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Article in *Chemical Geology* · November 2008

DOI: 10.1016/j.chemgeo.2008.09.002

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The effect of titanite and other HFSE-rich mineral (Ti-bearing andradite, zircon, eudialyte) fractionation on the geochemical evolution of silicate melts

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ARTICLE INFO

Article history:

Received 18 June 2008

Received in revised form 1 September 2008

Accepted 2 September 2008

Editor: R.L. Rudnick

Keywords:

Alkaline rocks

Titanite

Eudialyte

Ti-bearing andradite

High field strength elements

ABSTRACT

We present trace element data for HFSE-rich minerals (titanite, eudialyte, Ti-bearing andradite, zircon) from plutonic rocks of the Eocene Tamazeght complex, High Atlas Mountains, Morocco. In most lithologies significant amounts of titanite are present and as such, titanite fractionation played a major role in the evolution of the HFSE budget of the whole complex. By combining our data with published titanite–melt partition coefficients we explore the effects of titanite fractionation on the evolution of geochemical parameters (Zr/Hf, Nb/Ta, La/Lu and Th/U ratios) during differentiation of silicate melts in detail. Based upon this, we further discuss the genetic relationships between the various rock types present in the Tamazeght complex and show that the above-mentioned element ratios can potentially be useful for distinguishing geochemically distinct melt reservoirs within a given plutonic rock suite.

Zircon, eudialyte and Ti-bearing andradite are generally rare or are restricted to localized rock units. Despite their scarcity, each of them can have a significant effect upon the HFSE budget in their evolving magmas. Here, we derive first estimations of eudialyte–melt partition coefficients for REE. Application of these data to eudialyte-bearing rocks of the Ilimaussaq complex (South Greenland), and comparing the results to published estimations for the parental melts of these rocks yields consistent results and demonstrates the reliability of our estimations.

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1. Introduction

In the vast majority of plutonic rocks (including peraluminous, metaluminous, alkaline and peralkaline compositions) zircon and titanite are among the most common accessory minerals. These are rich in high field strength elements (HFSE; elements such as Zr, Hf, Nb, Th, U, REE) and generally dominate the HFSE budget of the whole-rock. In mafic alkaline rocks, Ti-bearing andradite may occur as well. A less common and geochemically highly evolved group of peralkaline rocks (igneous rocks with an aluminous index of >1 (Al; molar $\text{Na}_2\text{O} + \text{K}_2\text{O}/\text{Al}_2\text{O}_3$) contains a variety of structurally complex Na–Ca–HFSE silicates (mainly eudialyte, catapleite and others), for which the term apatitic rocks is used (Sørensen, 1997). Zircon and/or titanite bearing rocks, however, are called miaskitic rocks. Transitional rock types may contain HFSE-rich minerals typical of both groups.

The abundance ratios of geochemically very similar element pairs (e.g., Zr/Hf or Nb/Ta) can be used to elucidate the genetic relationships between various lithologies of a given igneous rock association and to track the geochemical evolution of silicate melts (Chakhmouradian and Williams, 2004; Bea et al., 2006; Claiborne et al., 2006). Since the

above-mentioned minerals often dominate the whole-rock HFSE budget, they can potentially affect such geochemical parameters. For example, significant fractionation of zircon was shown to decrease the Zr/Hf ratio in the residual melts (Linnen and Keppler, 2002; Bea et al., 2006; Claiborne et al., 2006). For other HFSE-rich minerals, similar effects are forecasted (Bea et al., 2006), but so far, no detailed investigations are available.

Understanding the solubility of HFSE in silicate melts and their partitioning behavior with respect to the above-mentioned minerals is essential, in particular to understand the commonly observed enrichment of HFSE in alkaline to peralkaline igneous rocks, which in cases reach high concentrations of potential economic interest (Kogarko, 1980; Sørensen, 1992; Oliva and Williams-Jones, 1999; Salvi et al., 2000). Experimental work has shown that aside from other factors (e.g., fluorine content; Keppler, 1993), the solubility of HFSE in silicate melts strongly depends upon their structural state (Watson and Harrison, 1983; Linnen and Keppler, 1997, 2002). For example, the solubility of Zr and Hf in peraluminous and metaluminous strongly polymerized melts is orders of magnitude lower than in strongly peralkaline and thus, less polymerized melts (Linnen and Keppler, 2002). Similarly, the incorporation of some trace elements in HFSE-rich phases depends on the degree of polymerization of the melt they crystallize from (Prowatke and Klemme, 2005).

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In the present study, we mainly utilize trace element data for titanite (but also for eudialyte, Ti-bearing andradite and zircon) from the Tamazeght complex, Morocco, to track the effect of HFSE-rich mineral fractionation on the evolution of geochemical parameters like Zr/Hf, Nb/Ta and other ratios and to discuss the genetic relationships between the various rock types present in the complex. The Tamazeght complex is well suited for such an investigation, since it contains most HFSE-rich minerals important for plutonic rocks. The Tamazeght rocks are metaluminous, alkaline and even peralkaline in composition and offer the unique possibility to study the geochemical evolution of silicate melts during a very long differentiation history. The implications derived from this study can potentially be applied to any igneous rock association undergoing significant titanite fractionation.

2. Geological setting

The Tamazeght complex is located in the Moroccan High Atlas Mountains and represents a multiphase plutonic to sub-volcanic complex comprising a wide range of plutonic rocks (including metaluminous, alkaline and peralkaline whole-rock compositions; Kchit, 1990). The complex consists of ultramafic, shonkinitic, gabbroic to monzonitic and various foid syenitic units, with the latter group dominating in outcrop (Kchit, 1990; Salvi et al., 2000; Marks et al., 2008). Several carbonatitic diatremes and numerous dykes of carbonatite, lamprophyre, phonolite, trachyte and nephelinite composition crosscut the complex (Bouabdli et al., 1988; Mourtada et al., 1997). The complex was emplaced into a graben-like structure, which

developed during the opening of the Atlantic Ocean (Laville, 1981; Laville and Harmand, 1982). Monzonitic rocks of the complex were dated at 44 ± 4 Ma (Rb/Sr) (Tisserant et al., 1976) whereas crosscutting dykes give an age of 35 Ma (Klein and Harmand, 1985). Our own U–Pb ion microprobe zircon analyses from a monzonitic sample (TMZ2) and a late-stage hydrothermal vein (TMZ234) yielded indistinguishable ages of 44.5 ± 2.2 Ma (2σ ; MSWD=1.3; $n=6$) and 43.1 ± 1.8 (2σ ; MSWD=1.6; $n=10$), respectively. Both ages are in excellent agreement with the published ages of Tisserant et al. (1976). The depth of intrusion is assumed to be less than 3 km (Salvi et al., 2000).

Recently, Marks et al. (2008) presented detailed studies on the mineral chemistry and the petrology of the silicate units. It was concluded that the large lithological variation found in the Tamazeght complex probably originated from distinct melt batches derived from a heterogeneous mantle source. Within specific rock groups, however, fractionation and accumulation processes also play a certain role. Four main rock suites in the Tamazeght complex are distinguished. The order of presentation here follows the relative age relations (from oldest to youngest rock types), based on field relations.

Glimmerites are interpreted to have originated from low-degree melts of a metasomatized and K-phase-bearing mantle domain (e.g., amphibole–spinel lherzolite; Bouabdli et al., 1988; Marks et al., 2008).

Pyroxenites and shonkinites (the latter are melanocratic nepheline syenites with a colour index >60 ; Le Maitre, 2002). share some similarities in terms of their crystallization conditions, their phase assemblages and the chemical composition of phases. Possibly, these rocks were derived from a common source and may represent different evolutionary stages of a common parental magma.

Table 1
Trace element composition of garnet from the Tamazeght complex, Morocco (b.d.l. = below detection limit)

	TMZ22		TMZ20			TMZ23c		TMZ25				TMZ12		
	Glimmerite		Glimmerite			Pyroxenite		Pyroxenite				Shonkinite		
	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$	LREE-rich rim	Mean	$\pm 2\sigma$	Mean	$\pm 2\sigma$	LREE-rich rim	$\pm 2\sigma$	Mean	$\pm 2\sigma$	LREE-rich rim
	($n=8$)		($n=5$)			($n=8$)		($n=6$)		($n=2$)		($n=6$)		
ppm														
Cs	b.d.l.		b.d.l.		b.d.l.	b.d.l.		b.d.l.		b.d.l.		b.d.l.		0.03
Rb	b.d.l.		b.d.l.		b.d.l.	b.d.l.		b.d.l.		b.d.l.		b.d.l.		b.d.l.
Ba	0.37	0.05	b.d.l.		0.24	b.d.l.		0.18	0.03	b.d.l.		b.d.l.		0.13
Be	0.50	0.20	0.24	0.03	b.d.l.	0.38	0.12	0.30	0.08	b.d.l.		b.d.l.		b.d.l.
B	1.13	0.94	0.86	0.07	b.d.l.	1.82	0.34	1.16	0.62	b.d.l.		b.d.l.		b.d.l.
Th	48.6	15.0	19.2	6.5	11.6	35.5	10.2	25.5	9.6	33.3	2.1	4.92	0.15	7.83
U	21.7	4.3	13.1	1.3	18.4	21.5	4.2	15.3	3.5	31.6	3.8	14.0	0.5	15.2
Nb	354	146	187	35	451	246	92	182	59	363	70	261	6	799
Ta	8.4	4.7	4.6	1.3	19.1	5.0	2.0	4.2	1.8	14.0	2.1	6.2	0.2	20.9
La	17.2	4.1	12.3	1.1	65.6	13.2	3.1	13.5	3.2	92.4	25.4	20.3	0.9	13.1
Ce	107	21	74.1	6.4	258	86.7	16.2	82.5	13.4	448	110	89.1	2.2	65
Pb	0.22	0.08	0.10	0.04	0.05	0.16	0.05	0.13	0.04	0.17	0.03	0.07	0.01	0.10
Pr	23.3	4.2	16.1	1.3	42.3	19.3	3.0	18.0	2.5	71.7	13.5	16.2	0.1	11.7
Sr	56.1	11.6	48.2	4.1	82.6	49.3	4.5	47.6	7.1	78.2	10.5	105	8	93
P	54.2	7.8	48.7	2.8	78.6	48.9	3.2	58.3	8.2	85.9	4.6	184	3	48.5
Nd	146	21	102	10	215	127	17	116	13	304	40	96	2	65
Zr	834	274	797	44	510	2366	874	871	439	717	78	7487	117	2470
Hf	14.6	8.1	17.8	5.6	11.2	20.5	8.2	13.9	7.4	24.8	4.5	117	1.1	41.1
Sm	48.1	2.5	34.4	7.0	49.1	46.5	3.0	38.1	4.4	43.4	0.4	37.1	0.4	17.6
Eu	18.0	0.5	12.5	3.1	15.3	18.3	1.0	14.0	2.0	11.8	0.5	17.5	0.0	5.7
Gd	47.9	2.6	33.7	10.1	36.2	52.2	3.4	37.6	7.2	28.1	1.5	53.0	0.8	13.9
Tb	7.77	0.87	5.40	1.86	4.75	9.09	0.86	6.11	1.40	3.27	0.42	11.6	0.10	1.92
Dy	45.0	7.7	31.5	12.3	21.9	56.7	7.4	35.6	9.5	16.4	3.0	84.1	0.2	9.5
Li	19.2	5.8	14.4	2.4	12.5	17.1	2.1	14.5	5.02	14.6	0.30	25.3	20.2	475
Y	306	61	211	86	76.2	365	36	238	65.2	70.4	29.2	706	6	37.3
Ho	9.33	2.14	6.44	2.70	3.49	12.4	1.8	7.36	2.24	2.72	0.80	21.0	0.2	1.76
Er	25.5	7.1	17.8	8.1	7.35	34.9	5.7	19.8	6.55	5.94	2.20	67.9	0.4	3.76
Tm	3.74	1.14	2.74	1.33	0.75	5.38	0.89	2.98	1.07	0.73	0.30	11.3	0.1	0.48
Yb	26.3	8.5	18.9	9.2	3.78	37.4	6.4	20.6	7.71	4.37	2.46	81.4	1.1	2.64
Lu	3.67	1.15	2.67	1.31	0.44	5.13	0.77	2.92	1.00	0.55	0.36	10.90	0.24	0.26
Sc	44.5	23.9	39.7	7.0	50.0	26.2	5.9	31.7	9.6	68.9	14.2	11.7	0.2	31.3
V	2312	437	2842	264	966	3039	547	2825	354	1112	351	3245	43	3103
Cr	1417	477	863	192	997	92	63	929	442	1177	173	120	44	494
Ni	9.14	5.19	2.65	0.20	3.61	0.89	0.60	2.78	1.75	4.37	0.37	12.7	0.1	3.28
Zn	404	107	307	30	69.0	246	24	286	78	142	66	134	2	229

Table 2

Trace element composition of titanite from the Tamazeght complex, Morocco (b.d.l. = below detection limit)

