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The lanthanide tetrad effect in highly evolved felsic igneous rocks – a reply to the comment by Y. Pan

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Discussing the Y-Ho, Zr-Hf, and lanthanide systematics of natural samples from aqueous and magmatic geological systems, it was shown (Bau 1996) that in contrast to the behaviour of isovalent elements in basic to intermediate melts, their behaviour in aqueous media cannot be explained adequately by variations between their ionic radii. Comparing Y/Ho and Zr/Hf ratios, and chondrite-normalized rare-earth element (REE_{CN}; C1-chondrite from Anders and Grevesse 1989) patterns of high-silica ($SiO_2 > 70\%$) felsic igneous rocks to those of samples from other geological environments, it was pointed out that the behaviour of these elements in highly evolved felsic magmatic systems is very similar to their behaviour in aqueous solutions, but considerably different from their behaviour in basic to intermediate melts. Moreover, it was shown that in high-silica felsic magmas "anomalous" behaviour of the REE (resulting in REE_{CN} patterns such as those shown in Fig. 1) is associated with "anomalous" fractionation of the geochemical twin pairs Y-Ho and Zr-Hf. Hence, it was suggested that in analogy to aqueous systems differences in the stabilities of chemical complexes may be responsible for the "anomalous" behaviour of Y, REE, Zr, and Hf in highly differentiated felsic and pegmatitic fluids.

From these subjects, it is the lanthanide tetrad effect that once more has become a matter of controversy. In his discussion and an adjoining paper (Pan and Breaks, in press), Yuanming Pan (1997) suggests "[...] that the discontinuity at Ho/Er in REE patterns of highly evolved leucogranites and pegmatites can be explained by conventional magmatic crystallization when appropriate partition coefficients are used, similar to Yurimoto et al. (1990) who showed that the discontinuity at Nd is attributable to fractional crystallization involving monazite." A model calculation was presented suggesting that at high degrees of (Rayleigh) fractional crystallization ($F < 0.3$) of a mineral assemblage comprising (amongst others) 0.03% monazite and 0.58% garnet, REE_{CN} patterns show discontinuities at Nd (due to monazite fractionation) and Er (due to garnet fractionation). It was concluded that there is no support for "[...] a lanthanide tetrad effect or fractionation of REE by chemical complexation in magmatic systems [...]" (Pan 1997).

The term "lanthanide tetrad effect" was initially used to describe the behaviour of the trivalent lanthanides during liquid-liquid extraction experiments (Peppard et al. 1969), and refers to the apparent sub-division of La and the fourteen 4*f* elements into four groups or tetrads (1.: La–Nd; 2.: Pm–Gd; 3.: Gd–Ho; 4.: Er–Lu; see also Fig. 1). This sub-division is well known in aqueous chemistry, where it is frequently met in sets of stability constants of organic REE complexes, for example (e.g. Martell and Smith 1974). In aqueous *geo*chemistry the tetrad effect and "unusual" REE anomalies, i.e. anomalies for the non-redox-sensitive lanthanides La, Gd, and Lu, are known from seawater and marine precipitates such as limestones, seamount phosphorites, and hydrous ferromanganese oxides (for a recent discussion see, e.g. Bau et al. 1996). In magmatic geochemistry no such features have been reported yet from basic or intermediate igneous rocks, but many highly evolved, silica-rich ($SiO_2 > 70\%$) rocks, such as leucogranites, rhyolites, and pegmatites, show "irregular" REE_{CN} patterns (see, e.g. Jolliff et al. 1989; Masuda and Akagi 1989; Bau 1996, Pan and Breaks, in press).

As stated previously (e.g. Akagi et al. 1993; Bau 1996), any detailed evaluation of the occurrence of the tetrad effect in REE_{CN} patterns requires excellent analytical precision and accuracy, and it is essential to aquire concentration data for the complete set of REE. However, even when assuming the absence of any analytical bias, it is of utmost importance to emphasize that

