# THE LANTHANIDE TETRAD EFFECT IN SOME PEGMATITE MINERALS FROM CONŢU-NEGOVANU (LOTRU-CIBIN MTS.)

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## Introduction

Masuda and Ikeuchi (1978) were the first to observe the lanthanide tetrad effect in the marine environment and before them, the same behavior of REEs was described in non–geological disciplines by Fidelis and Siekierski (1966) and Peppard *et al*. (1969) who observed the tetrad effect in patterns of liquid–liquid REE distribution coefficients. In non–geological disciplines it is also described as “*nephelauxetic effect*” (Jorgenson, 1970), “*inclined W effect*” (Sinha, 1978) or “*double–double effect*” (Mioduski, 1997).

The lanthanide tetrad effect is generally characterized by the subdivision of chondrite–normalized REE patterns into four segments called *tetrads* : La – Ce – Pr – Nd, (Pm) – Sm – Eu – Gd, Gd – Tb – Dy – Ho and Er – Tm – Yb – Lu. According to their apparent shape, Masuda *et al*. (1987) showed that there are two types of lanthanide tetrad effects: the W tetrad effect characterized by four convex curves and the M tetrad effect characterized by four concave curves. The W tetrad effect is observed in the natural waters and related materials and the M tetrad effect is observed in the solid products.

The presence of tetrad effect has been found in various environments with different extension. Found in various marine materials, including seawater, algae, sponges, limestone shells *etc*., the W–type REE tetrad effect was reported first by Masuda and Ikeuchi (1978). Soon, the M–type tetrad effect was found in granites from China (Masuda *et al*., 1987, 1990, 1994; Zhao and Cooper, 1992; Kawabe, 1995; Akagi *et al*., 2002; Zhenhua *et al*., 2002) and also in granites from Egypt (Bau, 1996) and Germany (Irber, 1999). In metamorphic rocks, the presence of the lanthanide tetrad effect was reported by Yurimoto *et al*. (1990) and Tang and Liu (2002). In sedimentary materials the presence of the lanthanide tetrad effect was also reported by Kawabe *et al*.

(1991), Hidaka *et al*. (1992), Akagi *et al*. (1993), Kawabe (1996) and Minami *et al*. (1998). Tanaka *et al*. (1990) observed clearly the third and the fourth tetrads in seawater samples collected around the Japanese islands. Intense interaction of seawater with blueschist-facies metabasite clasts has zig-zag REE patterns reflecting the lanthanide tetrad effect (Yamamoto *et al*., 1995). According to Kawabe (1996), REE abundances of the average NASC and PAAS shales present small but significant convex M-type tetrad effect relative to the chondritic REE. Both W-type and M-type REE pattern are observed in cherts from the Pilbara Block, Western Australia, in Triasic cherts from central Japan, in Cretaceous deep sea cherts from central Pacific and Caribbean Sea (Minami *et al*., 1998).

During the last years, discussions about the tetrad effect have been focused on highly evolved igneous rocks which are often interpreted as transition terms between the end-members of magmatic and high-temperature hydrothermal systems (Bau, 1996, 1997; Pan, 1997; Irber *et al*., 1997; Irber, 1999).

The cause of such behavior of lanthanide elements generating tetrad effects is assumed to be influenced by variations in the exchange interactions of unpaired 4f-electrons, spin-orbit coupling or crystal field stabilization (*e.g.*, Fidelis and Siekierski, 1966, 1971; Nugent, 1970; Siekierski, 1971; Sinha, 1978; Dzhurinskii, 1980; Mioduski, 1997).

Some authors argue against the presence of lanthanide tetrad effect in natural samples. They consider that anomalous behavior of lanthanide elements in natural samples cannot be convincingly proven as being controlled by the tetrad effect (McLennan, 1994).

The lanthanide tetrad effect appears to be a record of special petrogenetic and metallogenetic processes. It revises and complements the linear trend in Masuda – Coreyll diagram and can be used as an important tracer in petrogenetic and metallogenetic investigations (Zhenhua *et al*., 2002).

The aim of this paper is to provide data on the tetrad effect behavior of the REEs in the pegmatitic minerals from Conțu-Negovanu field (Lotru-Cibin Mts.).

## Geological background and sample description

Conțu-Negovanu granitic pegmatite field is located in the Lotru-Cibin Mts. of the Southern Carpathians. The pegmatite bodies are hosted by mesometamorphic rocks belonging to Sebeş-Lotru Group. The lithology of the Sebeş-Lotru Group is generally represented by a lower migmatitic complex and upper kyanite-staurolite-bearing micaschists alternating with biotite paragneisses (Berza *et al*., 1994). The genesis of the Conțu-Negovanu pegmatites is considered to be metamorphic, as they seem to have originated mainly, if not entirely, as a result of segregation within a fluid under preanatectic conditions (Săbău *et al*., 1987). The pegmatites display two distinct mineral assemblages, assigned to two different types of pegmatites: feldspar ± muscovite pegmatites and albite – spodumene pegmatites (Androne *et al*., 2005). In order to show the presence/absence of the lanthanide tetrad effect in the Conțu-Negovanu pegmatitic minerals, analithical data on the following minerals were used: quartz, feldspar, biotite, garnet (Androne, 2005), tourmaline (Androne *et al*., 2004), muscovite (Androne *et al*., 2005) and staurolite (unpubl. data). All the quantitative analyses were performed by ICP-MS at the University of Köln (Germany).