TMZ23c		TMZ68		TMZ139		TMZ307		TMZ308		TMZ320		TMZ321		TMZ2	
Pyroxenite		Shonkinite		Shonkinite		Shonkinite		Shonkinite		Monzogabbro		Monzonite		Monzonite	
Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ
(n=7)		(n=8)		(n=11)		(n=7)		(n=9)		(n=10)		(n=6)		(n=9)	
ppm															
Cs	0.02	0.02	b.d.l.		0.03	0.01	0.06	0.03	0.03	0.02	b.d.l.		0.13	0.10	0.02
Rb	b.d.l.		0.08		0.03	0.03	0.13	0.05	0.08	0.04	0.08	0.04	0.13	0.01	0.16
Ba	0.18	0.07	0.29	0.13	0.29	0.11	0.23	0.10	b.d.l.		b.d.l.		0.49	0.19	0.21
Be	b.d.l.		b.d.l.		0.40	0.12	0.28	0.07	0.18	0.00	0.43	0.14	0.36	0.00	0.15
B	1.55	0.73	2.01	0.45	1.67	0.42	2.01	0.55	1.00	0.01	3.51	1.00	2.16	0.98	1.82
Th	54.0	17.8	163	19	121	16	162	33	260	59	72.6	48.3	124	17	195
U	16.0	4.6	20.7	2.5	17.9	3.2	24.5	4.9	35.0	9.7	10.9	8.1	20.2	3.0	25.9
Nb	3825	476	2525	549	3095	461	4143	897	3408	1052	1550	379	3172	598	2469
Ta	57.8	15.4	175	100	212	81	198	36	210	185	197	61	152	19	214
La	274	34	1725	260	1262	113	2239	361	1657	362	801	208	1718	280	1937
Ce	714	97	3350	917	2677	382	4791	378	3555	960	2161	311	3937	439	5017
Pb	1.13	0.09	1.46	0.13	1.12	0.34	1.30	0.18	2.02	0.40	0.58	0.30	0.84	0.16	1.68
Pr	90.3	13.3	367	136	304	51	539	38	418	127	317	14	452	29	650
Sr	1225	41	808	168	1195	48	453	197	424	173	407	21	486	49	130
P	52.6	10.0	702	145	299	50	355	130	488	120	678	169	383	95	461
Nd	334	52.5	1350	625	1090	172	1988	285	1588	519	1411	65	1644	96	2655
Zr	547	177	4000	275	2986	61	5160	959	5589	490	3102	889	5356	595	4008
Hf	14.3	3.7	115	11.3	67.4	2.7	128	18	130	17	104	23	149	18	147
Sm	46.7	7.9	225	124	174	23	325	72	277	97	285	33	260	28	503
Eu	12.5	2.2	66.7	34.8	54.5	8.1	86.8	23.7	83.0	26.6	84.9	9.5	76.7	9.6	123
Gd	24.7	5.3	163	81	130	13	231	53	193	65	224	22	190	23	399
Tb	2.74	0.55	22.2	11.5	18.3	2.3	33.6	7.1	27.6	9.3	29.9	2.2	27.0	2.9	57.4
Dy	11.2	2.5	113	56	95.5	12.4	177	31	140	46	148	9	146	12	301
Li	b.d.l.		0.70	0.17	b.d.l.		b.d.l.		0.34	0.11	0.55	0.09	2.64	0.56	1.29
Y	43.8	8.6	504	192	439	47	811	86	605	164	586	20	716	39	1356
Ho	1.66	0.39	20.1	8.61	17.8	2.1	32.7	4.8	24.2	7.6	25.2	0.9	27.4	1.1	56.9
Er	3.17	0.69	46.4	17.2	41.4	4.6	77.0	8.3	55.4	15.8	53.4	2.2	66.4	1.9	134.9
Tm	0.35	0.09	6.05	1.77	5.39	0.46	10.1	0.8	7.01	1.76	6.34	0.79	8.91	0.31	18.6
Yb	1.88	0.38	35.3	8.06	29.4	2.1	59.3	4.4	39.9	8.7	33.1	7.2	52.3	2.9	109.0
Lu	0.18	0.04	4.33	0.59	3.36	0.30	6.71	0.55	4.29	0.73	3.89	1.08	6.26	0.47	14.11
Sc	12.9	4.51	7.32	1.22	4.88	0.69	6.65	0.58	6.73	0.81	6.28	0.50	6.06	0.82	15.8
V	916	68	610	42	612	21	544	36	455	23	622	68	790	33	679
Cr	1250	175	20.0	4.26	8.77	2.41	3.10	1.32	82	10	0.74	0.17	0.99	0.30	9.9
Ni	0.16	0.01	0.24	0.05	0.27	0.11	0.14	0.00	0.16	0.05	0.16	0.09	b.d.l.		0.21
Zn	4.60	0.40	5.73	0.69	5.99	0.87	5.02	0.31	5.19	1.10	6.17	0.59	6.55	0.67	6.54
TMZ313		TMZ219		TMZ157		TMZ318		TMZ312		TMZ161		TMZ95		TMZ94	
Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Nepheline syenite		Nepheline Syenite	
Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ	Mean	±2σ
(n=7)		(n=8)		(n=11)		(n=7)		(n=9)		(n=8)		(n=7)		(n=5)	
ppm															
Cs	0.03	0.01	0.02	0.01	b.d.l.		b.d.l.	0.06	0.02	b.d.l.		b.d.l.		b.d.l.	
Rb	0.12	0.05	0.11	0.06	0.07	0.01	0.09	0.05	0.09	0.06	0.16	0.12	0.07	0.02	0.07
Ba	0.47	0.07	0.32	0.18	0.28	0.03	0.20	0.08	0.41	0.11	0.75	0.56	b.d.l.	0.29	0.00
Be	0.26	0.06	b.d.l.		b.d.l.		b.d.l.		b.d.l.		0.21	0.02	b.d.l.		b.d.l.
B	2.58	0.85	1.32	0.00	0.68	0.00	1.36	0.53	0.87	0.00	1.95	1.00	1.29	0.42	1.53
Th	152	21	141	32	130	18	162	27	151	27	118	5	125	10	127
U	21.7	2.6	19.0	5.6	16.8	2.2	27.7	7.5	21.5	3.4	16.2	1.8	23.9	1.1	27.6
Nb	3021	436	3161	1035	2951	423	1674	621	3747	766	2842	148	4183	297	6134
Ta	198	40	151	35	270	59	138	115	199	7	265	47	129	15	123
La	1658	161	2154	748	1800	209	1188	307	1888	231	1786	69	1803	147	2214
Ce	3791	235	4267	1043	4366	302	2945	1247	4092	222	4254	246	3215	215	3535
Pb	1.08	0.14	1.24	0.41	1.00	0.14	1.69	0.40	1.10	0.19	0.98	0.16	1.16	0.25	1.12
Pr	461	41	455	93	545	38	404	204	449	17	535	45	314	16	303
Sr	294	83	575	217	718	65	200	31	540	141	718	39	627	163	315
P	461	90	362	172	624	167	505	53	357	73	827	145	172	40	100
Nd	1801	232	1590	382	2115	216	1750	939	1559	163	2100	201	1016	65	872
Zr	4921	671	4237	1096	3725	493	4810	278	4650	608	3320	60	4477	97	5644
Hf	142	18	121	23	115	13	132	21	118	12	98.0	2.4	94.8	2.4	112
Sm	311	55	243	79	358	55	341	195	239	43	362	39	148	11	112
Eu	87.5	15.7	69.7	24.4	108	16	96.4	51.2	71.2	14.8	108	11	43.5	3.8	32.5
Gd	245	43	187	61	265	43	267	148	169	32	249	25	113	7	86.8
Tb	33.3	5.9	25.3	7.9	35.9	5.4	35.6	20.1	25.6	4.6	35.3	3.3	16.4	0.8	13.1
Dy	177	29	134	37	184	23	179	100	139	21	177	15	88.4	3.1	76.6
Li	0.67	0.19	1.03	0.58	1.55	0.38	0.43	0.24	1.66	0.08	0.31	0.05	0.69	0.22	1.02
Y	803	85	633	121	791	82	749	401	686	55	742	42	465	7	431
Ho	33.2	4.5	25.4	6.3	32.9	3.8	32.3	17.5	26.4	3.2	31.2	2.0	17.7	0.2	15.7
Er	78.7	8.7	60.3	13.1	74.2	6.2	72.1	38.7	64.2	5.0	68.4	3.6	44.1	0.5	41.1
Tm	10.5	0.7	8.01	1.58	9.12	0.59	9.21	4.83	8.66	0.37	8.28	0.24	6.26	0.22	5.91

(continued on next page)

Table 2 (continued)

	TMZ313		TMZ219		TMZ157		TMZ318		TMZ312		TMZ161		TMZ95		TMZ94	
	Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Monzosyenite		Nepheline syenite		Nepheline Syenite	
	Mean (n=7)	±2σ	Mean (n=8)	±2σ	Mean (n=11)	±2σ	Mean (n=7)	±2σ	Mean (n=9)	±2σ	Mean (n=8)	±2σ	Mean (n=7)	±2σ	Mean (n=5)	±2σ
Yb	61.4	4.1	47.0	9.3	49.1	2.4	51.9	25.6	51.7	1.6	46.8	1.0	35.9	0.7	35.0	3.0
Lu	7.92	0.65	5.70	1.12	5.68	0.35	6.61	2.79	5.97	0.25	5.27	0.14	4.17	0.10	3.97	0.48
Sc	8.74	1.21	6.70	0.10	6.20	0.40	11.1	2.1	4.76	0.14	4.48	0.16	4.67	0.12	5.23	0.94
V	602	21	746	86	720	20	580	53	655	30	544	14	856	25	828	46
Cr	2.75	0.35	18.9	26.4	3.51	4.50	18.4	5.6	1.05	0.21	14.2	2.6	3.86	2.19	5.56	2.83
Ni	0.22	0.03	0.14	0.02	0.22	0.01	0.16	0.10	b.d.l.		0.28	0.09	0.18	0.11	0.24	0.07
Zn	6.33	0.90	6.25	0.07	6.55	0.77	6.47	0.42	4.31	0.48	4.82	1.05	5.83	0.40	5.94	0.54
	TMZ74		TMZ83		TMZ311		TMZ165		TMZ221		TMZ223		TMZ288		TMZ238	
	Nepheline syenite		Nepheline syenite		Nepheline syenite		Nepheline syenite		Nepheline syenite		Nepheline syenite		Miaskitic malignite		Agpaitic malignite	
	Mean (n=8)	±2σ	Mean (n=9)	±2σ	Mean (n=6)	±2σ	Mean (n=10)	±2σ	Mean (n=7)	±2σ	Mean (n=7)	±2σ	Mean (n=8)	±2σ	Mean (n=11)	±2σ
ppm																
Cs	0.05	0.01	b.d.l.		0.10	0.07	0.03	0.01	0.03	0.02	b.d.l.		0.03	0.02	0.08	0.06
Rb	0.66	0.96	0.09	0.03	0.10	0.06	0.15	0.15	0.20	0.18	0.07	0.01	0.08	0.01	1.38	0.85
Ba	20.0	4.7	0.34	0.25	0.16	0.01	0.16	0.02	1.01	1.18	b.d.l.		b.d.l.		1.30	0.84
Be	b.d.l.		b.d.l.		b.d.l.		0.28	0.00	b.d.l.	b.d.l.			0.23	0.07	0.72	0.46
B	1.44	0.34	0.93	0.11	2.16	0.54	1.69	0.58	2.40	0.75	1.92	1.10	1.24	0.00	3.02	1.09
Th	132	45	137	28	185	54	79.9	21.1	212	9	63.3	10.5	58.9	19.9	41.9	67.0
U	19.3	7.4	23.0	5.4	31.9	12.8	15.6	2.5	45.0	12.7	19.6	3.4	37.4	23.1	11.1	9.7
Nb	3329	893	3349	632	3631	415	4983	759	5248	445	6529	510	6004	2090	4150	1033
Ta	122	28	169	27	129	17	136	20	147	26	143	21	83.7	38.1	63.5	10.1
La	2480	519	1555	253	1925	101	2594	326	2774	218	2312	212	1807	259	1220	222
Ce	4504	482	3243	343	3630	209	4382	517	4673	376	3553	306	2648	401	1935	264
Pb	1.04	0.28	1.02	0.30	1.51	0.41	1.42	0.12	2.31	1.62	2.83	2.92	0.95	0.14	3.33	2.91
Pr	449	63	366	23	374	39	399	41	438	65	298	26	222	43	169	43
Sr	909	269	545	162	309	166	1462	137	556	114	305	24	202	17	2171	948
P	335	109	354	165	242	75	130	19	197	56	70.6	3.9	67.1	19.5	65.2	85.9
Nd	1486	318	1336	101	1268	165	1188	121	1399	282	830	83	636	144	513	230
Zr	4063	1041	5138	781	5879	1239	4840	488	5686	213	7325	1859	7862	1985	4358	1278
Hf	106	19	124	18	136	29	114	17	135	6	178	56	160	43	98.3	32.4
Sm	214	61	222	28	196	28	159	16	198	47	106	10	85.5	21.2	70.7	46.0
Eu	63.7	16.9	64.9	10.0	53.8	7.6	47.8	5.0	56.6	13.1	31.2	2.4	25.0	5.6	20.7	15.7
Gd	148	41	164	23	142	21	117	10	138	33	75.8	5.0	65.0	14.0	48.8	38.5
Tb	21.4	5.8	23.2	2.5	21.3	3.1	17.2	1.7	20.4	4.9	11.9	0.8	10.6	2.0	7.35	5.52
Dy	114	28	123	9	116	16	94.5	10.6	111	28	69.3	3.5	62.3	10.1	40.1	27.7
Li	1.31	0.55	0.27	0.05	0.35	0.09	1.26	0.26	2.38	0.46	0.32	0.02	0.63	0.18	0.71	0.28
Y	552	98	585	20	585	66	478	53	567	148	357	16	331	36	187	77
Ho	21.6	4.5	23.2	1.2	22.1	2.7	18.4	2.1	21.6	5.5	13.7	0.5	12.6	1.5	7.31	4.97
Er	52.3	9.3	55.1	3.0	55.0	5.3	44.3	5.5	54.4	14.3	34.7	1.6	32.8	4.2	18.2	11.6
Tm	7.00	1.10	7.48	0.55	7.59	0.61	5.80	0.67	7.64	2.18	4.70	0.19	4.69	0.58	2.30	1.51
Yb	41.7	6.0	44.1	4.8	45.3	2.5	31.8	4.6	46.9	13.4	26.8	1.9	27.2	2.9	12.5	8.9
Lu	4.89	0.83	5.16	0.55	5.19	0.38	3.36	0.43	5.55	1.69	2.78	0.23	2.80	0.29	1.19	1.08
Sc	5.26	0.54	5.45	0.74	6.09	0.88	4.47	0.54	5.65	0.28	5.78	1.27	5.78	1.15	2.47	1.06
V	730	29	610	10	548	64	759	27	729	15	743	34	466	43	618	164
Cr	2.16	0.60	2.01	1.15	4.19	1.73	6.18	0.85	3.65	1.98	0.81	0.09	0.59	0.14	50	56
Ni	0.22	0.06	0.20	0.05	b.d.l.		0.16	0.08	0.25	0.11	0.18	0.01	0.14	0.07	0.84	0.62
Zn	6.21	2.24	5.87	0.54	4.59	0.40	5.83	0.52	5.46	1.18	4.31	0.22	4.52	0.20	9.66	3.23

Rocks of a monzonitic group may reflect larger degrees of melting and the increased importance of a basaltic melt component. The variable plagioclase/alkali feldspar ratios and the similar petrographic appearance of the studied samples indicate that fractionation and accumulation processes were important in this group.

Nepheline syenites and malignites (the latter are mesocratic foid syenites with a colour index of 30–60; [Le Maitre, 2002](#)) are explained by lower degrees of melting and a more alkaline character of the parental melt of these rocks. Most textural varieties of nepheline syenites may have originated from a common melt reservoir. In one particular type (malignites) special circumstances – be they of a chemical or a physical nature or a combination of both – locally led to the development of an agpaitic (cf. eudialyte-bearing) mineral assemblage.

3. Petrography

Detailed petrographic descriptions and whole-rock data of the various lithologies of the Tamazeght complex are given by [Kchit](#)

(1990). The samples used in the present study are described in [Marks et al. \(2008\)](#). Thus, only very short descriptions are presented here and these focus on important textures related to HFSE-rich minerals in the various rock types. All samples were collected at a latitude between 32°36' and 35°31' and at a longitude between 4°37' and 4°44'.

Glimmerites (TMZ20 & 22) are dominated by poikilitic mica, garnet (Ti-bearing andradite) and clinopyroxene. Garnet is a major mineral (up to 15 vol.%) and grew early in the crystallization sequence. Feldspar, nepheline and amphibole are lacking. Accessory minerals are perovskite, titanite, magnetite, apatite and calcite. Scarce perovskite (generally <50 μm) is always overgrown by titanite.

