DYSPROSIAN XENOTIME-(Y) FROM THE ANNIE CLAIM #3 GRANITIC PEGMATITE, SOUTHEASTERN MANITOBA, CANADA: EVIDENCE OF THE TETRAD EFFECT?

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ABSTRACT

Dysprosian xenotime-(Y) was found in the Annie Claim #3 pod of lepidolite-subtype granitic pegmatite within the Greer Lake intrusion of pegmatitic granite, in the Archean Bird River Subprovince of the Superior Province, in southeastern Manitoba. It occurs as microscopic inclusions in spessartine and as discrete crystals, both enclosed in ferroan muscovite, also associated with manganocolumbite – manganotantalite, microlite, zircon and apatite. The xenotime-(Y) contains up to 14.88 wt.% Dy_2O_3 (and 7.59 wt.% Gd_2O_3, 3.31 wt.% Tb_2O_3), the highest concentration of Dy so far observed in this mineral. In chondrite-normalized *REE* patterns, the positive Tb anomaly is even higher than that of Dy. Along with xenotime-(Y) and xenotime-(Yb) from other granitic pegmatites, altered granites and alpine veins, the Annie Claim #3 xenotime-(Y) shows prominent double segmenting of the Gd to Lu sequence, ascribed by some authors to the tetrad effect in geological materials generated from, or affected, by aqueous media. Analytical problems could not produce this effect in the xenotime samples.

Keywords: xenotime-(Y), xenotime-(Yb), rare-earth elements, tetrad effect, granitic pegmatite, Annie Claim #3, Manitoba, Canada.

SOMMAIRE

Nous avons trouvé du xénotime-(Y) enrichi en dysprosium dans une lentille de pegmatite granitique de type lépidolite appelée Annie Claim #3, et faisant partie du massif intrusif du lac Greer, d'âge archéen, Sous-province de Bird River de la Province du Supérieur, dans le secteur sud-est du Manitoba. Les cristaux se présentent en inclusions dans la spessartine et en cristaux distincts, tous inclus dans des agrégats de muscovite ferreuse, en association avec manganocolumbite – manganotantalite, microlite, zircon et apatite. Le xénotime-(Y) contient jusqu'à 14.88% Dy_2O_3 en poids (et 7.59% Gd_2O_3, 3.31% Tb_2O_3), la teneur de Dy la plus élevée qui soit connue pour cette espèce. Les spectres de terres rares normalisés par rapport à une distribution chondritique montrent une anomalie positive en Tb même plus grande que l'anomalie en Dy. Comme c'est le cas pour le xénotime-(Y) et le xénotime-(Yb) provenant d'autres pegmatites granitiques, granites altérés et veines alpines, le xénotime-(Y) de la pegmatite Annie Claim #3 fait preuve d'une segmentation double des teneurs normalisées dans l'intervalle entre Gd et Lu, que certains ont attribué à l'effet de tétrade, reconnu dans les matériaux déposés à partir de milieux aqueux, ou bien affectés par ceux-ci. Les problèmes analytiques ne sauraient expliquer cet effet dans les échantillons de xénotime.

(Traduit par la Rédaction)

Mots-clés: xénotime-(Y), xénotime-(Yb), terres rares, effet de tétrade, pegmatite granitique, Annie Claim #3, Manitoba, Canada.

INTRODUCTION

Xenotime-(Y) normally shows low contents of heavy rare-earth elements (*HREE*) and negligible concentrations of their light counterparts (*LREE*). Increased quantities of individual *HREE*s, such as those in xenotime-(Yb) (Buck *et al.* 1999), are exceptional, although moderate enrichment in Yb, Dy and Gd has been occasionally noticed (Vlasov 1966, Sahama *et al.* 1973, Franz *et al.* 1996). Here we report on the occurrence of xenotime-(Y) with the highest content of Dy ever reported in this mineral, from a lepidolite-subtype granitic pegmatite in Manitoba. This example of xenotime-(Y) also shows potential evidence, along with some of its pegmatitic and hydrothermal counterparts, of the controversial tetrad effect in chondrite-normalized *REE* patterns.