## Quantification of the lanthanide tetrad effect

Masuda *et al*. (1994) proposed a method to quantify the lanthanide tetrad effect, by fitting the observed tetrads by a quadratic function. The resultant quadratic coefficients were used as a measure of the lanthanide tetrad effect. This method is of special advantage for IDMS analyses as it evades the problem of the missing monoisotopes Pr, Tb, Ho and Tm.

Irber (1999) proposed a method to quantify the lanthanide tetrad effect which determines the deviation of a REE pattern with tetrad effect from a hypothetical tetrad effect-free REE pattern. From the four tetrads, only the first and the third tetrad have been used for quantification of the tetrad effect as the second tetrad is camouflaged by the absence of Pm in nature and by the distinctive behavior of Eu depending on oxygen fugacities. The fourth tetrad is the least developed.

To determine the hypothetical tetrad effect-free REE pattern, the corner points of the single tetrads La-Nd (respectively Gd-Ho) serve as a respective reference. A virtual line is drawn between these corner points and the mean deviation of Ce and Pr (respectively Tb and Dy) from this line expresses the contribution to the respective tetrad (Irber 1999):

$$t_1 = (Ce/Ce^t \times Pr/Pr^t)^{0,5}$$

$$t_3 = (Tb/Tb^t \times Dy/Dy^t)^{0,5}$$

and $$Ce/Ce^t = Ce_n/(La_n^{2/3} \times Nd_n^{1/3}); \quad Pr/Pr^t = Pr_n/(La_n^{1/3} \times Nd_n^{2/3});$$

$$Tb/Tb^t = Tb_n/(Gd_n^{2/3} \times Ho_n^{1/3}); \quad Dy/Dy^t = Dy_n/(Gd_n^{1/3} \times Ho_n^{2/3});$$

where $REE_n$ is chondrite-normalized lanthanide concentration.

The geometric mean of both values for the first ($t_1$) and the third ($t_3$) tetrad yields the overall value of the tetrad effect, noted as $TE_{1,3}$:

$$TE_{1,3} = (t_1 \times t_3)^{0,5}$$

The values of $TE_{1,3}$ range from 1.00 for a hypothetical tetrad effect-free REE patern, towards higher values for REE patterns with tetrad effects. Only the samples with values $TE_{1,3} > 1.10$ were considered to show the tetrad effect, as an error of 10% usually occurs and therefore, this effect becomes quite visible at these values.

## Results and discussion

In order to emphasise the existence of the tetrad effect in the minerals belonging to the Conțu-Negovanu pegmatites, Irber's (1999) method was used, although it is mentioned as applicable for granitoids only. The reason for this is that if granitoids display lanthanide tetrad effect, it would be right to assume that at least one mineral in the specific assemblage presents it too. The $TE_{1,3}$ values have been determined for the main pegmatitic minerals, sampled both from the feldspar-muscovite pegmatites and albite-spodumene pegmatites. The samples with zig-zag REE patterns have been excluded for having the highest probability of analithical error.
The $TE_{1,3}$ values are presented in table 1 and are also plotted in fig.1.

Table 1. $TE_{1,3}$ values according to Irber (1999) for some minerals from Conțu-Negovanu pegmatites.

| | **Quartz** | | **Plagioclase** | | | | | **Alkali-feldspar** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *Sample* | *Q-16* | *Q-61* | *F-5A* | *F-7* | *F-32A* | *F-34* | *F-54* | *F-8* | *F-51* | *F-52* |
| ***$TE_{1,3}$*** | 0.93 | 1.00 | 1.00 | 0.94 | 0.94 | 1.03 | 1.01 | 0.81 | 0.99 | 0.85 |
| | **Muscovite** | | | | | | | **Biotite** | | |
| *Sample* | *M-46* | *M-93* | *M-53* | *M-84* | *M-88* | *M-91* | *M-94* | *B-34* | *B-36* | *B-54* |
| ***$TE_{1,3}$*** | 1.16 | 1.20 | 1.04 | 0.88 | 0.94 | 0.88 | 0.87 | 1.58 | 1.02 | 1.04 |
| | **Garnet** | | | | | **Staurolite** | | **Tourmaline** | | |
| *Sample* | *G-11* | *G-12* | *G-94* | *G-21* | *G-22* | *S-1* | *S-2* | *T-12* | *T-21* | *T-22* |
| ***$TE_{1,3}$*** | 1.23 | 1.13 | 1.05 | 1.24 | 1.26 | 1.04 | 1.00 | 0.96 | 1.01 | 1.01 |