Proxenites (TMZ23c & 25) are dominated by euhedral clinopyroxene, nepheline and euhedral to subhedral garnet. Minor minerals are apatite, calcite, mica and magnetite. Interstitial titanite is very rare and amphibole and feldspar are absent. In shonkinites (TMZ68, 139, 307 and 308), mafic minerals include amphibole, clinopyroxene, olivine, biotite and magnetite. Early magmatic titanite occurs frequently in these rocks (up to 5 vol.%) and reaches several

Table 3

Major, minor and trace element composition of eudialyte from agpaiteic malignites of the Tamazeght complex, Morocco (b.d.l. = below detection limit)

	TMZ 298		TMZ 238		TMZ 248		TMZ 177	
	Mean (n=8)	±2σ	Mean (n=10)	±2σ	Mean (n=7)	±2σ	Mean (n=8)	±2σ
wt.%								
SiO ₂	50.10	0.27	50.30	0.35	50.28	0.33	50.26	0.36
TiO ₂	0.28	0.02	0.42	0.05	0.82	0.03	0.32	0.08
ZrO ₂	10.29	0.10	10.35	0.62	9.47	0.41	10.89	0.36
HfO ₂	0.13	0.01	0.10	0.01	0.09	0.02	0.09	0.01
Nb ₂ O ₅	1.10	0.06	0.99	0.16	0.66	0.15	1.18	0.16
Al ₂ O ₃	0.15	0.02	0.13	0.06	0.12	0.02	0.11	0.03
La ₂ O ₃	0.17	0.02	0.28	0.19	0.06	0.01	0.72	0.11
Ce ₂ O ₃	0.15	0.02	0.21	0.15	0.03	0.01	0.75	0.12
Nd ₂ O ₃	0.01	0.00	0.01	0.01	0.00	0.00	0.08	0.01
Y ₂ O ₃	0.02	0.01	0.05	0.05	0.01	0.00	0.06	0.02
FeO	5.44	0.21	4.16	0.60	5.04	0.60	3.99	0.18
MnO	1.53	0.18	2.78	0.63	2.09	0.26	4.09	0.19
CaO	12.36	0.15	11.65	0.44	10.96	0.26	9.38	0.34
SrO	2.32	0.18	2.07	0.38	2.76	0.51	1.38	0.17
Na ₂ O	12.79	0.20	13.05	1.50	13.95	0.30	14.06	0.27
K ₂ O	0.24	0.05	0.42	0.08	0.33	0.03	0.54	0.02
Cl	1.47	0.03	1.19	0.06	1.24	0.04	0.34	0.02
Total	98.55		98.16		97.91		98.24	
ppm								
Cs	1.49	0.50	3.58	0.90	0.79	0.33	4.84	1.25
Rb	13.3	0.64	13.74	2.37	8.78	0.94	26.8	0.85
Ba	31.5	5.48	110.5	27.6	99.4	107	11.5	0.80
Be	1.24	0.57	0.66	0.32	0.44	0.11	0.51	0.20
B	13.0	7.18	9.91	4.81	13.4	6.81	9.22	4.10
Th	16.2	2.2	67.7	44.9	235	179	88.4	11.5
U	34.0	4.9	172.6	62.2	285	120	138	41.3
Nb	7700	425	6900	1125	4600	1000	8250	1100
Ta	63.6	11.3	30.0	16.9	13.6	4.68	46.9	11.1
La	1413	202	2397	1661	485	116	6146	897
Ce	1223	181	1675	1209	262	74.5	6080	984
Pb	80.9	7.15	103	64.2	46.4	10.9	205	15.4
Pr	64.5	7.32	71.5	53.6	14.1	4.30	351	38.1
Sr	19600	1520	17500	3200	23300	4200	11700	1400
P	20.65	1.02	21.45	2.01	18.95	1.39	23.73	1.39
Nd	87.2	23.0	84.9	24.8	14.5	4.7	652	106
Zr	76,200	800	76,600	4600	70,100	3000	80,600	2600
Hf	1220	93	879	108	834	140	867	77
Sm	17.83	1.32	16.12	15.62	3.40	1.46	70.24	8.83
Eu	5.82	0.69	5.24	5.41	1.13	0.55	19.58	2.40
Gd	19.33	2.17	18.63	20.51	3.90	2.23	51.18	6.60
Tb	4.15	0.42	4.30	5.13	0.94	0.63	8.17	0.99
Dy	33.33	3.95	37.34	46.52	8.35	6.00	51.98	6.43
Li	1.00	0.22	3.42	1.03	2.82	0.96	4.35	0.47
Y	194	54.5	380	88.4	47	36.4	468	67.3
Ho	9.73	1.18	11.60	14.96	2.69	2.05	12.20	1.56
Er	38.40	4.68	49.46	63.64	11.49	9.08	40.17	4.58
Tm	7.69	0.87	10.54	12.92	2.46	1.97	7.10	0.78
Yb	64.95	6.85	93.67	102.49	22.77	18.50	57.42	5.86
Lu	9.90	0.90	13.77	12.64	3.60	2.91	8.05	0.66
Sc	49.41	0.77	49.58	3.24	43.78	2.03	50.74	1.74
V	3.61	0.14	0.97	0.32	0.97	0.19	b.d.l.	
Cr	0.53	0.13	0.56	0.18	0.49	0.16	0.62	0.20
Ni	b.d.l.		0.15	0.03	b.d.l.		b.d.l.	
Zn	70.90	9.83	97.23	35.68	61.37	19.68	191.09	10.26

millimeters in size. Locally, titanite shows rounded inclusions of ilmenite and/or magnetite. Infrequently, garnet (variety schorlomite) occurs as an accessory mineral in shonkinitic rocks (TMZ12).

Monzonitic rocks (TMZ2, 157, 161, 219, 312, 313, 318, 320 and 321) are characterized by the occurrence of plagioclase and alkali feldspar in addition to foid minerals (nepheline±sodalite and cancrinite) in variable modal amounts and are subdivided into monzogabbros, monzonites and monzosyenites. Mafic minerals include clinopyroxene and magnetite with minor amphibole, mica and ilmenite. Garnet is not present, titanite is common (3–5 vol.%) and occurs as euhedral to subhedral crystals (up to 2 mm) in all investigated samples (see Fig. 4e in Marks et al., 2008). In monzogabbros and monzonites, some titanite contains rounded relics of earlier ilmenite. In monzosyenites,

however, titanite lacks such inclusions and no primary ilmenite is found. Restricted to monzogabbros, additional titanite rims (<200 µm wide) are observed around ilmenite. The petrological significance of these textures is discussed in Marks et al. (2008). In only one monzogabbro sample (TMZ2) few grains (generally <100 µm) of euhedral to subhedral zircon are present.

All samples of nepheline syenite (TMZ74, 83, 94, 95, 165, 221, 223, 238, 248, 288, 298, 311) are rich in alkali feldspar, nepheline and other foid minerals, but lack plagioclase. Mafic minerals are clinopyroxene and/or amphibole together with minor titanite (1–3 vol.%) and/or magnetite except in malignites (TMZ238, 248, 288 and 298), where titanite is scarce or absent. Titanite is euhedral to subhedral, up to 2 mm in size and shows generally no mineral inclusions, with the exception of scarce apatite (see Fig. 6a in Marks et al., 2008). It is interpreted as being of magmatic origin. In some malignites (TMZ238, 248 and 298) euhedral and/or poikilitic eudialyte was formed during a late-magmatic stage. These samples come from spatially restricted areas within otherwise miaskitic malignites, which are normally only a few tens of square meters in size. They are interpreted as the most evolved areas of this unit (Marks et al., 2008). In only one of these agpaiteic late-stage melt samples (TMZ238) are both titanite and eudialyte present. Here, both occur as euhedral to subhedral crystals and no reaction textures between them are observed.

Hydrothermal veins (TMZ177 and 234) occur within malignites and are generally rich in cm-sized alkali feldspar and aegirine. The most important HFSE-rich minerals in these hydrothermal veins are either zircon (TMZ234) or eudialyte (TMZ177).

4. Analytical methods

4.1. Microprobe

To avoid analytical uncertainties due to variations in the concentrations of the internal standard used for LA-ICP-MS analyses (see below), all analytical spots for LA-ICP-MS analyses were quantitatively analyzed by microprobe and then adjusted accordingly. The major and minor element composition of titanite, garnet and eudialyte were determined using a Jeol 8900 electron microprobe in wavelength-dispersion mode at the Institut für Geowissenschaften, Universität Tübingen, Germany. Acceleration voltage was 20 kV and beam current 20 nA. Major and minor elements were measured with variable counting times of 10 to 120 s (peak) and 5 to 30 s (background) depending on the abundance of the respective element. In eudialyte, Na was analyzed first with a counting time of 10 s (peak) and 5 s (upper and lower background) in order to avoid migration of Na. For Nd and Zr as well as for Ti and Hf an overlap correction was applied. For calibration, both synthetic and natural standards were used. Processing of the raw data was carried out with the internal φρZ correction method of JEOL (Armstrong, 1991). Most analyses were carried out with a defocused beam of 10 µm, except for eudialyte, where a beam diameter of 20 µm was used. Analytical uncertainties are below 1% relative for major elements and around 15–20% for minor elements.

4.2. LA-ICP-MS

In situ trace element analyses were carried out by Laser Ablation ICP-MS (LA-ICP-MS) at the Institut für Geowissenschaften at the Johannes Gutenberg Universität Mainz, Germany following methods described by Jacob (2006). The system consists of an Agilent 7500ce quadrupole ICP-MS coupled to a New Wave Research UP 213 laser ablation system with a frequency quintupled Nd:YAG laser with an output wavelength of 213 nm. Spot sizes during the analyses were 50 µm depending and were controlled by a rotating aperture that cuts out parts of the beam, while keeping the energy densities constant. Helium combined with Ar after the sample cell was used as carrier gas

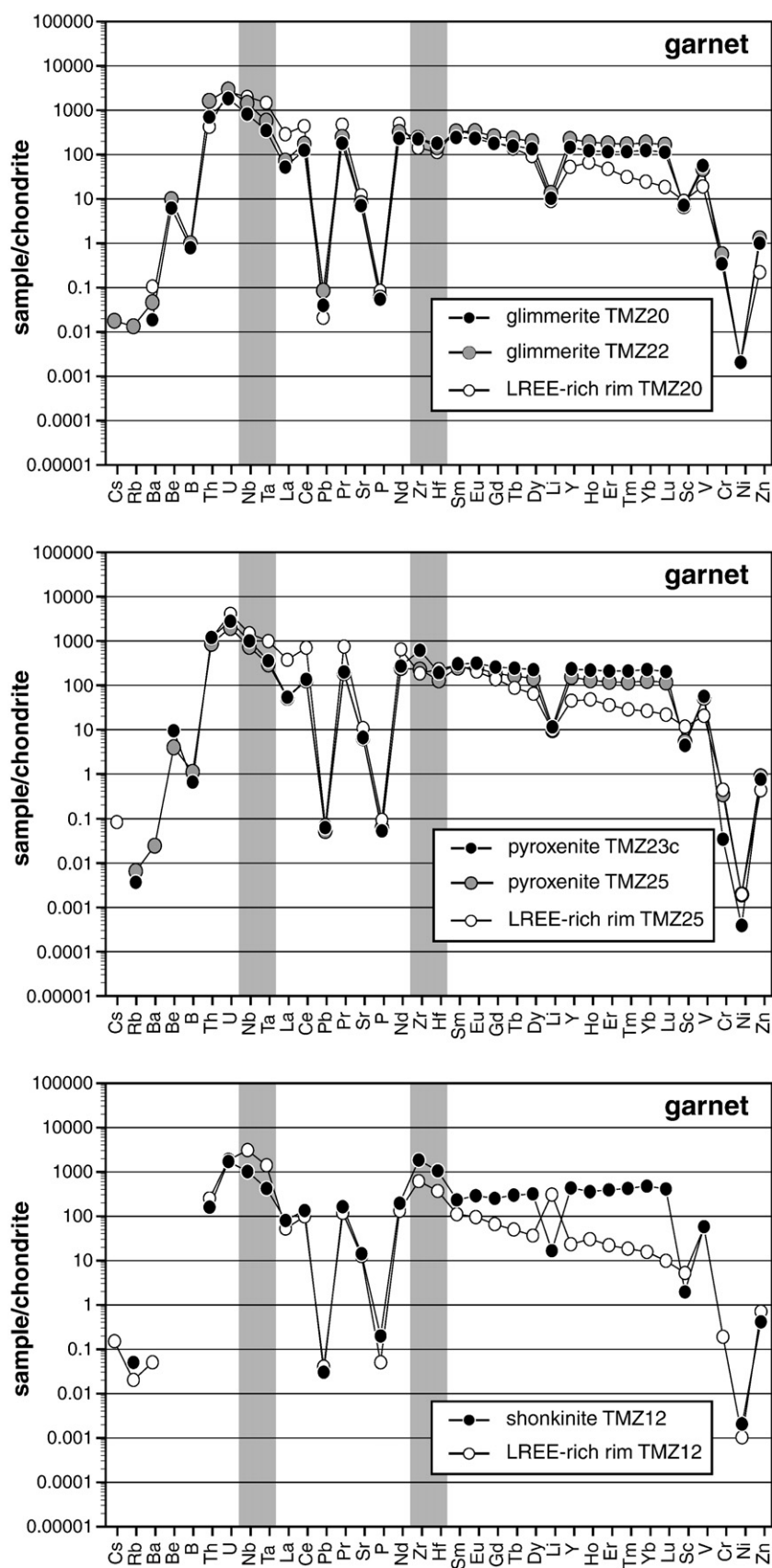


Fig. 1. Chondrite-normalized trace element diagrams for Ti-bearing andradite from the Tamazeght complex, Morocco.

and ablation was carried out at (4 J/cm^2) with a pulse rate of 10 Hz. The commercial software GLITTER 4.0 (Macquarie University) was used for data reduction with NIST SRM 612 as the external standard and ^{43}Ca as the internal standard using values for CaO from the electron microprobe analyses for the minerals. Data for NIST SRM 612 were taken from the GeoReM database (Jochum and Nohl, 2008). Based on the comparison of measured and recommended values for NIST SRM 612 and BCR 2-G reference glasses (Appendix A), the presented data are accurate to within 10% for most elements. A notable exception is B, which deviates from the recommended values by up to 50%. Precision, based on the 2 sigma deviations of the mean of pooled measurements of the two reference glasses is generally better than 10%, with exceptions for B, Zn, V, Sr, Ba, which have a poorer precision (Appendix A). Detection limits for most elements were between 0.004 and 0.1 ppm, depending on the mass number of the element. Notable exceptions are B and Zn having

detection limits between 0.1 and 1.5 ppm, and P, with a detection limit of up to 7 ppm.