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REGIONAL SETTING AND THE PARENT PEGMATITE

The parent pegmatite is located in southeastern Manitoba, very close to the southwestern margin of the Greer Lake pegmatitic granite, located in metabasalts of the Lamprey Falls Formation of the Bird River Greenstone Belt, in the Bird River Subprovince, western Superior Province of the Canadian Shield [*cf.* Černý *et al.* (1981) for details of regional geology].

The pegmatite forms a subellipsoidal, subhorizontal body approximately 10×7 meters in size, with distinct concentric zoning (Masau 1999). The zones show an inward progression of five main types of mica, from muscovite to lithian muscovite and lepidolite, associated mainly with quartz and several varieties of albite; K-feldspar is subordinate in the outermost zones and missing in the intermediate and inner zones. Accessory minerals include spessartine, cesian beryl, cassiterite, manganocolumbite, manganotantalite and rare microlite, uranpyrochlore, wodginite, ferrotapiolite, yttrotantalite or formanite-(Y), apatite, zircon, coffinite, uraninite and xenotime-(Y). Minerals of boron and phosphates of Li, Al, Fe or Mn are conspicuously absent.

The Dy-enriched xenotime-(Y) forms inclusions in garnet ($Sps_{64}Alm_{29}Grs_7$ to $Sps_{83}Alm_{11}Grs_6$, with up to 0.67 wt.% Y_2O_3), which is hosted by small subround nodules of dark brownish green ferroan muscovite (2.21 to 7.57 wt.% total Fe as FeO, 0.04 to 0.33 wt.% MnO, 0.58 to 1.66 wt.% Rb_2O, average Li_2O 0.63 wt.%). The mica aggregates also contain discrete crystals of dysprosian xenotime-(Y), and subhedral platy crystals of manganocolumbite–manganotantalite [Mn/(Mn + Fe) at. from 0.44 to 0.87, Ta/(Ta + Nb) at. from 0.18 to 0.85], in part replaced by microlite. Isolated grains of the xenotime-(Y) are rarely found scattered among the mica flakes. The paragenetic position of the micaceous nodules could not be precisely established, as they were found only in broken-up dump material. However, the nodules most probably crystallized in late stages of consolidation of the Annie Claim #3 pegmatite, as they locally cross-cut adjacent albite of the outer intermediate zone.

EXPERIMENTAL

The dysprosian xenotime-(Y) was analyzed using a Cameca SX–50 electron microprobe at the Department of Geological Sciences, University of Manitoba. The conditions of analysis in the wavelength-dispersion mode were the same as those applied to xenotime-(Yb) by Buck *et al.* (1999), except for an accelerating voltage of 15 kV and a beam current of 20 mA. The analytical data were reduced and corrected by the PAP method of Pouchou & Pichoir (1884, 1985). The values of Tm were adjusted for overlap with Sm using the method of Åmli & Griffin (1975), elaborated on by Nagy (1993), and processed by the XMAS option for overlap

deconvolution. Zr, Hf, Al, Sc and Ce (and, in most cases, La also) were found to be below detection limits; Pr and Eu were not sought. All of the minor Fe was assumed divalent.

Chondritic *REE* values of Taylor & McLennan (1985) were used to normalize the *REE* contents of xenotime-(Y) and xenotime-(Yb) from all localities cited.

DYSPROSIAN XENOTIME

The subhedral to anhedral inclusions of xenotime-(Y) in garnet embedded in micaceous aggregates range from 20 to 10 μm in size, and the xenotime-(Y) grains disseminated in those aggregates are somewhat larger, ≤150 μm. Internally, most of the grains are homogeneous, or they display only minor variations in the cation contents. Distinctly heterogeneous distribution of Y and the individual *HREE* is rarely observed.

Representative compositions of the Annie Claim #3 xenotime-(Y) are shown in Table 1. The content of Dy is variable, between 6.90 and 14.88 wt.% Dy_2O_3, and averaging about 8.5 wt.%. The 14.88 wt.% concentration is the highest ever observed; it amounts to 0.17 atoms per formula unit (*apfu*), alongside the dominant Y at 0.66. Gadolinium also is enriched at 7.59 wt.% oxide and 0.09 *apfu*. In contrast, the incorporation of Si, U and Th is negligible, and Zr may be present, if at all, only below detection limits of electron microprobe. Thus, departure of the compositions toward the coffinite and thorite components is not important, and a potential zircon component is undetectable. Also, the satisfactory analytical totals and stoichiometry of unit formulas indicate that the potential presence of hydroxyl must be negligible, even lower than that of the fluorine (maximum 0.31 wt.%, 0.032 *apfu*, and much less in all other compositions).

