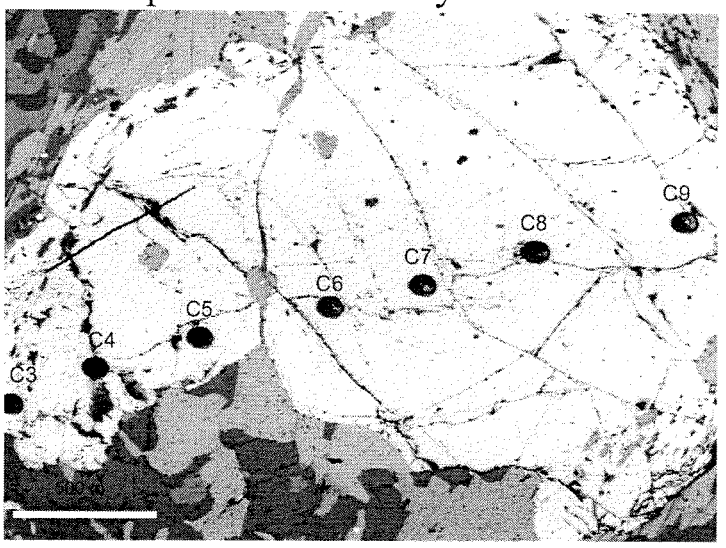
* The values are averages of bulk rock concentrations in subsolidus upper amphibolite facies gneisses from Sierra de Comechingones (Type I gneisses, see Otamendi and Patiño Douce, 2001, for petrographic details and full analyses). Concentration ranges in these rocks (in ppm) are as follow Gd: 5.6–7.9; Dy: 4.8–6.9; Er: 2.6–4.2; Yb: 2.3–4.0; Y: 24–36.

† The values used correspond to the spot analysis that yield the highest Y and heavy rare earth element concentration. These values were chosen because the strategy used to estimate values of D relies on using trace element concentrations at the beginning of garnet crystallization and these trace elements are known to be strongly compatible in garnet (see text). Typical uncertainties for our laser ablation microprobe analyses are: Gd: ± 5 ppm; Dy: ± 20 ppm; Er: ± 30 ppm; Yb: ± 40 ppm; Y: ± 150 ppm. Full analytical data, including discussion of analytical uncertainties, are given in this GSA Data Repository.

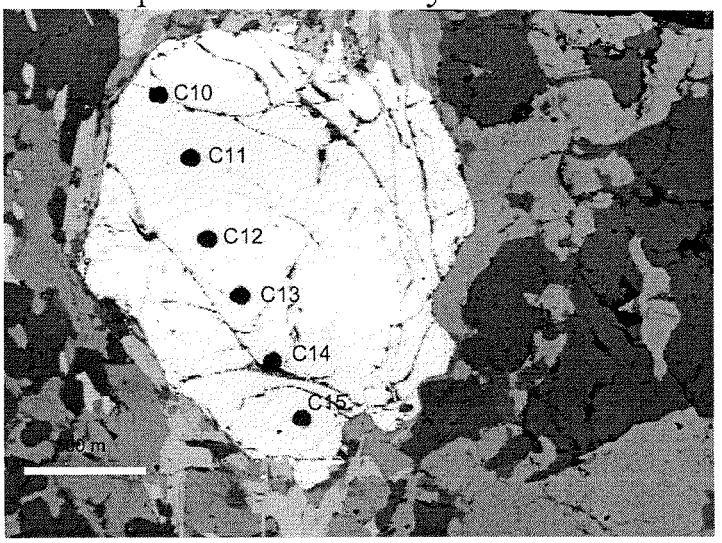
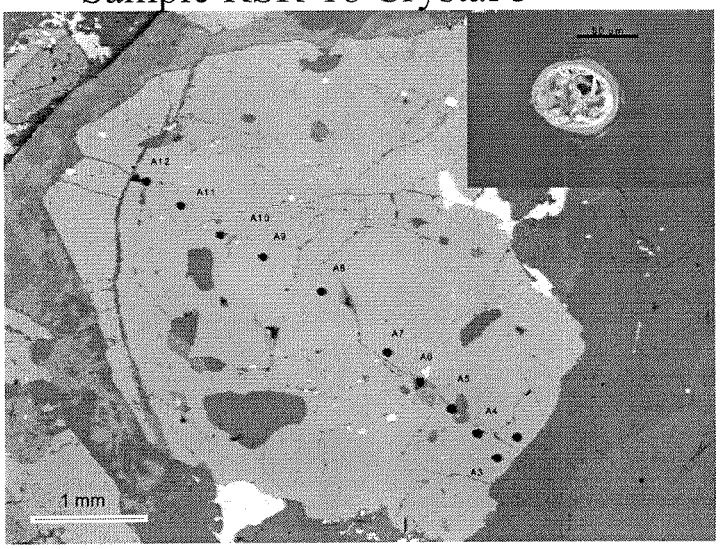
§ Effective garnet / matrix partition coefficients calculated with equation 1 (see text), for the limiting case $W^G = 0$ (i.e., at the beginning of garnet crystallization, see text)

Backscattered-electron images of analyzed garnet crystals

Sample RSR-31B Crystal 1



Sample RSR-31B Crystal 2



Sample RSR-18 Crystal 3