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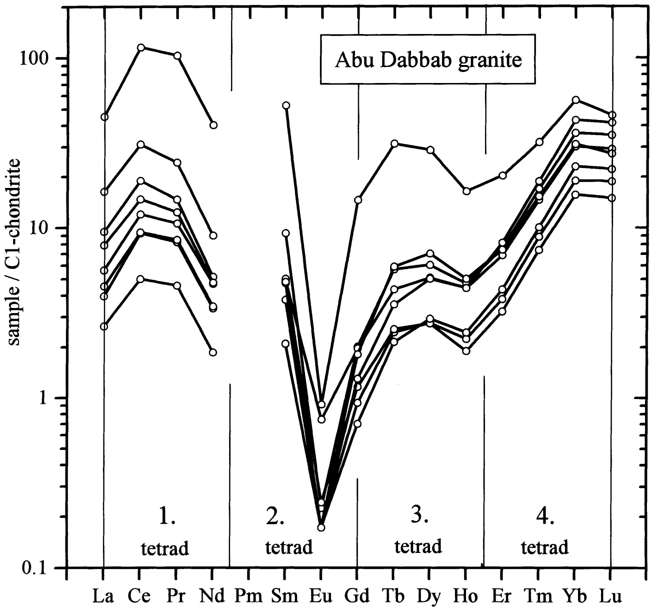

Fig. 1 REE_{CN} patterns for samples from the albite granite at Abu Dabbab, Eastern Desert, Egypt, showing a well-defined lanthanide tetrad effect with four convex-upward curved segments, and internal minima at La_{CN}, Nd_{CN}, Gd_{CN}, Ho_{CN}, and Lu_{CN} (modified after Bau 1996)

not every "irregular", "kinked", or "discontinuities-bearing" REE_{CN} pattern automatically justifies application of the term 'tetrad effect'! Unfortunately, this point is often overlooked by both opponents and promoters of the tetrad effect concept. Furthermore, over the years the discussion has suffered from the fact that in some cases occurrence of the tetrad effect has been claimed although it was too poorly developed to be thoroughly evaluated, and interpretations may have been (mis)guided by expectations. Hence, the occurrence of the lanthanide tetrad effect in geological samples is still not widely accepted (e.g. McLennan 1994), and there, indeed, is reason for a position of cautious scepticism.

However, the most extreme case reported yet of an "irregular" REE distribution that apparently displays the tetrad effect is shown by the albite granite of Abu Dabbab, Eastern Desert, Egypt (Fig. 1, and Bau 1996). Hence, this granite is an ideal test case for any model that tries to explain such "irregular" REE_{CN} patterns by fractional crystallization as envisaged by Pan (1997) and others. The REE_{CN} patterns of the Abu Dabbab granite (Fig. 1) are sub-divided into four convex-upward curved segments, and show internal minima at La_{CN}, Nd_{CN}, Gd_{CN}, Ho_{CN}, and Lu_{CN}. Moreover, these samples have non-chondritic Y/Ho and Zr/Hf ratios (Bau 1996). Following Masuda et al.'s (1987) terminology, the patterns show a well-defined M-type tetrad effect, and meet the prime criterion for application of the term 'tetrad effect': all four segments show the same type of curvature.

In detail, the 1. tetrad is characterized by $La_{CN} \ll Ce_{CN} > Pr_{CN} \gg Nd_{CN}$, and $La_{CN} > Nd_{CN}$. The depletion of La relative to Ce is so pronounced that the Ce_{CN}/Ce_{CN}^{*} ratio (with $Ce_{CN}^{*} = 0.5La_{CN} + 0.5Pr_{CN}$, or $La_{CN}^{0.5} \times Pr_{CN}^{0.5}$) is always considerably above unity. However, this decoupling of La from the other LREE cannot be produced by fractional crystallization of monazite. Although Rayleigh fractionation of monazite, as was explicitly shown by Yurimoto et al. (1990, Fig. 3) and re-emphasized by Pan (1997, Fig. 2), can generate $La_{CN}/Nd_{CN} > 1$ and $Nd_{CN}/Gd_{CN} < 1$, i.e. a "kink" at Nd, it cannot reproduce the REE distribution of the 1. tetrad in detail (Fig. 2).

