

Rare-earth element determination in minerals by electron-probe microanalysis: application of spectrum synthesis

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ABSTRACT

Electron-probe microanalysis (EPMA) is applicable to rare-earth elements (*REE*) in minerals with relatively high *REE* concentrations (e.g. hundreds of parts per million). However, given that each of the 14 *REE* has at least 12 X-ray lines in the *L* spectrum, finding peak-free regions for background measurement can be problematical. Also, measured peak intensities are liable to require correction for interferences. Hitherto, little attention has been paid to the optimisation of background offsets and the implications of the wide variation in *REE* distribution patterns in different minerals. The 'Virtual WDS' program, which enables complex multi-element spectra to be synthesised, has been used to refine the conditions used for different *REE* distributions. Choices include whether to use the $L\beta_1$ rather than the $L\alpha_1$ line, background offsets, and counting times for comparable relative precision. Correction factors for interferences affecting peak and background measurements have also been derived.

KEYWORDS: electron-probe microanalysis, rare-earth elements, Virtual WDS.

Introduction

ELECTRON-PROBE microanalysis of minerals containing rare-earth elements requires careful selection of conditions, owing to the multiplicity of X-ray lines. Energy-dispersive (ED) analysis is applicable only at percent concentration levels, which is a severe limitation. The present discussion is therefore concerned with wavelength-dispersive (WD) analysis, where small peaks are more easily detectable owing to the higher peak to background ratio compared to ED analysis, and the spectral resolution is much better (though interferences affecting either peak or background measurements can still occur).

Various approaches to the problem of interferences have been devised. Amli and Griffin (1975) used empirical factors to determine the amount which should be deducted from the measured $L\alpha_1$ intensity of a given element to allow for interference by another element, expressed as a fraction of the $L\alpha_1$ intensity of the latter. Roeder (1985) derived similar factors from a mathematical peak-shape expression adjustable to allow for differences in spectro-

meter resolution. Exley (1980), on the other hand, used the $L\beta_1$ line for several of the *REE*, with the object of avoiding the need for such corrections. More recently, Williams (1996) has described an analytical scheme involving suitable choice of $L\alpha_1$ or $L\beta_1$ line, together with empirical corrections for interferences from *REE* and other commonly associated elements.

Such procedures take no account of the wide variation in *REE* abundance patterns for different minerals, which can affect the choice of $L\alpha_1$ or $L\beta_1$ line and optimum background offsets. In order to investigate this, spectra have been simulated for different *REE* distributions with the aid of the 'Virtual WDS' computer program for WD spectrum simulation (Reed and Buckley, 1996). Background offsets have been chosen to minimise interferences from *REE* and other elements. Where interferences cannot be avoided completely, correction factors have been determined. Relative counting times required for equal statistical precision have been estimated, enabling counting strategies to be devised to suit different minerals.

Trace element analysis — general considerations

REE concentrations in minerals are often (though not always) low, in which case the following general considerations for minor or trace element analysis apply. To obtain the best possible counting precision and minimum detection limits, the highest practicable beam current should be used (consistent with the avoidance of damage to the specimen). It may be desirable to use a separate routine for major elements to avoid excessive dead-time and pulse-height distortion occurring at very high count-rates. Also a high electron accelerating voltage improves trace element detectability, but may entail some loss of accuracy for the major elements, owing to errors in the 'ZAF' corrections.

The normal procedure for background determination is to interpolate from intensity measurements with the spectrometer offset on each side of the peak. Background offsets should not be greater than necessary, owing to the possibility of errors due to non-linearity of the continuum. It is acceptable (and sometimes advantageous) for a background position to be on the 'tail' of the measured peak. The contribution of the 'tail' cancels out in the ratio of intensities measured on standard and 'unknown', assuming the peak profile is the same (a 'tail' intensity of more than, say, 10% of the peak should be avoided, however).

For small peaks the optimum strategy is to use a total background counting time equal to that for the peak, divided equally between positive and negative offset positions. For single-sided background measurements (used when no interference-free location is available on one side) the whole time is devoted to measuring background at one position. For higher concentrations (e.g. above 1%) background counting time can be reduced.

A peak may be defined as being just detectable when it is equivalent to 3 times the standard deviation of the background, as determined by counting statistics. The detection limit (>99% confidence) can thus be expressed in terms of concentration as: $C_{DL} = 3[(n_p^2/n_b)t]^{-0.5}$, where n_p is the peak count-rate for the pure element, n_b is the sample background count-rate, and t is the counting time used for peak and background. (For some purposes it is more appropriate to use a figure of $2C_{DL}$, representing the minimum concentration required for meaningful quantitative determination.)