4.3. Secondary ionization mass spectrometry

REE and U–Th–Pb analysis by secondary ionization mass spectrometry (SIMS) was conducted using the Cameca ims 1270 ion microprobe at UCLA. *In situ* SIMS analyses were carried out in two analytical sessions using pieces of petrographic thin-sections cut by a diamond saw and mounted in epoxy together with polished grains of reference zircon AS-3. We followed analytical protocols in Monteleone et al. (2007) and Grove et al. (2003) for REE and U–Th–Pb analysis, respectively. In both sessions, the spot size for the $\sim 15 \text{ nA } ^{16}\text{O}^-$ primary beam used was $\sim 15 \mu\text{m}$ in diameter, and the total depth of each sputter crater was $< 2 \mu\text{m}$. This ensured that the beam was entirely

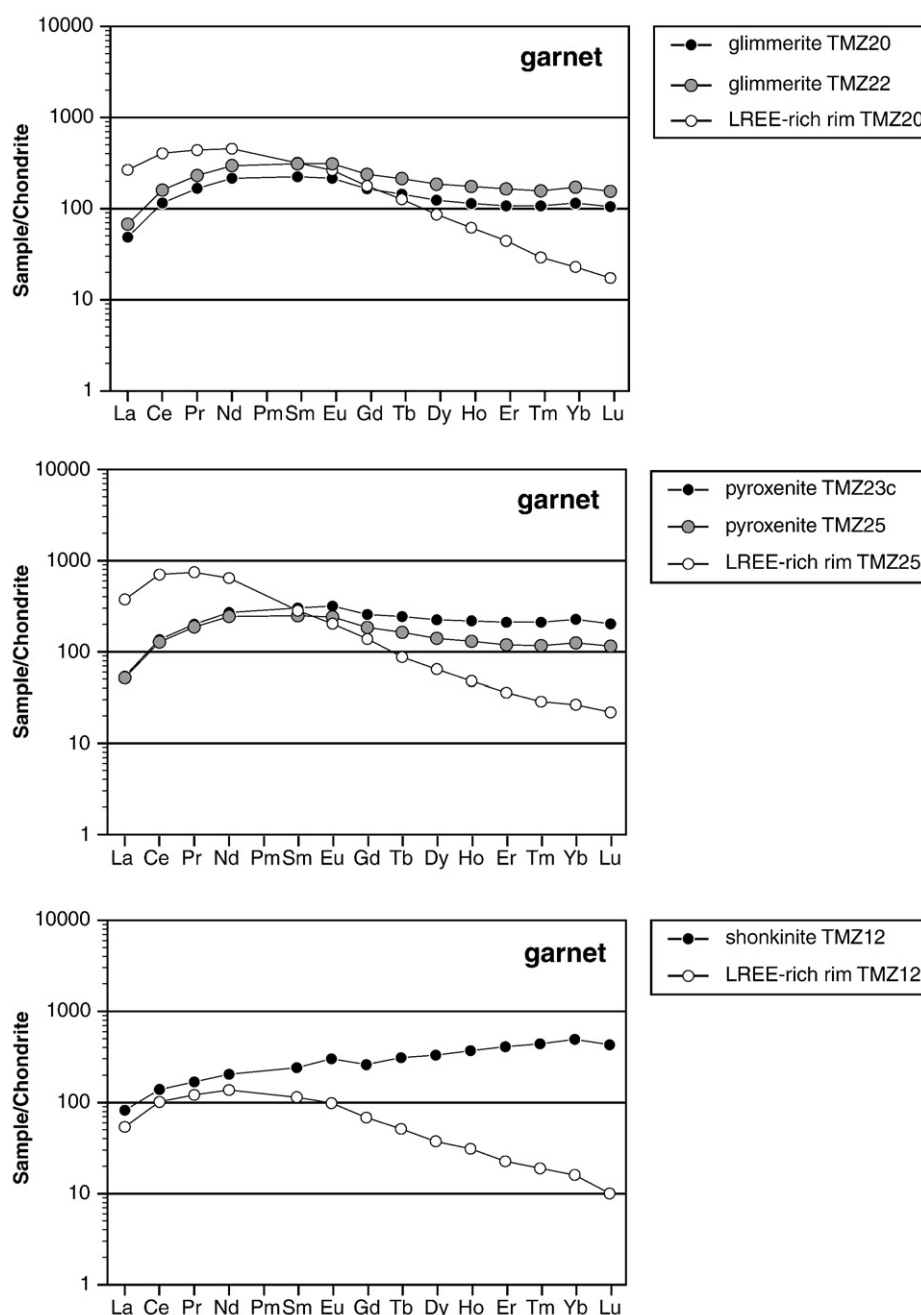


Fig. 2. Chondrite-normalized rare earth element diagrams for Ti-bearing andradite from the Tamazeght complex, Morocco.

contained within zircon. Analytical accuracy and precision of REE analysis is estimated from replicate analysis of reference zircon 91500 (Wiedenbeck et al., 2004), and range between ~5 and 10% (1 standard deviation) for intermediate to heavy REE and up to ~200% for La. The reproducibility of U–Pb relative sensitivity calibration measurements on AS-3 zircons (1099.1 Ma; *Paces and Miller, 1993*) was ~1.7% (1 standard deviation).

5. Trace element concentrations

In total we performed LA-ICP-MS trace element analyses of garnet ($n=37$), titanite ($n=195$) and eudialyte ($n=33$). In order to give a representative overview on the whole data set, we present here the averages of analyses for the respective minerals of each sample studied. Mean analyses together with information on the variability of the data within individual rock samples are presented in *Tables 1–3* and are illustrated in *Figs. 1–6*. For zircon, SIMS trace elements analyses were performed. The data are shown

in *Fig. 7* and representative analyses are given in *Table 4*. All rare earth element (REE) and trace element (TE) patterns are normalized to C1-chondritic abundance values of *Palme and O'Neill (2003)*.

5.1. Garnet

Tamazeght garnets are Ca-, Ti- and Fe^{3+} -rich, spanning the compositional range between Ti-bearing andradite and schorlomite (*Marks et al., 2008*). In terms of TE and REE characteristics, garnet from glimmerite, pyroxenite and shonkinite samples generally show remarkable similarity, both in terms of overall abundance (*Table 1*) and chondrite-normalized patterns (*Figs. 1 and 2*). The majority of the garnets display convex upwards chondrite-normalized REE patterns that are relatively flat from Sm to Lu and show some depletion of LREE relative to MREE and HREE (<140 ppm Ce and $(\text{La/Lu})_N=0.15\text{--}1.3$; *Fig. 2*). In contrast, the rims of some crystals are LREE-enriched (260–530 ppm Ce and $(\text{La/Lu})_N$ of 5–38; *Fig. 2*).

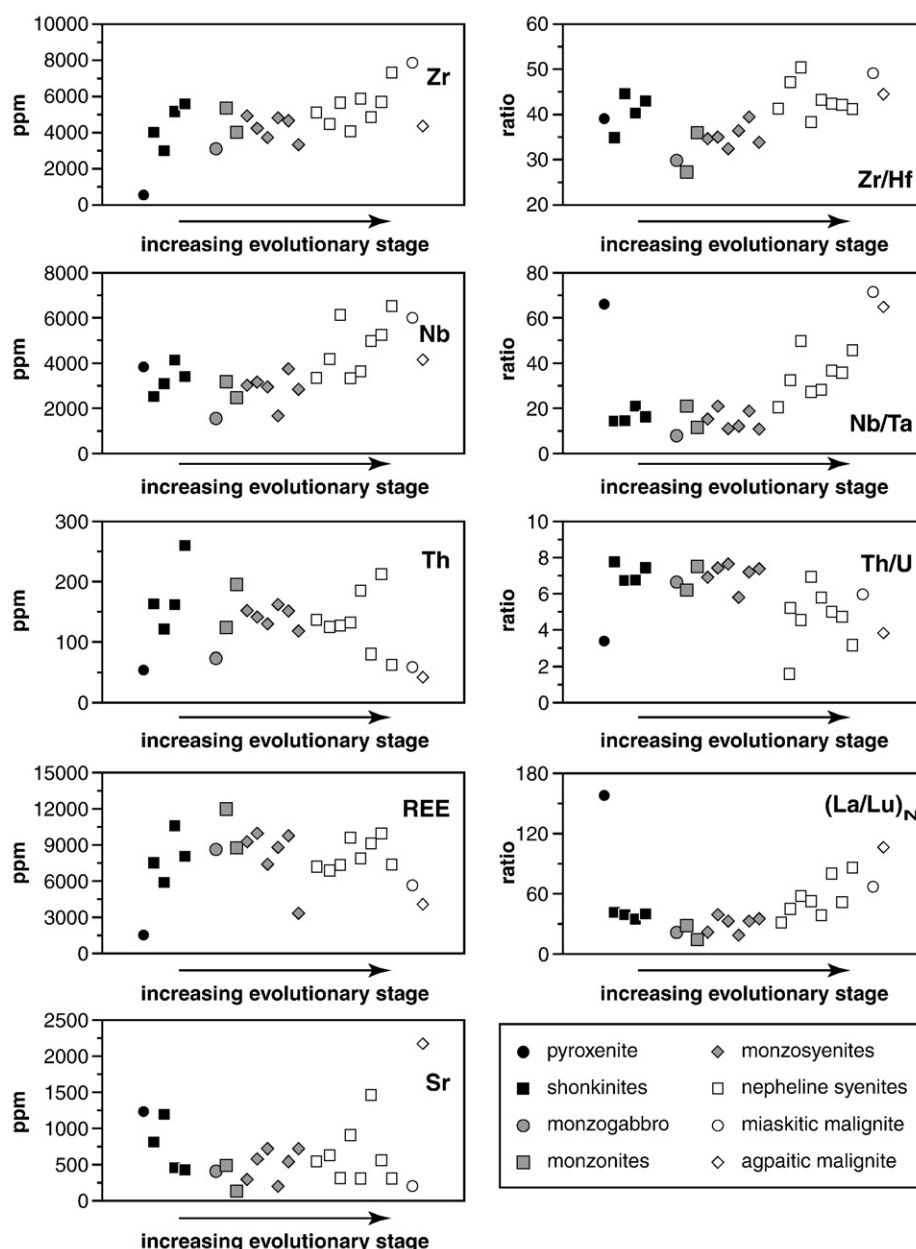


Fig. 3. Concentrations and element ratios of selected trace elements in titanite from the Tamazeght complex, Morocco.

Zr/Hf ratios are quite variable (33–190), although variation in the LREE-enriched rims is more limited and restricted to relatively low Zr/Hf ratios (28–60). For Nb/Ta, ratios range from 36–61 and 24–26, respectively.

The abundances of the other studied TE, however, are comparable in both garnet varieties and between the three rock types. The Tamazeght garnets are characterized by high V and Cr (up to 3000 and 1400 ppm, respectively), Zr and Hf (up to 7500 and 115 ppm,

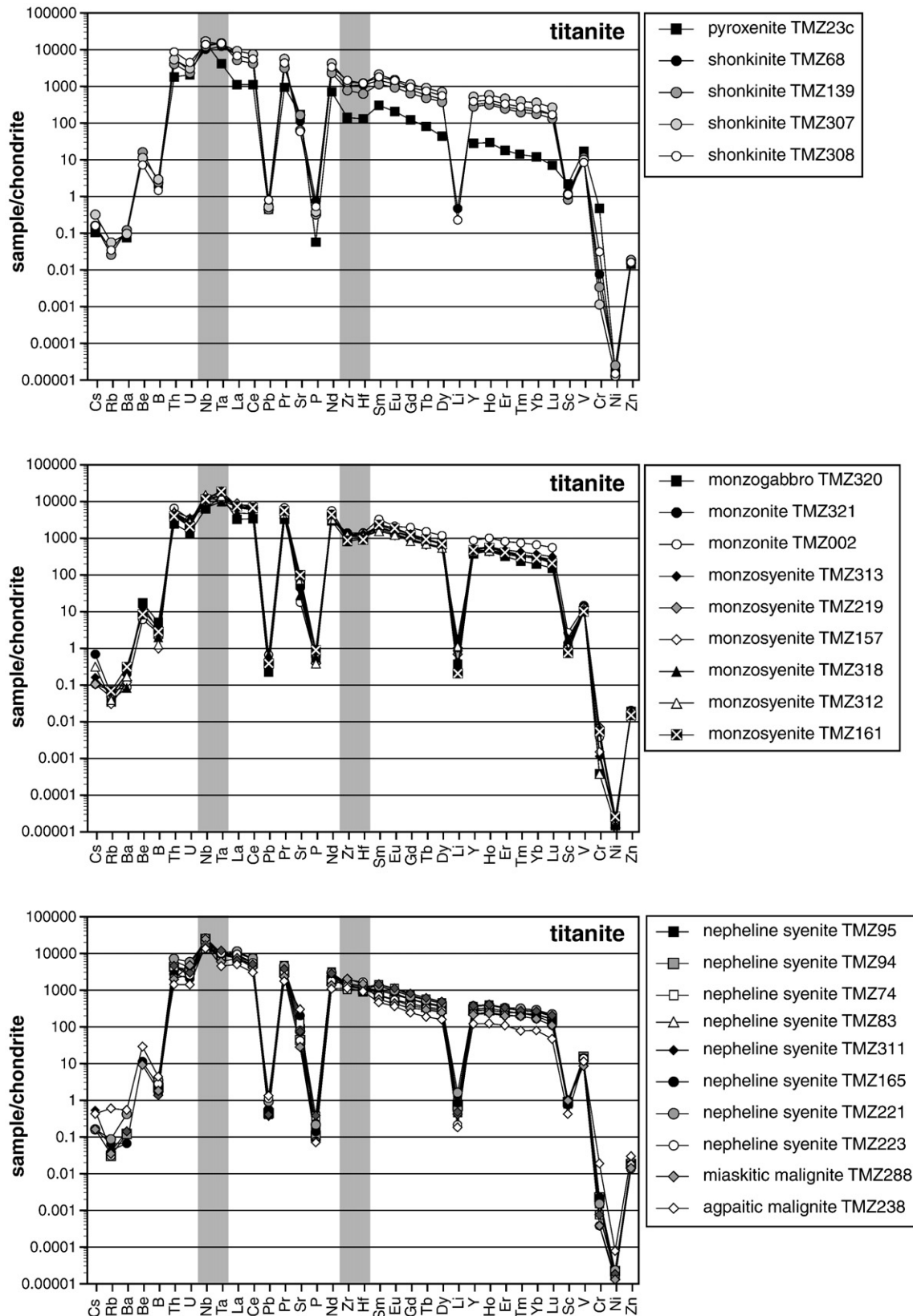


Fig. 4. Chondrite-normalized trace element diagrams for titanite from the Tamazeght complex, Morocco.

respectively), Nb and Ta (up to 800 and 20 ppm, respectively), Y (up to 700 ppm), Zn (up to 400 ppm), P (up to 185 ppm), and Th and U contents (up to 50 and 20 ppm, respectively). Other TE are uniformly low and generally do not exceed 10 ppm.