The 2. tetrad is generally only poorly defined, due to missing data for Pm, and the presence of a large negative anomaly for redox-sensitive Eu (Fig. 1). However, an order of $Nd_{CN} \le Sm_{CN} > Gd_{CN}$ is obvious. The 3. tetrad is characterized by $Gd_{CN} \ll Tb_{CN} < Dy_{CN} > Ho_{CN}$, and $Gd_{CN} \ll Ho_{CN}$, whereas the 4. tetrad shows $Ho_{CN} < Er_{CN} < Tm_{CN} < Yb_{CN} \ge Lu_{CN}$. Again, fractionation of monazite and garnet (or any other mineral with a maximum REE partition coefficient at Ho or Er) cannot reproduce such REE_{CN} patterns. Instead, REE_{CN} patterns modelled by Pan (1997), for example, decrease systematically from La_{CN} to Nd_{CN}, increase from Nd_{CN} to Gd_{CN}, then decrease again to Er_{CN}, and increase to Lu_{CN} (Fig. 2). They define a convex-upward trend for the 1. and 2. tetrad, but only one single concave-upward curve from Gd_{CN} to Lu_{CN}.

To explain the discrepancies between his modelled REE_{CN} distribution and that shown by natural samples

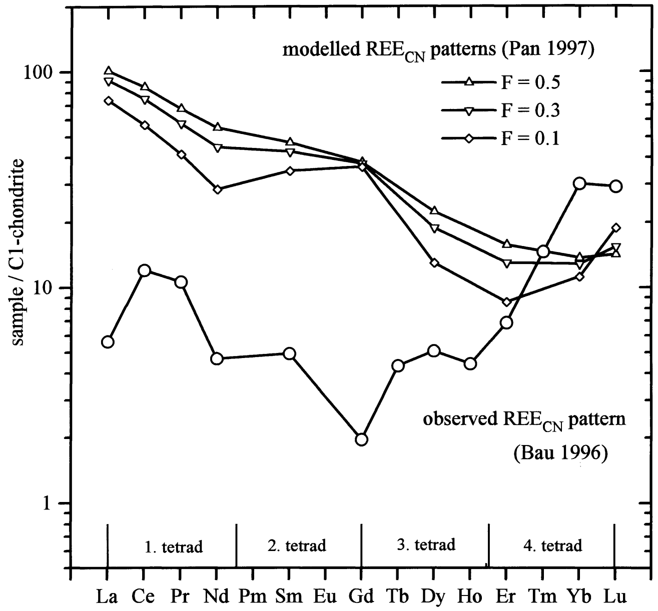

Fig. 2 REE_{CN} patterns modelled assuming high degrees of fractional crystallization (*F* = 0.1, 0.3, and 0.5) of a mineral assemblage comprising (amongst others) monazite and garnet from average S-type granite (see Pan, 1997, for data and details), compared to an observed REE_{CN} pattern of the Abu Dabbab granite, that shows the tetrad effect (note that data for redox-sensitive Eu have been omitted). Apparently, there is a pronounced difference between the modelled and the observed REE_{CN} patterns

which give no indication for garnet fractionation, Pan (1997) speculated that the peculiar HREE distribution might be generated by fractional crystallization of xenotime or fergusonite. This, however, may produce a discontinuity at Er, but cannot generate the two convex-upward curves of the 3. and 4. tetrad. Moreover, the convex-upward trend shown by each tetrad in the $\mathrm{REE_{CN}}$ patterns of the Abu Dabbab granite requires that the bulk partition coefficients, D, of the fractionating mineral assemblage must show four concave-upward curved segments when plotted versus ionic radius. This is in marked disagreement with available experimental and theoretical data on REE partitioning between minerals and silicate melts (e.g., Onuma et al. 1968; Blundy and Wood 1994; Purton et al. 1996), which show convex-upward parabolae in Onuma diagrams.

This is further illustrated in Fig. 3 in which the modelled bulk distribution coefficients for the REE, D*(REE), are plotted in order of increasing REE atomic number. Values of D*(REE) were calculated from the equation for Rayleigh fractional cystallization

$$C_L/C_0 = F^{(D-1)} \tag{1}$$

rearranged to

$$D^* = \frac{lg(C_L/C_0)}{lgF} + 1 \tag{2}$$

where D^* is the modelled bulk partition coefficient, C_0 is the concentration of a trace element in the primary magma (here in average S-type granite from Table 1 in Pan (1997); data for Tb, Ho, and Tm derived by linear interpolation between their respective neighbours in the REE series, and Y calculated assuming a chondritic Y/Ho ratio of 28), C_L is the concentration in the remaining liquid (here in sample AD-37 from the Abu Dabbab granite from Table 1 in Bau 1996), and F is the fraction of melt remaining (here $F = 0.1$, following Pan (1997) in considering a high degree of fractional crystallization).