Choice of conditions for *REE* analysis

The *K* lines of *REE* are not excited at normal electron beam accelerating voltages, and *M* lines are ruled out by self-absorption which distorts peak shapes and reduces intensities, especially those of *LREE* (Lábár and Salter, 1991). For analytical purposes the $L\alpha_1$ line is thus the first choice, but if it is affected by interferences the $L\beta_1$ line may be preferable. For example Pr- $L\alpha_1$ is overlapped by La- $L\beta_1$ (Fig. 1), whereas Pr- $L\beta_1$ is interference-free, though its intensity is some 25% lower.

All the *REE L* lines lie within the wavelength range of the LiF (200) crystal. *LREE* are also covered by PET, but the higher intensities obtained with this crystal are offset by lower peak to background ratios and broader peaks that are more susceptible to interferences (Fig. 2). Williams (1996) proposed using PET for La and Ce, but Ce is then susceptible to much more serious interferences from Ba and Ti than with LiF. In the subsequent discussion it is assumed that only LiF is used.

Background measurement

REE (and other) lines in the spectra of natural minerals, it is sometimes difficult to find suitable places for background measurements. Interferences which affect the background may lead to under-estimation of the concentration, which is just as important as over-estimation caused by interferences affecting the peak. However, background interferences can be minimised by optimal choice of offsets, taking into account the other elements present and their relative concentrations. Also, when such interferences occur on one side of the peak, they can be avoided by measuring back-

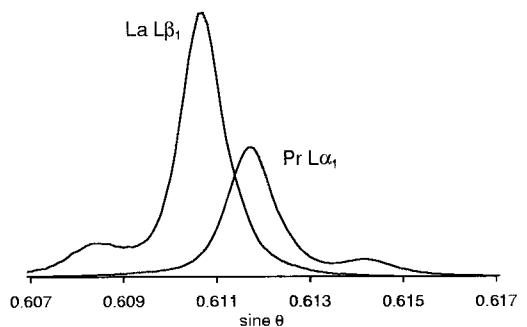


FIG. 1. The Pr- $L\alpha_1$ peak with interfering La- $L\beta_1$ (chondritic relative concentrations of Pr and La).

ground only on the other side. In this case, allowance should be made for slope, which may affect the background intensity by several percent (see Table 1). If measurements are made on both sides, interpolation takes account of slope. The error in the background due to curvature is less than 1% of the background intensity and can be neglected.

A potential cause of continuum non-linearity is the presence of steps due to absorption edges lying between peak and background positions. The L edges of *REE* can be discounted on the grounds that the steps are not large enough relative to the peaks to be important. However, more significant effects can arise from non-*REE* elements present in much higher relative concentrations: for example, the Ba- L_2 edge is close to Sm- $L\alpha_1$ (+0.0013 in sine θ units) and the Ba- L_3 edge is close to Nd- $L\alpha_1$ (-0.0019), also the Mn- K edge is close to Dy- $L\alpha_1$ (-0.0031).

Detection limits and counting times

The $L\alpha_1$ peak intensities for pure *REEs* recorded with a LiF crystal increase from La to Lu owing to the increase in the spectrometer efficiency with decreasing Bragg angle, which outweighs the decrease in excitation efficiency (the La- $L\alpha_1$ intensity is about one third that of Lu- $L\alpha_1$). The background intensity increases considerably more, however; hence the detection limit as given by the expression above remains fairly constant. With an accelerating voltage of 25 kV, a beam current of 100 nA, and a counting time of 100 s each for peak and background, the average value of C_{DL} (as obtained from the expression given above) is 150 ppm for a sample with a

mean atomic number (Z) of 30. For *REE*-containing minerals Z covers a wide range, e.g. from apatite (14) to uraninite (72), requiring a factor ranging from 0.7 to 1.5 to be applied to C_{DL} (owing to the proportionality of the continuum to Z). C_{DL} also varies inversely as the square root of beam current and counting time (which may be constrained by damage caused to the specimen by the bombarding electrons). If the $L\beta_1$ line is used, the detection limit is up to 1.5 times higher owing to its lower intensity compared to $L\alpha_1$. Also, detection limits are adversely affected by interferences.

REE distributions in natural minerals reflect 'solar system' abundances as found in chondritic meteorites, which cover a range of 30:1. Often the main object of analysis is to determine the shape of the chondrite-normalised distribution, in which case it is desirable to aim for constant relative precision as far as possible, and *REE* with low chondritic abundances thus require longer counting times. Fig. 3 shows the relative counting times required to achieve this object for different 'model' distributions. For some elements the times required would be impracticably long, so that compromise is necessary. Further, given that chondrite-normalised *REE* distributions are mostly smooth (apart from Eu), it may be inappropriate to include an element for which the precision is much poorer than its neighbours (owing to the alternation of high and low abundances for even and odd atomic numbers).