DISCUSSION

Absolute REE concentrations

Slight selective enrichment in Dy was reported in xenotime-(Y) by Demartin *et al.* (1991) from granitic pegmatites and alpine veins, by Förster & Rhede (1995), Sabourdy *et al.* (1997) and Förster (1998) from granites, and by Franz *et al.* (1996) from metapelites. However, concentrations of Dy comparable to those reported in xenotime-(Y) from the Annie Claim #3 have not been so far encountered in any environment. Representative data quoted in Table 1 (compositions 1 to 4) are shown graphically in Figure 1A, using the style favored by, *e.g.*, Vlasov (1966): the sum of even-numbered medium and heavy *REE*, complemented by Y, is normalized to a total of 100. This representation reflects the absolute abundances of individual *REE* + Y relative to each other.

Table 1 also lists representative Yb-enriched compositions quoted by Jefford (1962), Voloshin & Pakhomovskii (1986), Belolipetskii & Voloshin (1996)

TABLE 1. REPRESENTATIVE COMPOSITIONS OF DYSPROSIAN XENOTIME-(Y)
FROM THE ANNIE CLAIM #3 GRANITIC PEGMATITE
AND OF OTHER Dy-, Yb-, AND Gd-ENRICHED SAMPLES

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
P_2O_5	36.73	35.43	35.13	33.92	34.90	32.60	33.57	33.64	32.90	31.80	29.46	27.25	29.03	28.82	24.47
SiO_2	0.12	0.03	0.04	0.00	0.00	1.00	0.27	0.68	0.74	n.d.	2.93	n.d.	n.d.	0.00	n.d.
ZrO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.	2.66	n.d.	n.d.	n.d.	n.d.
ThO_2	0.00	0.00	0.22	0.44	0.30	0.10	0.8	1.75	0.00	0.84	0.95	n.d.	n.d.	0.00	n.d.
Al_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.00	n.d.	n.d.	n.d.	n.d.
Fe_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35	n.d.	n.d.	n.d.	n.d.
UO_2	0.27	0.17	0.02	0.37	1.00	0.20	0.21	0.26	0.32	0.25	0.22	n.d.	n.d.	n.d.	n.d.
Y_2O_3	48.93	41.87	39.73	34.79	47.50	42.90	38.97	40.57	30.40	26.80	33.99	8.75	12.51	25.28	10.32
La_2O_3	0.00	0.00	0.00	0.00	n.d.	n.d.	0.02	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ce_2O_3	0.00	0.00	0.00	0.00	n.d.	n.d.	0.00	0.11	0.00	0.06	n.d.	n.d.	n.d.	n.d.	n.d.
Pr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.01	0.03	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Nd_2O_3	0.07	0.20	0.00	0.00	n.d.	0.50	0.07	0.10	0.19	0.16	0.33	n.d.	n.d.	n.d.	n.d.
Sm_2O_3	0.00	1.19	0.29	0.73	n.d.	1.20	1.03	0.56	0.22	0.24	0.46	n.d.	n.d.	0.26	n.d.
Eu_2O_3	n.d.	n.d.	n.d.	n.d.	0.10	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	n.d.
Gd_2O_3	2.29	6.38	5.78	7.59	2.40	3.50	8.60	7.34	5.43	2.71	0.90	0.26	0.23	1.36	0.09
Tb_2O_3	1.16	1.64	2.53	3.31	0.90	0.90	1.24	1.16	1.05	0.61	0.48	0.19	n.d.	0.15	n.d.
Dy_2O_3	6.90	8.45	11.69	14.88	7.20	6.90	6.44	6.71	8.61	5.61	5.02	3.72	3.57	5.53	0.86
Ho_2O_3	0.60	0.54	0.78	0.87	1.20	1.20	1.11	1.23	2.00	1.30	0.64	0.94	0.61	2.33	n.d.
Er_2O_3	1.42	1.62	1.18	1.53	4.00	3.80	3.78	3.16	7.23	7.37	4.87	8.29	7.69	9.23	5.87
Tm_2O_3	0.21	0.27	0.20	0.11	n.d.	n.d.	n.d.	n.d.	1.13	1.69	1.13	2.86	2.52	1.86	3.33