5.2. Titanite

Absolute concentrations for selected TE and chondrite-normalized REE patterns are shown in Figs. 3–5. The grouping of the data (black, grey and white symbols) reflects the relative age relations of the three major rock groups. Within one rock group the data points are placed in order of increasing evolutionary stage, based on mineral chemistry and petrography (Marks et al., 2008).

The analyzed titanites are characterized by high concentrations of Zr (up to 7,900 ppm), Nb (up to 6500 ppm), REE_{total} (up to 12,000 ppm)

and Sr (up to 2200 ppm), and moderate amounts of V (up to 900 ppm), P (up to 800 ppm), Th (up to 260 ppm), Hf (up to 180) and U (up to 45 ppm). Elements such as Li, Cs, Rb, Be, Ba, B, Zn, Ni or Sc are low and generally do not exceed the sub-ppm to ppm-level. Compared to available literature data (e.g., Chakhmouradian et al., 2003; Arzamastsev et al., 2005; Liferovich and Mitchell, 2005; Vuorinen and Hålenius, 2005) these trace element characteristics are typical of titanite. When compared to chondritic values of Zr/Hf (~36), Nb/Ta (~17) and Th/U (~4) ratios, our data show considerable variation with Zr/Hf=27–66, Nb/Ta=8–71 and Th/U=2–8 (Fig. 3).

Chondrite-normalized REE patterns are LREE-enriched (Fig. 5) and fall into a range comparable to titanites from alkaline rocks of the Alnö Complex, Sweden (Vuorinen and Hålenius, 2005) and the Khibina Complex, Russia (Arzamastsev et al., 2005). Normalized La/Lu ratios $(La/Lu)_N$ display large variations (Fig. 3). The highest value (158) is

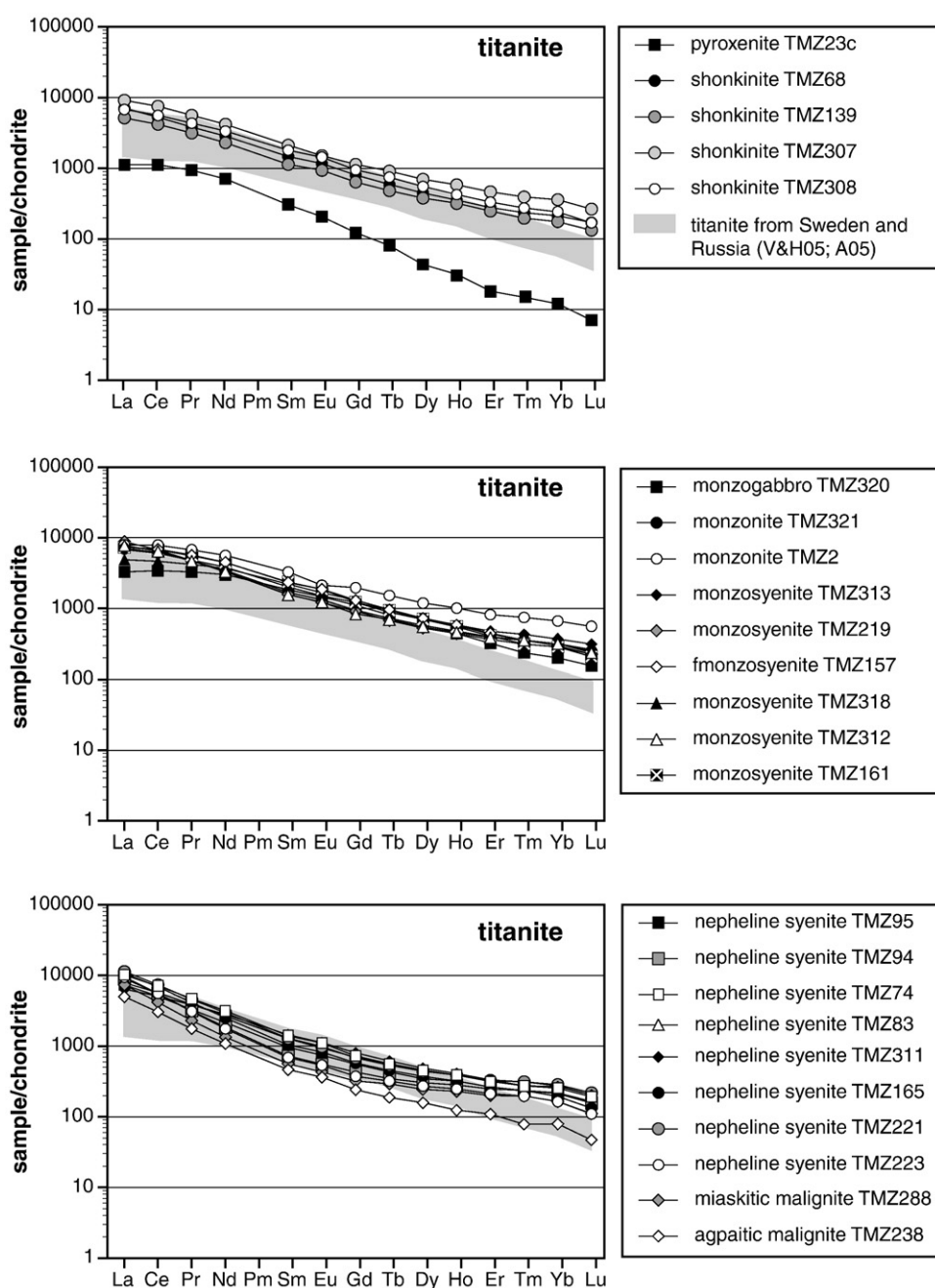


Fig. 5. Chondrite-normalized rare earth element diagrams for titanite from the Tamazeght complex, Morocco. For comparison, data for titanites from the Alnö complex, Sweden (Vuorinen and Hålenius, 2005) and from the Khibina complex, Russia (Arzamastsev et al., 2005) are shown as grey field.

found in a pyroxenite sample, which yields the lowest REE concentrations of the whole suite. In shonkinites, $(\text{La/Lu})_N$ ratios are relatively constant (35–41) being generally higher than in rocks of the monzonitic group (14–39). In contrast, $(\text{La/Lu})_N$ ratios in titanite from nepheline syenites show a large variation (32–106), with the highest ratio but the lowest concentrations in the most evolved (agpaitic) sample.

5.3. Eudialyte

Chondrite-normalized TE and REE patterns of eudialyte are shown in Fig. 6. The Tamazeght eudialytes are characterized by high concentrations of Zr (~10 wt.% ZrO_2), Hf (up to 1220 ppm), Nb (up to 8250 ppm), $\text{REE}_{\text{total}}$ (up to 13,500 ppm) and Sr (up to 23,300 ppm) and moderate amounts of Th (up to 235 ppm) and U (up to 285 ppm). Elements such as Li, Cs, Be, B, V, Ni or Cr are generally below 10 ppm.

Chondrite-normalized REE patterns have an asymmetrical concave pattern (Fig. 6b). Three of the four samples (TMZ298, 238 and 248) are very similar: After a strong decline from La to Nd, the patterns flatten towards Eu/Gd and rise slowly again towards Yb and Lu. The $(\text{La/Lu})_N$ ratios of these three patterns are very similar (14–18). The pattern of TMZ177 is slightly different: the lowest level is reached for Dy and the

rise towards Yb and Lu is weaker compared to the other three patterns, resulting in an exceptionally high $(\text{La/Lu})_N$ ratio of 79. Eudialyte from this sample is clearly hydrothermal in origin, whereas in the three other samples eudialyte is considered to be of late-magmatic origin.

Compared to data from the Ilímaussaq complex, South Greenland (Pfaff et al., in press) and from the Khibina massif, Russia (Arzamastsev et al., 2005), eudialyte from Tamazeght shows several differences (Fig. 6):

- Relatively low REE_{tot} concentrations compared to Ilímaussaq (up to 65,000 ppm) and Khibina (up to 20,000 ppm). Also, the shape of the REE patterns and the lack of a significant Eu anomaly distinguish them from eudialyte from Ilímaussaq and Khibina (Fig. 6b).
- Very high Nb/Ta ratios of 121–336 compared to Ilímaussaq (8–22) and Khibina (4–12). These result from unusually low Ta concentrations (<80 ppm) but Nb concentrations similar to Ilímaussaq and Khibina.
- High Zr/Hf ratios of 62–93 compared to Ilímaussaq (35–70) and Khibina (12–30) caused by similar Zr, but relatively low Hf concentrations (<1300 ppm).
- High Sr contents compared to Ilímaussaq (up to 1500 ppm) and Khibina (up to 14,000 ppm).

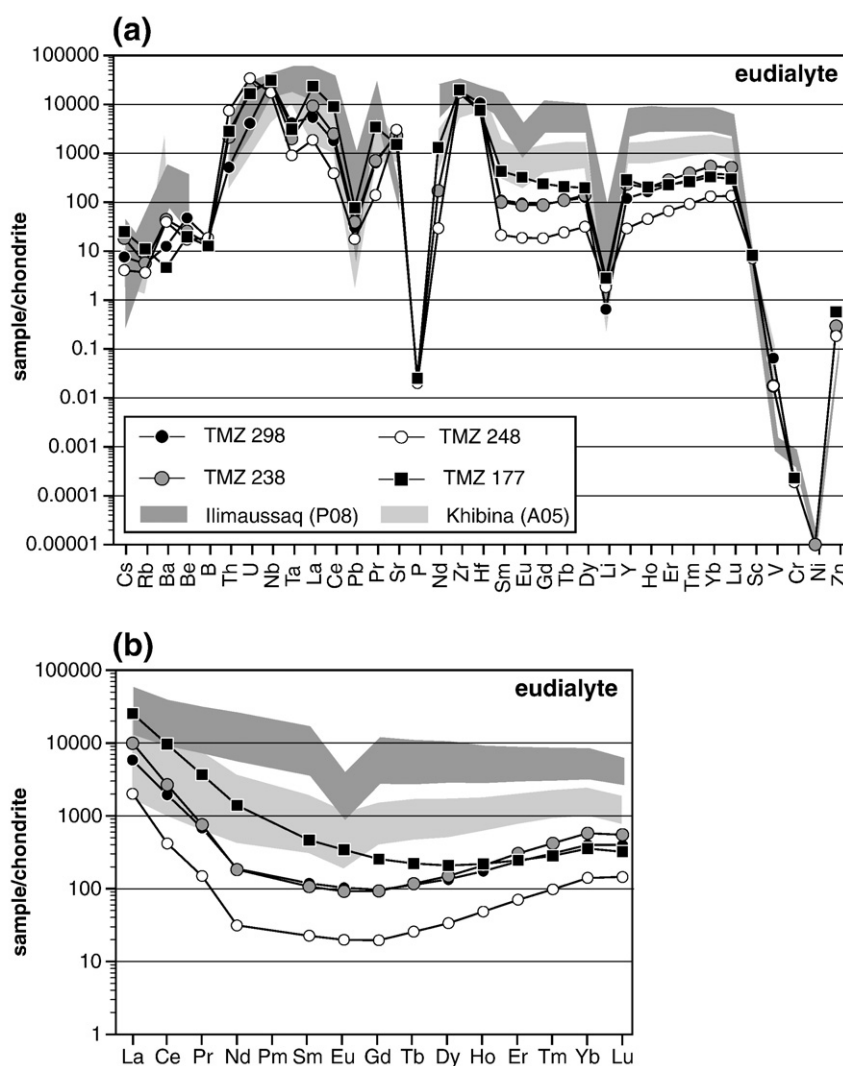


Fig. 6. Chondrite-normalized trace element diagram (a) and rare earth element diagram (b) for eudialyte from the Tamazeght complex, Morocco. For comparison, data for eudialytes from the Ilímaussaq complex, South Greenland (Pfaff et al., in press) and from the Khibina complex, Russia (Arzamastsev et al., 2005) are shown.

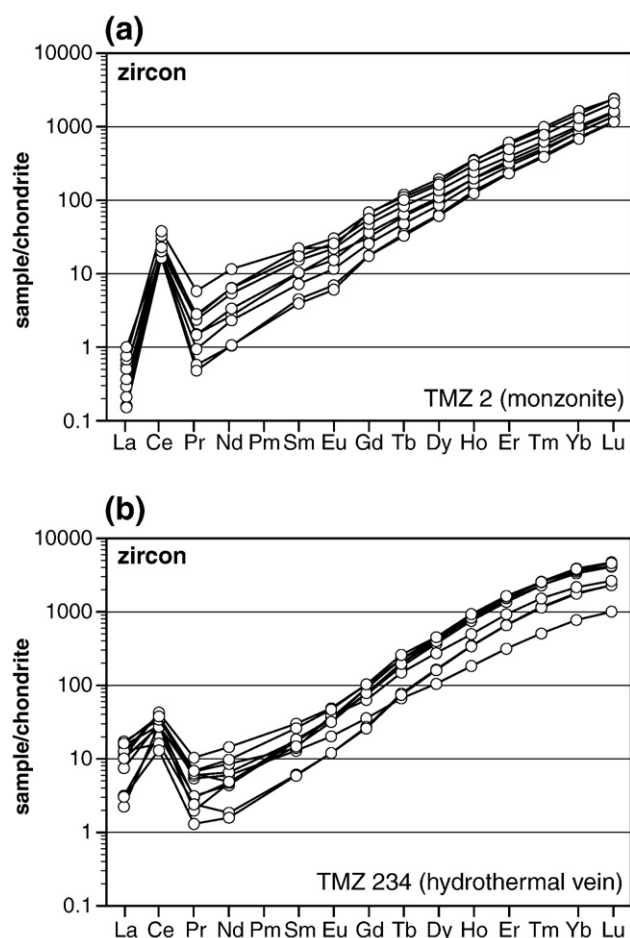


Fig. 7. Chondrite-normalized rare earth element diagram for (a) magmatic zircon from a monzonite sample (TMZ2) and (b) hydrothermal zircon from a late-stage vein (TMZ234) from the Tamazeght complex, Morocco.

5.4. Zircon

Chondrite-normalized REE patterns for zircon from two samples are characterized by a steeply rising slope from LREE to HREE (Fig. 9). They show a positive Ce anomaly but a very weakly developed Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.8\text{--}0.9$). In detail, there are some differences between the two samples. The patterns of magmatic zircon (TMZ2) are regular and smooth with Ce/Ce^* values of 14–61 and $(\text{La}/\text{Lu})_{\text{N}}$ ratios of 0.005–0.001 (Fig. 7a). Such a shape and enrichment level is typical of igneous zircon (see review of Hoskin and Schaltegger, 2003). In contrast, the patterns of the hydrothermal zircon (TMZ234) show higher levels of La than expected in a regular and smooth pattern (Fig. 7b). Consequently, calculated Ce/Ce^* values (3–14) and $\text{La}_{\text{N}}/\text{Lu}_{\text{N}}$ ratios (0.01–0.005) are lower than for magmatic zircon.