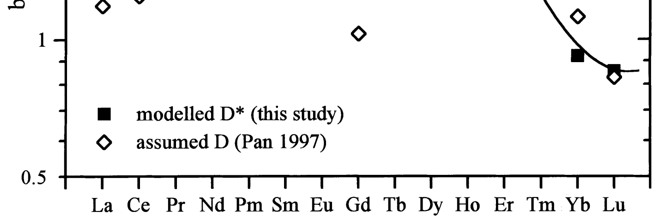

Fig. 3 Modelled bulk partition coefficients for REE and Y, D^*(REE) and D^*(Y), assuming hypothetical differentiation of Abu Dabbab granite (sample AD-37) from average S-type granite (data from Pan, 1997; Tb, Ho, and Tm interpolated from their respective REE neighbours, Y calculated assuming a chondritic Y/Ho ratio of 28) by a high degree of Rayleigh fractional crystallization ($F = 0.1$). Calculations followed Eq. (2); the bulk partition coefficients used by Pan (1997) are given for comparison; the parabolae emphasize the concave-upward curvature of the four segments (tetrads) in the pattern of D^*(REE) values. For further explanations see text

Not only is there an apparent large discrepancy between the bulk partition coefficients modelled from the Abu Dabbab data and those considered by Pan (1997), but there also is a substantial difference between D^*(Y) and D^*(Ho). To my knowledge, neither concave-upward curves of partition coefficients of the REE in Onuma diagrams, nor significant differences between partition coefficients of Y and Ho have been reported yet. Thus, while fractional crystallization of accessory minerals may generate discontinuities in $\mathrm{REE_{CN}}$ patterns of felsic magmas (I fully agree with Y. Pan), I find no evidence for the ability of this process to produce $\mathrm{REE_{CN}}$ patterns that show the lanthanide tetrad effect.

Further evidence against a dominant role of fractional crystallization comes from the covariation of Eu and Sr. Due to the equal charges and similar radii of $\mathrm{Sr^{2+}}$ and $\mathrm{Eu^{2+}}$, which both preferentially partition into feldspars, Sr/Eu ratios decrease only slightly from 300 to 100 during fractional crystallization. In granites which are characterized by non-chondritic Zr/Hf and Y/Ho ratios, and by the lanthanide tetrad effect, however, this covariation breaks down, and Sr/Eu ratios may increase significantly to values of up to 5000 (Irber 1996; W. Irber, work in preparation).

Moreover, any model that successfully tries to explain a REE distribution such as that of the Abu Dabbab granite, must also be able to explain the fractionation of *both* of the geochemical twin pairs Y-Ho and Zr-Hf (note that fractionation of Zr-Hf but not of Y-Ho is observed in carbonatites, e.g. Bau 1996; Andrade et al. 1997). Both pairs comprise isovalent elements (Y and Ho: trivalent; Zr and Hf: tetravalent) that are of almost equal ionic radii. Hence, mineral/melt partition coefficients which are controlled by size and charge of the cation considered and by the size and elasticity of the lattice site into which it is to be incorporated (e.g. Goldschmidt 1937; Möller 1988; Blundy and Wood 1994; Purton et al. 1996), are very similar for Y-Ho and Zr-Hf, respectively, and cannot induce significant fractionation of Y/Ho and Zr/Hf ratios. As documented previously from aqueous systems (Bau and Dulski 1995; Bau 1996; Bau et al. 1996), chemical complexation is able to fractionate Y from Ho and Zr from Hf, and may generate anomalies for the non-redox-sensitive lanthanides La, Gd, and Lu.

Hence, I conclude that in contrast to suggestions by Y. Pan (1997), fractional crystallization of accessory minerals cannot adequately explain the distribution of Y, REE, Zr, and Hf in some highly evolved felsic igneous rocks. Even at high degrees of fractional crystallization ($F < 0.3$) this process does neither generate

$\mathrm{REE_{CN}}$ patterns that are sub-divided into four convex-upward curved segments (tetrads) with minima at $\mathrm{La_{CN}}$, $\mathrm{Nd_{CN}}$, $\mathrm{Gd_{CN}}$, $\mathrm{Ho_{CN}}$, and $\mathrm{Lu_{CN}}$, nor does it induce significant decoupling of *both* of the geochemical twin pairs Y-Ho and Zr-Hf.

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