Yb_2O_3	1.07	1.62	1.00	1.07	2.20	3.00	2.68	1.85	7.82	15.10	11.73	36.37	32.27	18.69	43.38
Lu_2O_3	0.01	0.00	0.00	0.00	0.20	0.30	0.70	0.61	1.30	2.27	0.96	7.12	9.84	2.26	8.48
CaO	0.00	0.03	0.03	0.13	0.00	0.10	0.03	0.09	0.08	0.17	n.d.	n.d.	n.d.	0.15	0.24
FeO	0.28	0.00	0.08	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.00	0.00	0.13	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PbO	0.05	0.00	0.00	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
F	0.03	0.06	0.00	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
O=F	-0.01	-0.03	0.00	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	100.13	99.47	98.83	99.87	101.70	98.30	99.58	98.88	98.97	97.76	99.59	95.75	98.27	95.92	97.04
					atoms per formula unit (normalized to 4 anion atoms)										
Zr	-	-	-	-	-	-	-	-	-	-	0.045	-	-	-	-
Th	0.000	0.000	0.002	0.003	0.002	0.001	0.007	0.006	0.000	0.007	0.008	-	-	0.000	-
U	0.002	0.001	0.000	0.003	0.007	0.002	0.002	0.002	0.003	0.002	0.002	-	-	-	-
Al	-	-	-	-	-	-	-	-	-	-	0.082	-	-	-	-
Fe^{2+}	-	-	-	-	-	-	-	-	-	-	0.009	-	-	-	-
Y	0.839	0.747	0.718	0.645	0.835	0.789	0.717	0.741	0.581	0.527	0.630	0.202	0.272	0.534	0.248
La	0.000	0.000	0.000	0.000	-	-	0.000	0.001	-	-	-	-	-	-	-
Ce	0.000	0.000	0.000	0.000	-	-	0.000	0.001	0.000	0.001	-	-	-	-	-
Pr	-	-	-	-	-	-	0.000	0.000	0.000	0.001	-	-	-	-	-
Nd	0.001	0.002	0.000	0.000	-	0.006	0.001	0.001	0.002	0.002	0.004	-	-	-	-
Sm	0.000	0.014	0.003	0.009	-	0.014	0.012	0.007	0.003	0.003	0.006	-	-	0.004	-
Eu	-	-	-	-	0.001	0.001	-	-	0.000	0.000	-	-	-	0.000	-
Gd	0.024	0.071	0.065	0.088	0.026	0.040	0.099	0.083	0.065	0.033	0.010	0.004	0.003	0.018	0.001
Tb	0.012	0.018	0.028	0.038	0.010	0.010	0.014	0.013	0.012	0.007	0.005	0.003	-	0.002	-
Dy	0.072	0.091	0.128	0.167	0.077	0.077	0.072	0.074	0.100	0.067	0.056	0.052	0.047	0.071	0.012
Ho	0.006	0.006	0.008	0.010	0.013	0.013	0.012	0.013	0.023	0.015	0.007	0.013	0.008	0.029	-
Er	0.014	0.017	0.013	0.017	0.042	0.041	0.041	0.034	0.082	0.086	0.053	0.113	0.117	0.115	0.083
Tm	0.002	0.003	0.002	0.001	-	-	-	-	0.013	0.019	0.012	0.039	0.039	0.023	0.047
Yb	0.011	0.017	0.010	0.012	0.022	0.032	0.028	0.019	0.086	0.170	0.125	0.481	0.402	0.226	0.596
Lu	0.000	0.000	0.000	0.000	0.002	0.003	0.007	0.006	0.014	0.025	0.010	0.093	0.121	0.027	0.115
Ca	0.000	0.001	0.001	0.005	0.000	0.004	0.001	0.003	0.003	0.007	-	-	-	0.006	0.012
Fe^{3+}	0.008	0.000	0.002	0.004	-	-	-	-	-	-	-	-	-	-	-
Mn	0.000	0.000	0.004	0.000	-	-	-	-	-	-	-	-	-	-	-
Pb	0.000	0.000	0.000	0.000	-	-	-	-	-	-	-	-	-	-	-
Sum A site	0.991	0.988	0.984	1.001	1.037	1.033	1.013	1.004	0.987	0.972	1.064	1.000	1.009	1.055	1.114
P	1.002	1.005	1.009	1.000	0.976	0.953	0.983	0.977	1.001	0.994	0.869	1.001	1.005	0.968	0.934
Si	0.004	0.001	0.001	0.000	0.000	0.035	0.009	0.023	0.009	0.027	0.102	0.000	0.000	0.000	-
Sum T site	1.006	1.006	1.010	1.000	0.976	0.988	0.992	1.000	1.010	1.021	0.971	1.001	1.005	0.968	0.934
F	0.003	0.006	0.000	0.000	-	-	-	-	-	-	-	-	-	-	-
O	3.997	3.994	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000