6. Discussion

Zr/Hf ratios and similar geochemical parameters (Nb/Ta , Th/U , La/Lu) can be used to discuss magmatic processes like, for example, the nature of fractionating mineral assemblages and the resulting differentiation paths of magmas (e.g., Bea et al., 2006; Claiborne et al., 2006). For example, experimental and field-based work showed that significant zircon fractionation leads to decreasing Zr/Hf ratios in the residual melts since $K_{\text{D}}^{\text{Zr}}/K_{\text{D}}^{\text{Hf}}$ ratios for zircon are >1 (e.g., Linnen and Keppler, 2002; Claiborne et al., 2006). Based on a large amount of Zr and Hf data from various rock-forming and accessory minerals, Bea et al. (2006) discuss these effects. Their work forecasts that other HFSE-rich minerals should

have similar effects, depending on the differences of the partition behavior between the two element pair members. Titanite in particular was proposed to play an important role. Detailed investigations of other TE ratios (e.g., Nb/Ta , Th/U and others) in HFSE-rich minerals are scarce, but in general, similar effects should be expected. Here, we attempt to substantiate this idea, since titanite fractionation during magmatic differentiation may be important for calc-alkaline rock suites (Piccoli et al., 2001; Broska et al., 2007) as well as for some peralkaline ones (Arzamastsev et al., 2005; Vuorinen and Hålenius, 2005).

6.1. Identifying the major HFSE carrier mineral in the various Tamazeght lithologies

In the Tamazeght rocks, zircon is very rare. Although it is a common mineral in some late-stage pegmatites and veins of nepheline syenites (Kchit, 1990; Marks et al., 2008), we found zircon only in one monzonitic rock, occurring very rarely and apparently coexisting with titanite. Thus, zircon fractionation should not be an important process during the evolution of the majority of the Tamazeght rocks. Instead, unusually large amounts of titanite are present in most rock types (shonkinites, rocks of the monzonitic group and in most nepheline syenites) and obviously, titanite fractionation played a major role in the HFSE evolution of these rocks. In the most evolved rocks (agpaitic malignites) titanite is unstable with respect to eudialyte, which is the major HFSE-host in these rock types. In one sample, however, both titanite and eudialyte do occur. Ti-bearing andradite is an important cumulus phase in the oldest and least evolved rock types (glimmerites, pyroxenites) and most likely represents the major HFSE-sink in these rocks. Accessory perovskite in some of these samples may also contribute to the HFSE budget of these rocks; unfortunately, it could not be analyzed due to both strong alteration and small size. Titanite is very rare in these rocks. In all, the important mineral assemblages when discussing the HFSE budget of the Tamazeght melt(s) are

- Ti-bearing andradite $\pm$ perovskite/titanite in glimmerites and pyroxenites,
- titanite $\pm$ Ti-bearing andradite in shonkinites,
- titanite $\pm$ zircon in monzonitic rocks,
- titanite in miaskitic nepheline syenites,
- eudialyte $\pm$ titanite in agpaitic and transitional nepheline syenites and
- zircon or eudialyte $\pm$ catapleite in late-stage hydrothermal veins.

In the following, we will discuss the possible effect of these minerals on the evolution of geochemical parameters, such as Zr/Hf, Nb/Ta, Th/U and La/Lu ratios in alkaline to peralkaline melts of the Tamazeght complex and in general.

Table 4

Rare earth element (REE) content of zircon from the Tamazeght complex, Morocco

Sample analysis	TMZ234				TMZ2			
	2–10–2	$\pm 2\sigma$	2–12–2	$\pm 2\sigma$	F-1	$\pm 2\sigma$	D-3	$\pm 2\sigma$
ppm								
La	0.77	0.30	4.20	0.42	0.04	0.01	0.25	0.06
Ce	13.6	0.7	21.7	1.1	11.0	0.2	14.6	0.4
Pr	0.30	0.12	0.61	0.17	0.06	0.01	0.27	0.03
Nd	2.07	0.93	2.31	0.85	0.50	0.09	3.01	0.24
Sm	2.66	0.22	2.27	0.88	0.69	0.11	2.67	0.23
Eu	1.99	0.14	1.84	0.41	0.40	0.07	1.50	0.09
Gd	15.7	3.2	15.9	3.1	3.59	0.35	11.4	0.6
Tb	7.58	3.42	7.34	2.92	1.31	0.25	3.79	0.35
Dy	104	4	101	7	16	0.54	41.4	2.0
Ho	48.4	4.4	46.8	18.6	7.63	1.23	17.1	1.7
Er	254	9	256	10	39.3	2.9	82.0	3.3
Tm	65.5	5.3	64.8	14.9	10.4	1.9	19.8	1.7
Yb	639	134	638	128	118	14	216	15
Lu	117	5	119	7	30.2	2.1	53.0	2.1

6.2. Effect of titanite fractionation on Zr/Hf, Nb/Ta, Th/U and La/Lu ratios

In this section we investigate the influence of titanite fractionation on the geochemical evolution of the Tamazeght melts. The experimental work of Prowatke and Klemme (2005) showed that for some trace elements (e.g., Sr, Zr, Hf) the respective titanite–melt partition coefficients are not significantly affected by melt composition. Thus, the observed concentration differences in titanite for these elements directly correspond to concentration differences in the melts from which titanite crystallized (Fig. 3).

For other elements (Nb, Ta, Th, U and REE) the partition coefficients between titanite and melt are strongly influenced by the melt composition and increase with degree of polymerization, for which the alumina saturation index ($ASI = \text{molar Al}_2\text{O}_3 / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$) is used as a proxy. The concentration differences of these elements in titanites might partly be a result of changes of the respective partition coefficients because of distinct melt compositions (Fig. 3). The variability of titanite–melt partition coefficients for these elements is up to two orders of magnitude, making a quantitative treatment of melt evolution difficult (Prowatke and Klemme, 2005). However, variability of the K_D value ratios for Nb/Ta, Th/U and La/Lu are much smaller (significantly less than one order of magnitude) and thus allows a quantitative treatment.

Based on the evaluation of several thousands of whole-rock compositions of a large variety of volcanic rocks types (GEOROC-database), melt compositions with $ASI < 0.5$ are only scarcely observed and seem unrealistic as parental melts for most of the Tamazeght rocks. Consequently, the reported partition coefficients (Prowatke and Klemme, 2005) for such compositions were neglected. Moreover, the values given for a rhyolitic composition were excluded, since no quartz-rich compositions are known from the Tamazeght complex. Based on this, we use average K_D value ratios of 0.55 for Zr/Hf (range of 0.51–0.57), of 0.1 for Nb/Ta (0.07–0.16), of 4.5 for Th/U (2–9) and of 0.48 for La/Lu (0.16–0.78) for our geochemical modelling.

The calculated Zr/Hf, Nb/Ta, Th/U and La/Lu ratios of the respective melts for the individual samples are illustrated in Fig. 8, a plot of the measured Zr, Nb, Th and REE_{tot} concentrations in titanite versus the respective element ratios is shown in Fig. 9, while Fig. 10 illustrates correlations between Zr/Hf ratios and ratios of Nb/Ta, Th/U and La/Lu. The indicated “error bars” for these data points are estimated from the uncertainty introduced by averaging the measured element concentrations within individual samples and from the variability of K_D ratios for Zr/Hf, Nb/Ta, Th/U and La/Lu (see above). Based on Figs. 8–10, the following general statements can be made.

- All calculated Zr/Hf, Nb/Ta and most La/Lu ratios are super-chondritic, while Th/U ratios are sub-chondritic. Within and between the three rock groups, significant variability in calculated element ratios exist, although not for all element ratios in the same scale and matter. However, the observed variability between the rock groups does not follow a strict systematic order with relative differentiation stage of the rocks (Fig. 8).
- The correlations between the calculated element ratio and its numerator are of different quality for the Zr/Hf, Nb/Ta, La/Lu and Th/U systems (Fig. 9).
- Zr/Hf ratios correlate roughly positive with Nb/Ta and La/Lu ratios and negative with Th/U ratios (Fig. 10).

These findings have the following implications: First of all, we attribute the high Zr/Hf, Nb/Ta and La/Lu, the low Th/U ratios and the observed variation of these ratios within one rock group largely to the fractionation of titanite, since the K_D ratios of titanite for Zr/Hf, Nb/Ta and La/Lu are < 1 and > 1 for Th/U (Tiepolo et al., 2002; Prowatke and Klemme, 2005). Significant fractionation of titanite (as is evident from petrography) should thus lead to increasing Zr/Hf ratios with ongoing melt evolution. This is in accordance with our observations: for

example, within the monzonitic group, a monzogabbro has a relatively low Zr/Hf, whereas a monzonite and all monzoesyenites show higher Zr/Hf ratios (Fig. 8). One monzonite has the lowest Zr/Hf ratio within this rock group and this sample (TMZ2) bears additional zircon, which was shown to potentially decrease the Zr/Hf ratio in the melt (e.g., Claiborne et al., 2006). Similar relations are present within the nepheline syenitic and malignitic group. Some of the highest Zr/Hf ratios are found in the (based on petrography and mineral chemistry) most evolved samples of this group. Similar systematics are observed for Nb/Ta and La/Lu ratios and a reverse behavior for Th/U ratios. Such an effect of titanite fractionation on Zr/Hf ratios was proposed by Bea et al. (2006) and we find that our data support this forecast and expand it to cover Nb/Ta, U/Th and La/Lu ratios, which show comparable behavior. The roughly positive correlations between Zr/Hf, Nb/Ta and La/Lu ratios and the negative ones for Zr/Hf and Th/U ratios (Fig. 10) are further support of this interpretation.

Interestingly, the three rock groups do not show a continuous trend in terms of element ratios and concentrations (Fig. 8). This is best seen in the Zr/Hf plot, where Zr/Hf ratios are lowest for the intermediate rock types, intermediate for the oldest and most primitive units and highest for the most evolved group. Similar systematics are observed for Nb/Ta and La/Lu ratios and a reverse behavior (although less obvious) for Th/U ratios. If titanite fractionation from one common parental melt is the only process responsible for the observed variability of the element ratios of interest, one would expect a continuous evolution from the oldest to the youngest units and strong correlations between the element ratio and the numerator of the respective ratio. We conclude, that geochemically distinct melt reservoirs (in terms of element ratios and concentrations) play a role for the genesis of the investigated sample suite. This is in accordance with petrological results (Marks et al., 2008) and Nd and O isotopic data (Marks, unpublished data), and provides further evidence for source heterogeneity being important for the genesis of the Tamazeght complex. This conclusion does not prevent the use of the above-mentioned data but should be regarded as a useful tool for such investigations.

Theoretically, good correlations between the calculated element ratio (e.g., Zr/Hf) and its numerator (e.g., Zr) should be expected, since the concentration of these elements should increase during differentiation, as they are generally incompatible. However, the observed correlations (Fig. 9) are of different quality for the Zr/Hf, Nb/Ta, La/Lu and Th/U systems.

Our data imply that the Nb/Ta system is the best indicator to monitor titanite fractionation. It shows the most pronounced variation (which probably results from the lowest K_D value ratio) with high magnitude and a good correlation with Nb concentration (Fig. 9). This is taken as a proof for the assumption, that titanite dominates the Nb–Ta budget in most of our samples. The two most significant outliers from this otherwise well-defined trend are samples, where other minerals (Ti-bearing andradite for the pyroxenite and eudialyte for the agpaitic malignite) contribute to the HFSE budget of the rock. Although we cannot prove equilibrium between them and titanite beyond all doubt, their deviation from this trend is a good indicator, since in these two cases titanite competes for Nb with garnet and eudialyte, respectively. This should, however, not influence the calculated Nb/Ta ratio in the melt (since the K_D value ratio for titanite should not change), but will shift the absolute concentration of Nb in titanite towards lower values. This might explain their deviation from the otherwise well-defined correlation.

The relatively poor correlation for the Zr/Hf system may be explained by the additional influence of clinopyroxene, which contains up to a few hundreds of ppm Zr (Marks et al., 2008). Given the high modal amount of clinopyroxene compared to titanite, clinopyroxene might thus contribute significantly to the Zr/Hf budget of some rocks (roughly up to 40 % of the total Zr) and this explains the significant scatter for the Zr/Hf system (Fig. 9a).

The lack of a significant correlation for the Th/U and La/Lu systems may be explained by the influence of other minerals (e.g., apatite), larger errors of these calculations (Fig. 9) or by the fact that these systems are more fragile against geochemical heterogeneities in the respective melt reservoirs from which the various samples crystallized. Alternatively, for La/Lu ratios, the absence of a correlation between La/Lu and REE_{tot} (Fig. 9) might partly be a result of not fulfilling Henry's law conditions, given the high REE_{tot} concentrations in some titanites (Fig. 3; Prowatke and Klemme, 2006).

6.3. The role of Ti-bearing andradite

REE patterns in garnet evolve from typically convex upwards LREE-depleted ones to LREE-enriched patterns at the rim of crystals (Fig. 2). Similar characteristics are found in Ti-bearing andradite from other alkaline complexes (e.g., Alnö complex, Sweden), where these patterns are thought to reflect both the Ti-rich nature of the garnet and the magma composition (Vuorinen et al., 2005). Most likely, this mimics an evolving melt that is undergoing HREE depletion through garnet fractionation – a likely explanation, since pyroxenites display clear cumulate textures (Marks et al., 2008; Fig. 1). A recent study of Ti-bearing andradite from Mt. Somma-Vesuvius, Italy (Scheibner et al., 2007; see their Fig. 10) comes to similar conclusions. These

profiles are identical to the garnet REE characteristics displayed at Tamazeght (Fig. 2).

Fig. 11 illustrates a plot of both Zr concentration and Zr/Hf ratio in garnet against their $(\text{La/Lu})_{\text{N}}$ ratios. The latter was shown to increase during differentiation (Scheibner et al., 2007). Thus, Zr concentrations and Zr/Hf in garnet appears to decrease with ongoing differentiation, similar to the trend seen in zircon (Claiborne et al., 2006) but opposite to that seen in titanite.

6.4. REE distribution between titanite and zircon

Only in one monzonite sample (TMZ2) magmatic zircon is present. However, compared to titanite (~3 vol.%), zircon is very rare in this sample. As a test for the chemical equilibrium between them, we apply titanite–melt partitioning data of Prowatke and Klemme (2005) and zircon–melt partitioning data of Ballard et al. (2002) and Thomas et al. (2002) to calculate the REE pattern for the melts in equilibrium with titanite and zircon, respectively (Fig. 12).