Application of 'Virtual WDS'

Recording spectra from actual samples, with a view to investigating interferences, is extremely

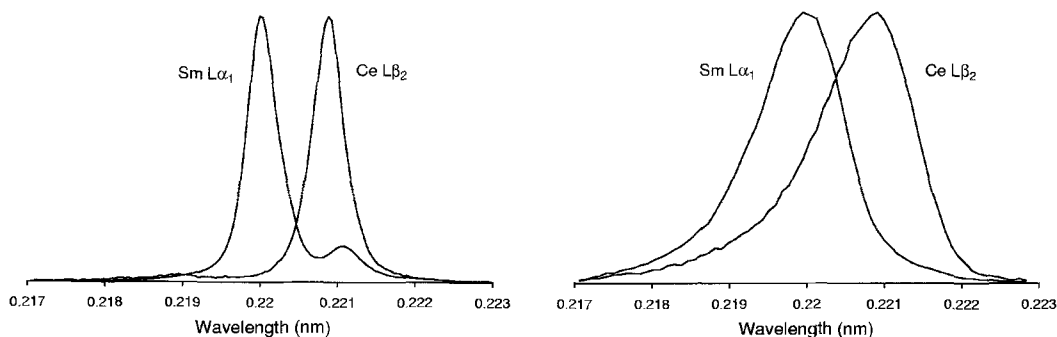


FIG. 2. Sm- $L\alpha_1$ and Ce- $L\beta_2$ peaks recorded with (a) LiF, (b) PET, crystals.

TABLE 1. Analysis conditions for *REE* (LiF crystal): choice of $L\alpha_1$ or $L\beta_1$ line, and background offsets (in sine θ units) for minimum interferences (zero indicates no background measurement), and value of background slope factor. Selection criteria expressed as ratio of mass concentrations

Element	Option no.	Line	Bgrnd offsets		Slope factor	Selection criteria
			-	+		
La	1	α	0.003	0.006	1	
Ce	1	α	0.002	0.0035	1	Ba/Ce<20
	2	β	0.004	0	0.97	Ba/Ce>20
Pr	1	β	0.002	0.002	1	Cs/Pr<60 & Ba/Pr<15
	2	β	0	0.002	1.02	Cs/Pr>60 or Ba/Pr>15
Nd	1	α	0.007	0.0045	1	
Sm	1	α	0.003	0.0055	1	
Eu	1	α	0.0025	0.004	1	Yb/Gd>5 & Mn/Eu<1 & Ba/Eu<15
	2	α	0	0.004	1.03	Yb/Gd>5 & Mn/Eu>1 & Ba/Eu<15
	3	α	0.0025	0	0.98	Yb/Gd>5 & Mn/Eu<1 & Ba/Eu>15
	4	β	0	0.0025	1.02	Ce/Gd>20 & Fe/Eu<0.3
	5	β	0.0055	0	0.95	Ce/Gd>20 & Fe/Eu>0.3
Gd	1	α	0.005	0.0045	1	Yb/Gd>1
	2	β	0.003	0.0035	1	Ce/Gd>6
Tb	1	α	0.002	0	0.99	
Dy	1	α	0.0025	0.004	1	Fe/Dy<7
	2	α	0.0025	0	0.98	Fe/Dy>7
	3	β	0.0025	0	0.98	Mn/Dy>0.3
Ho	1	β	0.002	0	0.99	
Er	1	α	0.004	0.0055	1	Yb/Gd>0.2
	2	α	0.004	0	0.98	Ce/Gd>15
Tm	1	α	0.007	0.002	1	
Yb	1	α	0.0025	0.0055	1	Yb/Gd>1 & Ni/Yb<0.1
	2	α	0.008	0.0055	1	Yb/Gd<1 or Ni/Yb>0.1
Lu	1	α	0.0025	0.005	1	

time-consuming if statistical precision commensurate with that of analytical measurements at trace levels is to be obtained. It is thus much better to use stored pure-element spectra and scale these according to concentration, as in the 'Virtual WDS' program (Reed and Buckley, 1996), which has been used to simulate spectra for different *REE* abundance patterns. Preferred analytical lines based on these simulations are given in Table 1: $L\alpha_1$ is first choice, unless it is significantly affected by interferences, in which case $L\beta_1$ may be preferable. Selection criteria are expressed in terms of Ce/Gd and Yb/Gd ratios, for *LREE*- and *HREE*-enriched distributions respectively (in the model distributions the ratio of the chondrite-normalised abundances of neighbouring elements is constant). Non-*REE* elements are also taken into account where these have a significant influence.

Background offsets given in Table 1 have been selected on the basis of minimal interferences from other *REE*. For each element the first option is that which applies to a flat chondrite-normalised distribution. Alternative options are given where necessitated by changes in the slope of the distribution.