Columns: 1 to 4: Annie Claim #3, this study; 5, 6: Demartin *et al.* (1991), their samples 11 and 6, from alpine veins; 7, 8: Franz *et al.* (1996), their samples 17329.1 and 14529.1, respectively, from metasediments; 9,10: Förster (1998), his samples 1141-FS and 1157-FS, respectively, from granites; 11: Jefford (1962), his sample 1, total includes 0.51 wt.% by ignition loss, from an alkaline granite; 12, 13: Buck *et al.* (1999), their samples YB1 and YB2, respectively, from a granitic pegmatite; 14: Voloshin & Pakhomovskii (1986), their sample 2, from a granitic pegmatite; 15: Belolipetskii & Voloshin (1996), their sample 1, from a granitic pegmatite. 0.00: below detection limit; n.d.: not determined. Compositions reported in wt.% oxides + fluorine.
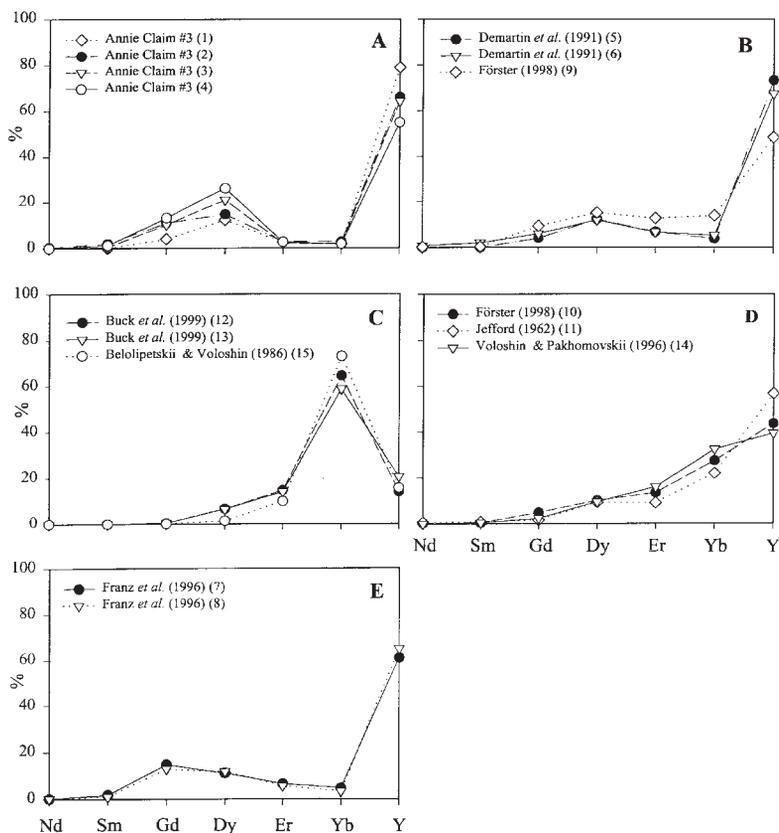
FIG. 1. Concentrations of middle and heavy even-numbered *REE* and Y, normalized to a
total of 100, in selected samples of xenotime-(Y) and xenotime-(Yb); numbers in brack-
ets after the references correspond to those of compositions quoted in Table 1.

and Buck *et al.* (1999). Some of those compositions also
show exceptional enrichment in Er and Lu, but the Dy
and Gd contents are invariably low (Table 1, composi-
tions 11 to 15, Figs. 1C, D).