The data for zircon of Ballard et al. (2002) nicely reproduce the slightly arched REE patterns calculated with the titanite data (Prowatke and Klemme, 2005). They reproduce best the characteristic $(\text{La/Lu})_{\text{N}}$ ratios > 1 and overlap with patterns calculated for relatively polymerized melts, which is in accordance with whole-rock data for

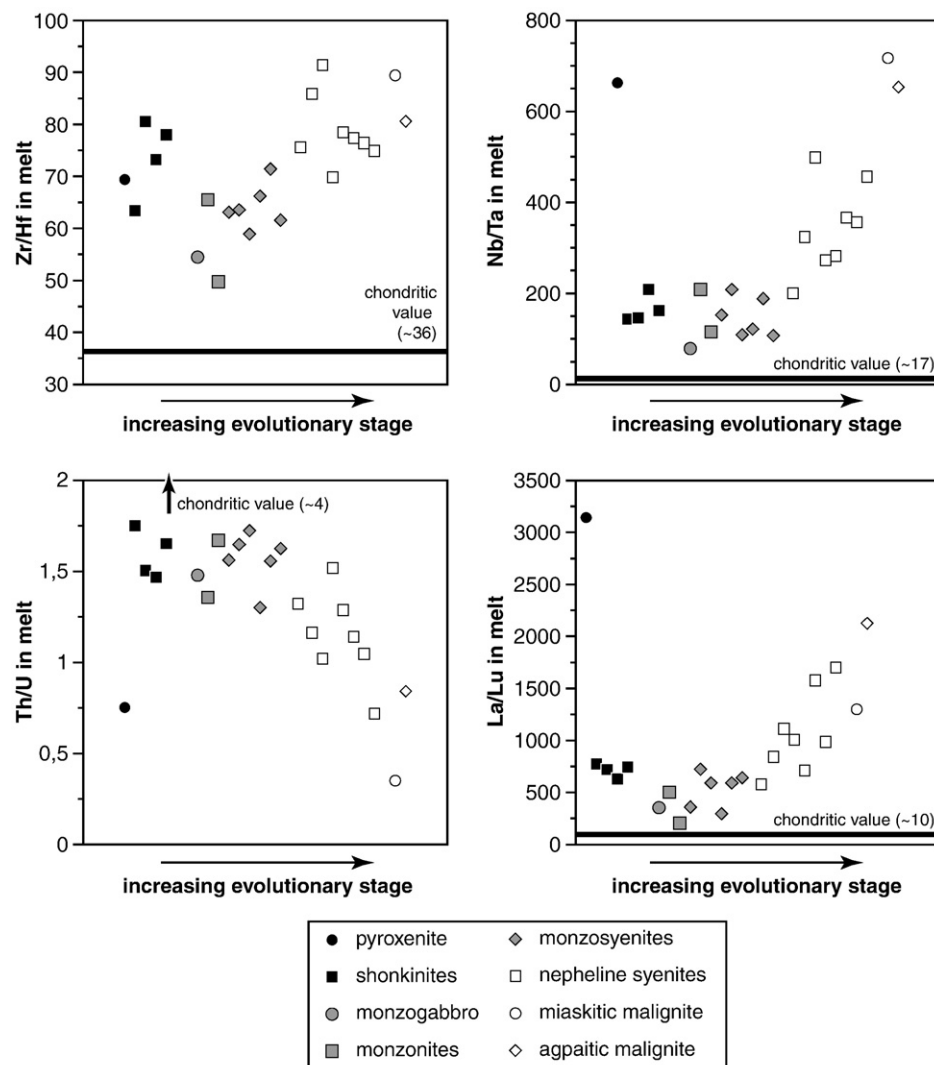


Fig. 8. Calculated Zr/Hf, Nb/Ta, Th/U and La/Lu ratios for the respective melts of the different rock types.

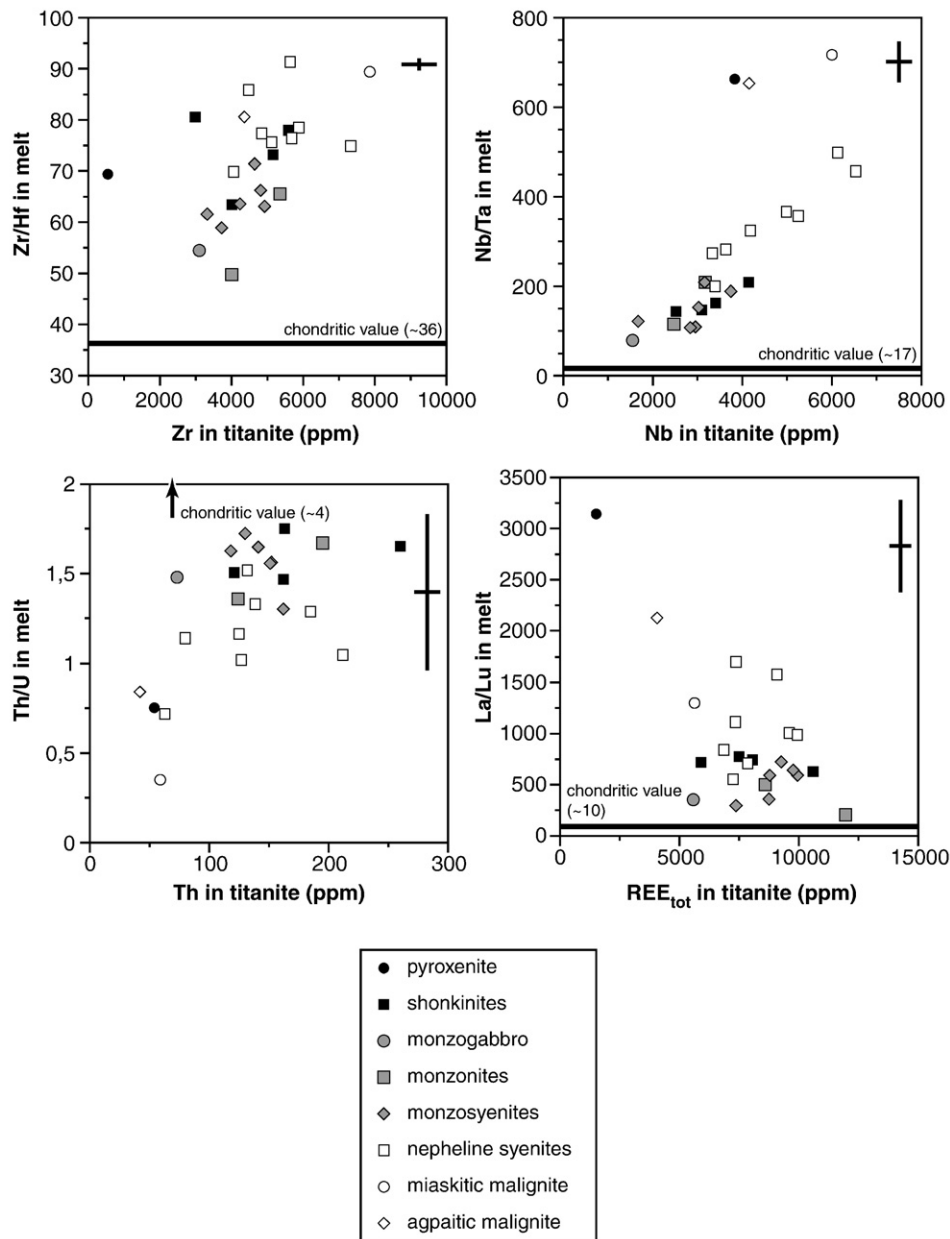


Fig. 9. Measured Zr, Nb, Th and REE_{tot} concentrations in titanite versus the calculated respective element ratios for the corresponding melts.

monzonites of the Tamazeght complex (ASI=0.7–0.9; Kchit, 1990). The data of Thomas et al. (2002) however, show significant misfit. The most obvious difference is their (La/Lu)_N ratio <1. Reasons for this misfit are not completely clear to us, but may potentially result from the different analytical methods used or from the compositional variations of the melts/whole-rocks investigated: Whereas the data of Ballard et al. (2002) were derived by the comparison of REE concentrations in whole-rock samples and their respective zircons, Thomas et al. (2002) used the melt inclusion-mineral (MIM) technique.

Whole-rock data from the rocks of Ballard et al. (2002) have ASI values between 0.8 and 0.9 (J. Michael Palin, pers. communication), whereas the ASI values for the melt inclusions reported in Thomas et al. (2002) are higher (0.9–1.4, with nearly all analyses being >1 [Additional studies on zircon–melt REE partitioning (Murali et al., 1983; Bea et al., 1994; Rubatto and Hermann, 2007) were not used here, since they either do not report whole-rock or matrix data or

present only data for too few REE.]. The melt inclusion data reported by Thomas et al. (2002) are significantly different from ASI values reported for the monzonitic rocks of the Tamazeght complex (0.7–0.9; Kchit, 1990) and this may be a reason for the observed misfit (Fig. 12). Murali et al. (1983) proposed, that the melt composition may have an influence on the REE partitioning behavior of zircon. However, to date there is no detailed study investigating these potential effects (in terms of ASI or AI) on the REE partitioning of zircon, as is available for titanite (Prowatke and Klemme, 2005). In any case, the method and samples used by Ballard et al. (2002) provide reliable results and yield results consistent with our data.

6.5. HFSE distribution between titanite and eudialyte

In one malignite sample (TMZ238) both titanite and eudialyte are present. Both occur as euhedral to subhedral crystals and no reaction

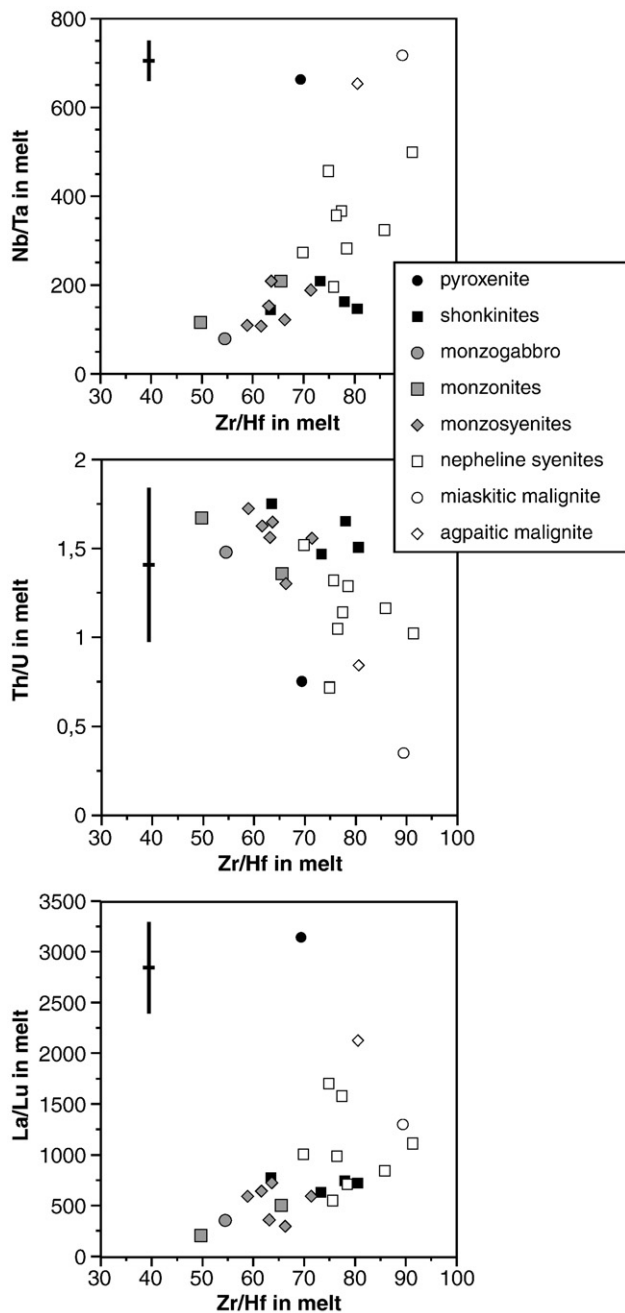


Fig. 10. Correlations between Zr/Hf ratios and ratios of Nb/Ta, Th/U and La/Lu. The “error bars” indicated are estimations of the uncertainty of these data points introduced by averaging the measured element concentrations in titanite and by the variability of K_D ratios for Zr/Hf, Nb/Ta, Th/U and La/Lu (see text for details).

textures between them are observed. The observed deviation of this sample from the Nb in titanite versus Nb/Ta in melt plot (Fig. 9) is a further hint to assume near-equilibrium between titanite and eudialyte. Calculated titanite–eudialyte distribution coefficients for this sample are given in Table 5.

The very high Zr/Hf and Nb/Ta ratios found in Tamzeght eudialyte (compared to titanite of the complex and compared to eudialyte from Ilímaussaq and Khibina (Arzamastsev et al., 2005, Pfaff et al., in press)) can be interpreted as a direct result of significant titanite fractionation prior to eudialyte precipitation. In the eudialyte-bearing rocks from Ilímaussaq, no titanite is present and in the Khibina rocks, titanite is

present in only some of the rocks (Arzamastsev et al., 2005) locally coexisting with eudialyte. However, as no detailed information on age relations or modal variations of titanite and eudialyte are provided (Arzamastsev et al., 2005), this limits our possibilities for discussion of these data.

6.6. REE partitioning behavior of eudialyte

Using the partitioning data of Prowatke and Klemme (2005) we calculated the REE patterns for the possible melts from which titanite crystallized from (Fig. 13a). With increasing assumed degree of depolymerization (low ASI and high AI), the relative position of the calculated melt patterns shift towards higher levels. Since agpaite melts are strongly depolymerized ($AI > 1$), we conclude that only the upper part of the theoretical range might represent realistic melt compositions. It is interesting to note that the general shape of the calculated REE patterns for the melt is very similar compared to measured REE patterns for magmatic eudialyte of this (TMZ238; Fig. 13a) and the two other investigated samples (TMZ248 and 298; Fig. 6b).

Using the REE data of eudialyte from sample TMZ238 and realistic melt compositions, we calculated then the distribution coefficients for REE between eudialyte and melts (Table 5). With decreasing degree of polymerization of the melt, REE distribution coefficients decline from about 5–18 ($ASI=0.57$, $AI=0.75$) to values between 0.3 and 1.5 ($ASI=0.11$, $AI=4.58$). Given this relatively large range (Fig. 13b), a detailed quantification of eudialyte–melt distribution coefficients seems difficult. Also, taking the uncertainty introduced by the

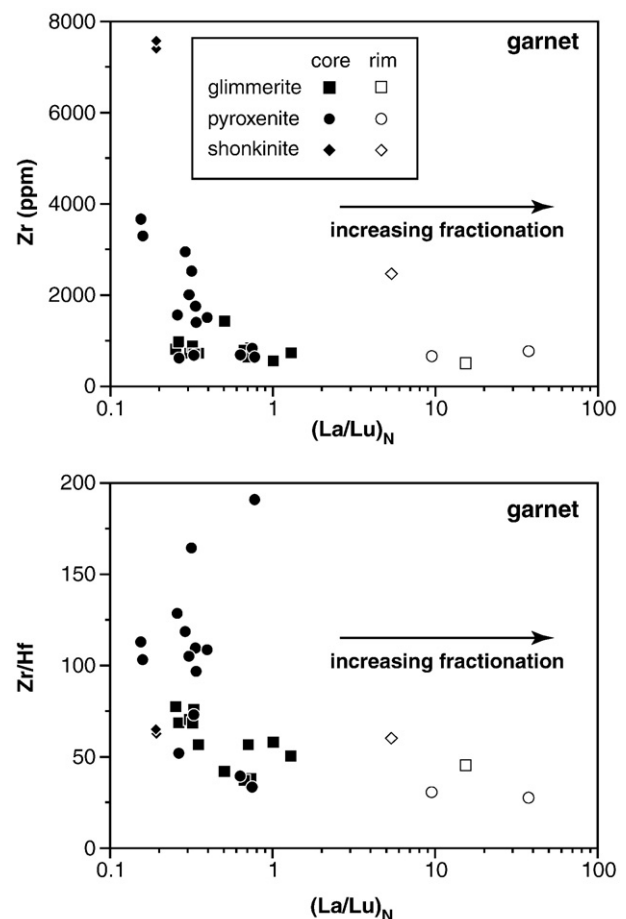


Fig. 11. Correlations between Zr concentration and Zr/Hf ratios with $(La/Lu)_N$ ratios for garnet from the Tamazeght complex.