The main minerals from both pegmatite types, *i.e.* quartz, alkali-feldspar (albite, microcline) and plagioclase do not display the tetrad effect, as the $TE_{1,3}$ values in some samples are < 1, suggesting an almost zig-zag pattern. The muscovite from the feldspar-muscovite pegmatites presents a clear tetrad effect (fig. 1, samples 11 and 12), whereas the muscovite from the albite-spodumene pegmatites does not.. Normally, the muscovite REE patterns should display a more intense M-type tetrad effect in the samples of late crystallization, *i.e.* belonging to the albite-spodumene pegmatites. The rather bizarre situation where the lanthanide tetrad effect is visible only in the muscovite from the early crystallized feldspar-muscovite pegmatites may be explained by the virtual presence of some relict inclusions of highly REE concentrating minerals *e.g.* orthite, monazite, xenotime *etc.* responsible for this effect. In the feldspar-muscovite pegmatite samples, muscovite is often intergrown with biotite and therefore, it is likely for it to have crystallised from biotite, preserving some of its inclusions. This hypothesis is consistent with the fact that only one biotite sample displays the tetrad effect (with the highest $TE_{1,3}$ value) which may also be due to some REE concentrating mineral inclusions. As for the general presence of the lanthanide tetrad effect in micas, up to now there are no published data available.

Tourmaline and staurolite do not present the lanthanide tetrad effect.

The garnet, with one exception, presents the tetrad effect, with a similar amplitude both in the pegmatite and metamorphic samples. The garnet sample G-94 has a $TE_{1,3}$ value which can be accepted as the inferior limit of the tetrad effect (according to Irber, 1999), considering a 10% analithical error.

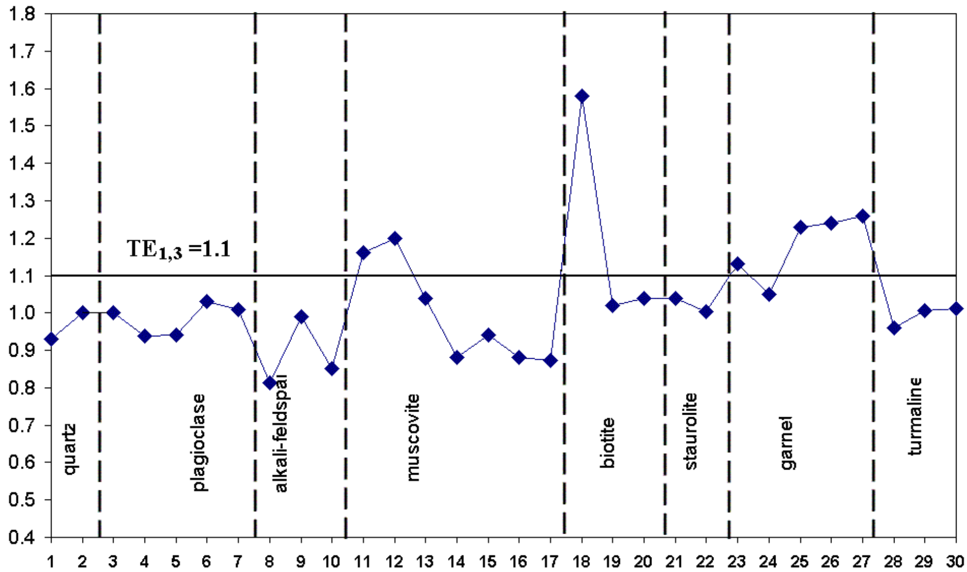


Fig. 1. $TE_{1,3}$ values according to Irber (1999) for the main minerals from Conțu-Negovanu pegmatites

## Conclusions

From all the minerals belonging to the Conțu-Negovanu pegmatites, the garnet is the only one which displays the lanthanide tetrad effect. The existence of the tetrad effect in garnet has already been documented (*e.g.* Pan, 1997; Tang and Liu, 2002). The feldspars, quartz, tourmaline and staurolite do not present the lanthanide tetrad effect. As for the micas, this effect may be observed only in some samples. Considering that the tetrad effect is present only in the muscovite intergrown with biotite, we may assume that this effect is consistent with the REE concentrating mineral inclusions in biotite and therefore, in the muscovite crystallised from the biotite too.

We consider that the hypothesis of the lanthanide tetrad effect due to the presence of the highly REE concentrating minerals (*e.g*. Jollif *et al*., 1989; Zhao and Cooper, 1992; Yurimoto *et al*., 1990; Pan, 1997) is also confirmed to some extent by the REE distribution within the minerals belonging to the Conțu-Negovanu pegmatites.


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