A strong positive Gd anomaly was recorded by
Sahama *et al.* (1973) in xenotime-(Y) from the Morrua
pegmatite, Mozambique, but only in terms of relative
abundance compared to other *REE*; quantitative data
were not obtained. Otherwise, moderately Gd-enriched
xenotime was encountered only by Franz *et al.* (1996)
in metapelitic lithologies (Table 1, compositions 7 and
8, Fig. 1E).

The selective enrichments in individual *HREE* do not
seem to be related to specific environments that gener-
ate xenotime. In contrast, some of the *REE* tend to cor-
relate in samples of various provenances. A link may
possibly exist among the positive anomalies of Yb, Er
and Lu, which are found mainly in Dy- and Gd-depleted
samples. On the other hand, Dy and Gd locally both tend
to show an enrichment.

Chondrite-normalized REE abundances

It is noteworthy that the Dy + Gd and Yb + Er + Lu
associations suggested above coincide with two of the
four *REE* tetrads, based on the periodicity and rhyth-
mics of ground-state total orbital quantum numbers of
free trivalent *REE* cations (Sinha 1975, and reviewed in
Sinha 1983). Expression of this tetrad effect in geologi-
cal materials was reported by, *e.g.*, Masuda & Ikeuchi
(1979), Masuda *et al.* (1987) and Masuda & Akagi
(1989), doubted by McLennan (1994) and Pan (1997),
but reaffirmed by Bau (1996, 1997) and Möller (1997)
specifically for mineral assemblages and whole-rock
overprints generated in aqueous environments (post-
magmatic fluids, hydrothermal solutions, and surface
waters).

The tetrad effect is best revealed in the classic chon-
drite-normalized patterns, shown in Figure 2 for the
third- and fourth-tetrad elements (Gd to Ho and Er to
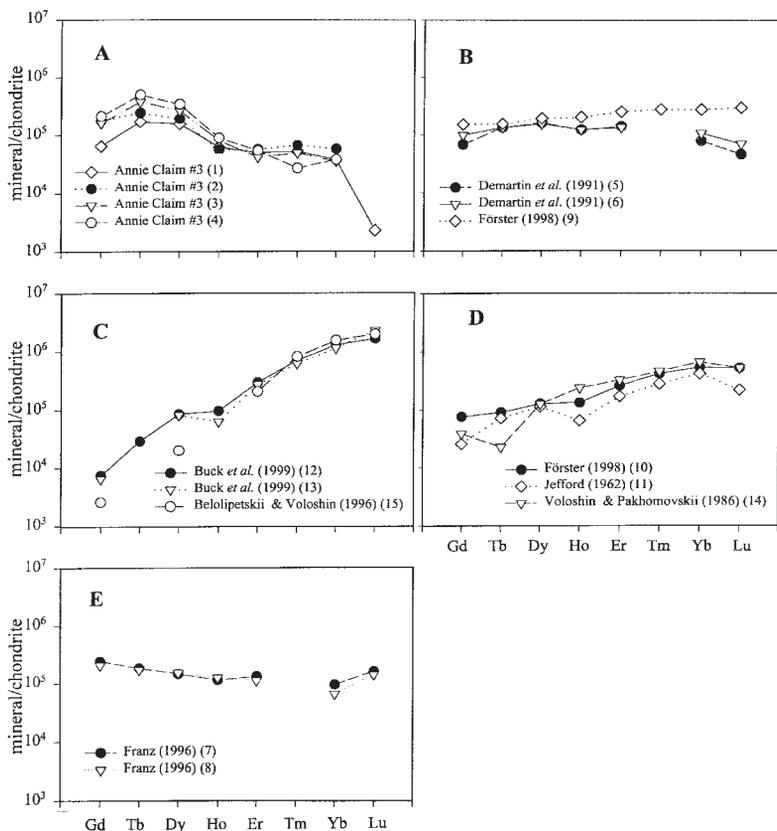Lu, respectively) for the compositions listed in Table 1.

Fig. 2. Chondrite-normalized *REE* abundances (Gd to Lu) in compositions of selected samples of xenotime-(Y) and xenotime-(Yb); numbers in brackets after the references correspond to those of compositions quoted in Table 1. The patterns are grouped as in Figure 1.