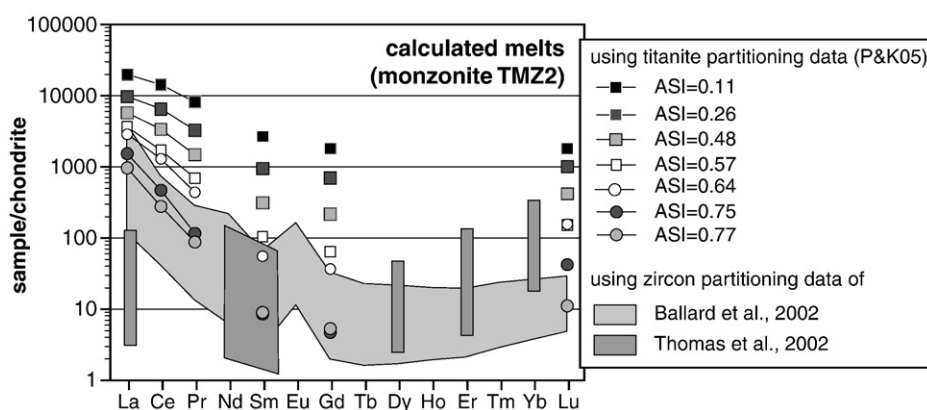


Fig. 12. Calculated REE patterns for the melts in equilibrium with titanite and zircon from sample TMZ2, respectively, based on titanite–melt partitioning data of Prowatke and Klemme (2005) and zircon–melt partitioning data of Ballard et al. (2002) and Thomas et al. (2002).

assumption of a chemically identical melt for eudialyte and titanite into account (see above), the distribution coefficients are possibly underestimated for LREE and overestimated for MREE and HREE. However, for a given melt composition, the relative differences of distribution coefficients for the various REE are rather small and vary from La to Lu by a factor of about 3–5. Also, the relative differences are highest for extremely high AI values getting smaller with decreasing AI (Fig. 13b).

As an independent test for the reliability of the different sets of eudialyte–melt distribution coefficients, we applied these to eudialyte-bearing rocks from the Ilímaussaq complex, South Greenland. We

used REE data of eudialyte from Pfaff et al. (in press) and data for rocks that might represent their parental melt (Sørensen, 2006). The observed REE patterns of these whole-rock data are reproduced best if the distribution coefficient sets for melt compositions with AI values between 0.75 and 1.32 are used (Fig. 13c). Only if these sets are used is the calculated normalized La concentration larger than that of Ce, a feature that is typical of the assumed Ilímaussaq melts. Since the AI values of the whole-rock data are in the same range (AI = 1.0–1.3), we conclude that these distribution coefficient sets for eudialyte are the most reliable estimations.

In summary, our calculations suggest that REE behave compatibly during crystallization of eudialyte and realistic distribution coefficients for REE are estimated to vary between 2 and 20 for most apatitic melt compositions. For a given melt composition D_{La} is generally $<D_{Lu}$ and a slight maximum in D -values is observed for MREE (Gd).

Table 5
Calculated titanite–eudialyte and eudialyte–melt distribution coefficients

Titanite–eudialyte distribution coefficient					
TMZ238					
La	0.51				
Ce	1.16				
Pr	2.36				
Nd	6.04				
Sm	4.39				
Eu	3.95				
Gd	2.62				
Tb	1.71				
Dy	1.07				
Ho	0.63				
Er	0.37				
Tm	0.22				
Yb	0.13				
Lu	0.09				
Eudialyte–melt distribution coefficient					
ASI	0.11	0.26	0.48	0.64	0.57
Al	4.58	2.23	1.32	1.04	0.75
La	0.79	1.59	2.71	4.26	5.42
Ce	0.48	1.05	2.03	3.98	5.27
Pr	0.35	0.88	1.93	4.11	6.51
Nd					
Sm	0.28	0.78	2.38	7.11	13.44
Eu					
Gd	0.42	1.08	3.46	11.64	20.39
Tb					
Dy					
Ho					
Er					
Tm					
Yb					
Lu	1.53	2.72	6.58	18.06	17.62

7. Summary and conclusions

Zr and Hf behave nearly identical in terms of geochemical behavior and, consequently most of the crust maintains near-chondritic Zr/Hf ratios of ~35–40. In contrast, the calculated melts of the Tamazeght complex, Morocco have super-chondritic and highly variable Zr/Hf ratios of ~50–90. As titanite is the primary reservoir for both Zr and Hf in most of these rocks and preferentially incorporates Hf, the crystallization of titanite leads to these elevated Zr/Hf ratio in the residual melt. Thus, high Zr/Hf is a fingerprint for the fractionation of titanite. In that sense, titanite fractionation in magmatic systems has the opposite effect to zircon fractionation (e.g., Claiborne et al., 2006), and our results support the work of Bea et al. (2006). Comparable behavior is observed for Nb/Ta and La/Lu, while the opposite (although less obvious) is visible for Th/U ratios.

However, if all of the investigated rocks units were to have been derived from a common parental melt, Zr/Hf ratios should systematically increase from oldest to youngest rock types and excellent correlations between Zr/Hf ratios and Zr concentration in titanite and the other element ratios would be expected. This, however, is not the case and the four investigated element ratios (Zr/Hf, Nb/Ta, Th/U and La/Lu) show variably disturbed behavior. We interpret this as indication of the influence of geochemically distinct melt batches (both in terms of element concentrations and element ratios), which is in accordance with the interpretations given by Marks et al. (2008) based on mineral chemistry and petrology of the rocks. In general, this means that the investigated element ratios cannot on their own be used to monitor fractionation of HFSE-rich mineral phases within a given magmatic suite,

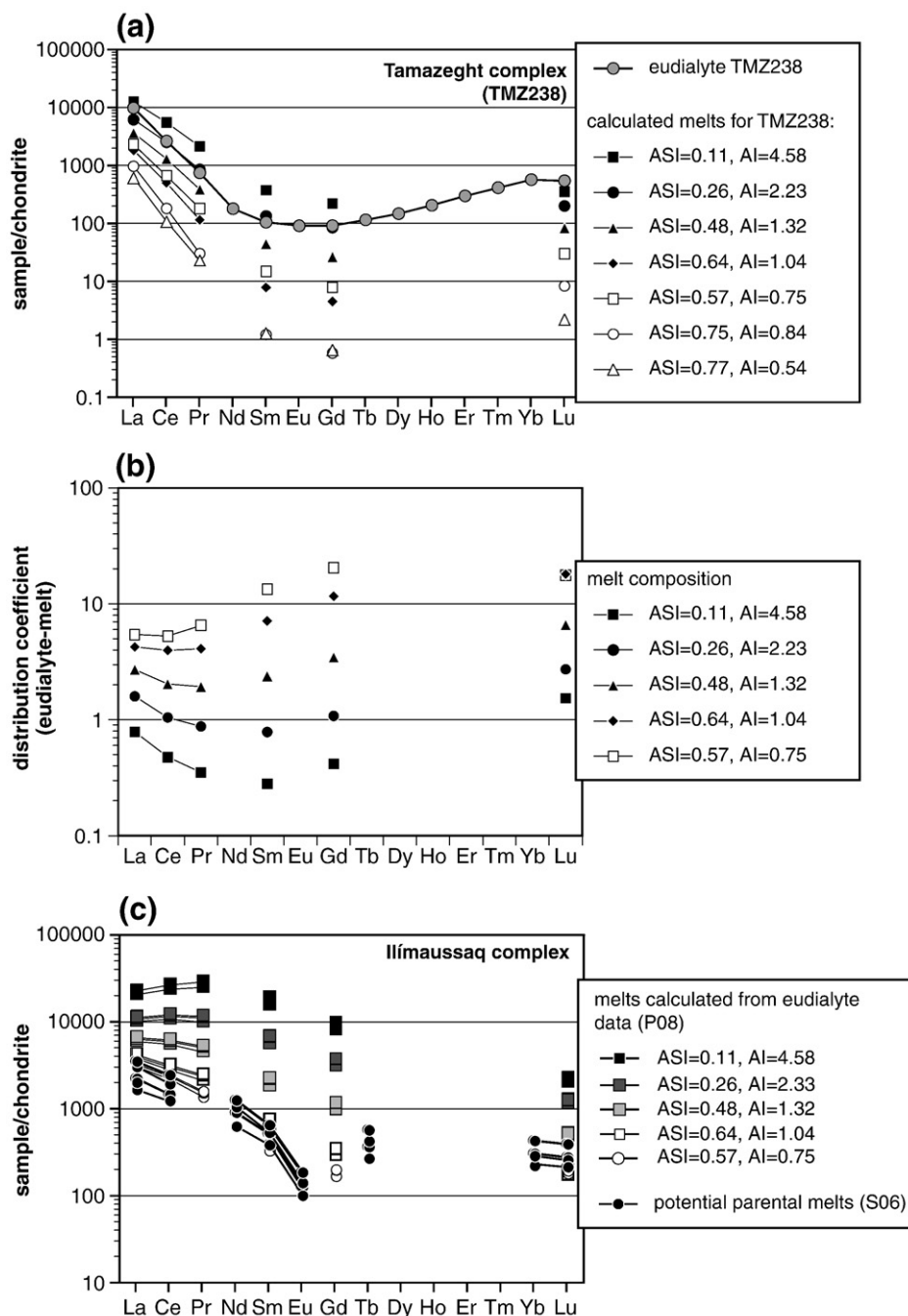


Fig. 13. a) Chondrite-normalized REE patterns for the possible melts from which titanite in sample TMZ238 crystallized (partitioning data from Prowatke and Klemme, 2005). b) Calculated distribution coefficients for REE between eudialyte and various melts. c) Comparison between calculated and postulated melt compositions (in terms of REE) for eudialyte-bearing rocks of the Ilímaussaq Complex, South Greenland using the estimated eudialyte–melt partition coefficients. REE data of eudialyte from these rocks from Pfaff et al. (in press), data for potential parental melts for these rocks from Sørensen (2006).

but that they are useful for distinguishing geochemically different melt reservoirs of a given rock series.

Acknowledgements

Funding for this work by the Deutsche Forschungsgemeinschaft (grant Ma 2135/11-1 and 11-2) and the Natural Sciences and Engineering Research Council of Canada (IMC: Discovery grant funds) is gratefully acknowledged. The ion microprobe facility at UCLA is partly supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, National Science Foundation. M.M. especially thanks Annabel Händel for the careful and time-consuming hand picking of the

large number of mineral separates used in this study and Thomas Wenzel and Ron Frost for insightful discussions. We also acknowledge the support of Francois Fontan (who passed away in August 2007), Pierre Monchoux and Stefano Salvi (Toulouse, France) to investigate this intrusive complex in more detail. Ali Bajja (Marrakesh, Morocco) is thanked for his co-operation, which facilitated the field trip in May 2006. We also thank the citizens of the small Berber village of Anougal for their hospitality, and Boujemaa Boudaoud (Azrou, Morocco) for being our guide in the High Atlas Mountains and for supplying important infrastructure in the field. We acknowledge the editorial handling of Roberta Rudnick and the constructive comments of Calvin Miller and one anonymous reviewer.

Appendix A

Laser ablation ICP-MS results for NIST SRM 612 and BCR 2-G glasses. Preferred values are from Jochum and Nohl (2008) and the GeoRem webpage (www.georem.mainz.mpch-mainz.gwdg.de).

NIST SRM 612					BCR 2-G			
	Preferred values	Mean (n=29)	±2σ	1 RSD (%)	Preferred values	Mean (n=24)	±2σ	1 RSD (%)
ppm								
Li	42	44	3	4.9	9	10	1	2.1
Be	38	39	2	2.4	2.3	2.1	0.3	−12.5
B	35	54	31	54.1	6	7	3	−27.3
P	51	57	9	3.6				
Sc	41	40	5	−2.5	33	34	2	2.7
V	39	39	2	−0.3	416	419	26	−0.5
Cr	36	38	2	−5.8	17	16	1	−5.3
Ni	38.8	39	3	1.7	13	12	2	−1.7
Zn	38	43	9	12.3	125	146	23	−0.4
Rb	31.4	34	2	6.7	47	50	4	3.1
Sr	78.4	80	5	4.6	342	334	27	0.3
Y	38	38	2	−1.0	35	34	2	−1.8
Zr	38	37	2	3.4	184	180	9	−2.3
Nb	38	35	1	−7.7	12.5	11	1	−17.8
Cs	42	44	1	4.8	1.16	1.2	0.2	0.3
Ba	39.7	38	3	−0.1	663	646	36	−3.3
La	35.8	38	2	6.5	24.7	27	2	9.4
Ce	38.7	39	2	2.0	53.3	53	3	2.8
Pr	37.2	37	2	0.5	6.7	6.5	0.4	−3.1
Nd	35.9	35	2	0.4	28.9	28	2	0.6
Sm	38.1	37	2	0.9	6.59	6.5	0.4	−0.3
Eu	35	37	2	6.7	1.97	2.0	0.1	2.8
Gd	36.7	36	3	−3.5	6.71	6.4	0.7	−4.3
Tb	36	38	2	5.0	1.02	1.00	0.1	−0.3
Dy	36	35	2	−3.8	6.44	6.3	0.5	−1.1
Ho	38	38	2	1.2	1.27	1.3	0.1	3.4
Er	37	35	2	−5.4	3.7	3.5	0.3	−2.9
Tm	38	36	2	−4.6	0.51	0.50	0.04	−0.3
Yb	39.2	38	2	−3.7	3.39	3.4	0.2	2.4
Lu	36.9	36	2	−3.3	0.503	0.51	0.01	1.9
Hf	35	35	3	1.4	4.84	4.8	0.5	−0.2
Ta	40	33	7	−18.1	0.78	0.6	0.2	−15.8
Pb	38.6	41	4	5.6	11	11	2	−3.9
Th	37.79	37	3	0.0	5.9	6.0	0.6	0.4
U	37.38	39	2	5.2	1.69	1.7	0.2	0.4

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