The tetrad effect is apparently well expressed in xenotime-(Y) from the Annie Claim #3 pegmatite, from alpine veins (Demartin *et al.* 1991), and from an alkaline pegmatite (Jefford 1962), and in xenotime-(Yb) from the Shatford Lake pegmatite group (Buck *et al.* 1999) (Figs. 2A, B, C). In contrast, it is not observed in samples from granites (Förster 1998) and metamorphic rocks (Franz *et al.* 1996) (Figs. 2D, E). Xenotime-(Yb) from granitic pegmatites of Kola Peninsula generates irregular (Voloshin & Pakhomovskii 1986) or smooth-looking (Belolipetskii & Voloshin 1996) patterns (Figs. 2C, D).

Magmas consolidating into more or less highly fractionated granitic pegmatites do not rank with aqueous systems *sensu stricto*, but they differ distinctly from plutonic batches of granitic melts by considerable enrichment in H_2O, promoted by the presence of F, B, P and Li (*e.g.*, London 1986a, b, 1990). Experimental evidence shows that homogeneous residual F,B,P,Li-rich pegmatite-forming melts may contain up to ~15 wt.% (approx. 40 vol.%) dissolved H_2O (London *et al.* 1989). The Annie Claim #3 pegmatite could not attain this experimentally established maximum, as it is very poor in P and B, but it must have crystallized from a Li- and F-rich and consequently H_2O-rich magma, as indicated by the abundance of Li- and F-rich micas. In general, pegmatite-forming magmas should qualify as substantially aqueous systems with respect to *REE* behavior (*cf.* Bau 1996), despite being phase-homogeneous throughout most of their consolidation (before they become volatile-oversaturated and exsolve a supercritical fluid; *e.g.*, London *et al.* 1989).

The number of data summarized in Table 1 and represented in Figures 1 and 2 is not sufficiently significant to substantially contribute to the argument for or against the geological expression of the tetrad effect, all the more that they are restricted to only the heavy half of the *REE* spectrum. Nevertheless, the coincidence of

the apparent tetrad effect with xenotime formed from aqueous environments is unmistakable. Analytical problems inherent to inductively-coupled-plasma and spark-source mass spectrometries as a cause of unusual *REE* patterns (McLennan 1994) do not apply, as the data considered here were generated by electron-microprobe analysis in different laboratories, using in part different analytical techniques and different methods of calibration. Virtually perfect stoichiometry of the Annie Claim #3 and Shatford Lake xenotime also indicates that the analytical procedures are above reproach.

Comparison of the absolute concentration and chondrite-normalized patterns

The differences between some of the patterns of Figure 1 and their counterparts in Figure 2 are remarkable, but generally expectable because of the different methods of normalization. For example, the positive Gd anomalies in the samples of Franz *et al.* (1996), the positive Dy anomalies in the alpine-vein samples (Demartin *et al.* 1991) and the positive Yb anomalies in the samples of Förster (1998), Jefford (1962) and Voloshin & Pakhomovskii (1986) are preserved in the chondrite-normalized patterns. In contrast, the moderate Dy anomaly in sample 1141–FS (Förster 1998) is barely noticeable in the chondrite-normalized plot, the very prominent enrichment in Yb in samples of Belolipetskii & Voloshin (1996) and Buck *et al.* (1999) is balanced by Tm and Lu, and a prominent Tb maximum dominates the chondrite-normalized plots of the Annie Claim #3 samples, overshadowing the wt.%-dominant enrichment in Dy.

The *tetrad* effect is an intrinsic property rooted in the periodicity of atomic structure of the *REE*, probably leading to differential complexation of *REE* in highly evolved, ligand-rich and hydrous granitic and pegmatite-forming melts, and in hydrothermal fluids (Bau 1996). In this context, the tetrad effect may explain the segmented *REE* abundances in geological products of the above environments. However, no data or hypotheses are currently available to explain the observed enrichment and depletion in *individual REE*. The available literature on experimental studies deals only with low-temperature hydrothermal and surface conditions (*cf.* Möller 1983, Byrne & Li 1995, among others). Selective complexing and differential stabilities of the complexes of individual *REE* could be responsible, as proposed by Gramaccioli & Pezzotta (1997) and Pezzotta *et al.* (1999). Broadly based experimental evidence on *REE* behavior with inorganic ligands at conditions corresponding to consolidation of hydrous and volatile-rich pegmatite-forming melts, supercritical fluids and high-temperature hydrothermal solutions is desirable. The recent work of Wood (*e.g.*, 1990, 1996) is most promising in this respect.

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