A good example is the application to Eu. The Eu- $L\alpha_1$ line is subject to interference from other *REE*, notably Pr and Nd (Fig. 4a). The effect of these elements on background measurements can be avoided to a large extent by suitable choice of offsets, but a correction is needed for their contribution to the apparent Eu- $L\alpha_1$ intensity. For *LREE*-enriched minerals, the concentrations of Pr and Nd are enhanced relative to Eu and the interferences are more serious. The $L\beta_1$ line also suffers interference, mainly from Dy (Fig. 4b), and thus is suitable only when *HREE* are strongly

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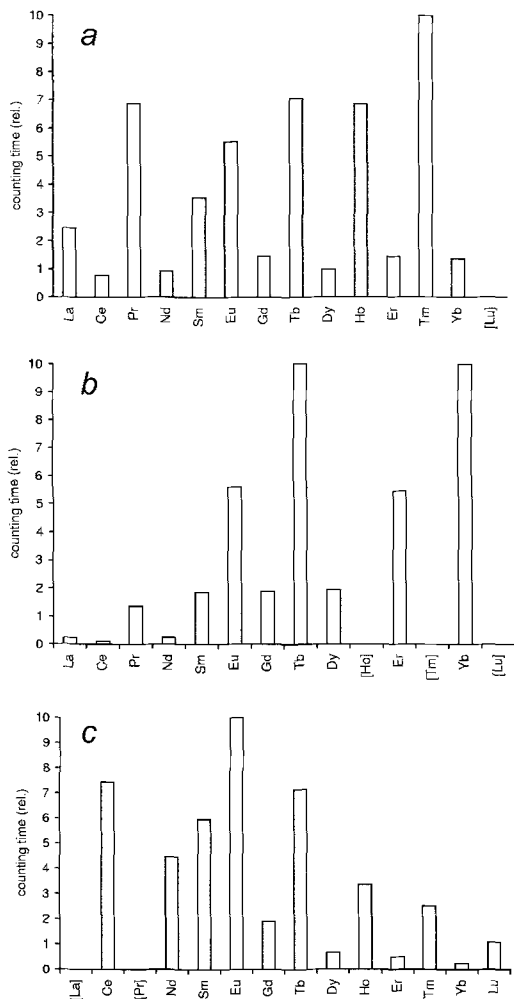


FIG. 3. Relative counting times required to give equal relative precision for different REE distributions: (a) equal chondrite-normalised concentrations; (b) LREE-enriched (chondrite-normalised La/Lu = 10^3); (c) HREE-enriched (chondrite-normalised Lu/La = 10^3). (Elements suffering prohibitive interferences or requiring impracticably long counting times excluded.)

depleted relative to LREE (Fig. 4a and b are based on a 'flat' distribution). Interferences by Mn, Fe and Ba, can also affect the choice of conditions (see Table 1). The relative depletion of Eu which sometimes occurs in minerals makes it even more difficult to determine this element.

Another example is illustrated in Fig. 5, which shows interferences affecting both the $L\alpha_1$ and

$L\beta_1$ lines of Tm, which (together with the low abundance of this element) suggest exclusion from the analysis routine in most cases, given that the neighbouring elements Er and Yb are less problematical. (The least unfavourable situation is where there is strong HREE-enrichment, all the interfering elements being lighter than Tm.)

Lines of other elements in the relevant wavelength range, namely the K lines of V-Ni, as well as the L lines of Sb-Ba (affecting LREE) and Hf-Re (affecting HREE), have also been considered. Fig. 6 illustrates an example of interference by the non-REE element Ba (the effect can be much larger than that shown, when the Ba/Ce ratio is higher). In this case (and some others) the interference effect may be greatly reduced by selecting background offsets such that the interfering element has an equal influence on both peak and background (Solberg, 1988). Note, though, that this approach is susceptible to errors due to differences in line profiles and therefore should be used with caution.

Interferences

The 'Virtual WDS' program has been used to derive factors from which corrections for interferences can be estimated (see Table 2). The amount by which the concentration of the analysed REE is enhanced owing to the interference is equal to the concentration of the interfering element multiplied by the interference factor (this does not take account of differential absorption effects, which may be significant for some sample compositions). A negative factor indicates that background is affected by interference more than the peak, leading to underestimation of the peak intensity. The correction strictly should be included in the iterative ZAF procedure, with allowance for differential absorption, etc. (Donovan *et al.*, 1993). It is permissible, however, where the correction is not large, to calculate it retrospectively from the normal output. Interference factors are sensitive to spectrometer resolution: the values given refer to a particular instrument and are intended mainly to indicate which interferences need correction (analytical data should be corrected using factors determined experimentally for the particular instrument used). Table 2 includes all potentially interfering elements, including for completeness some not likely to occur in natural REE-bearing minerals. The values are similar to those listed by Williams (1996) in some cases and smaller in

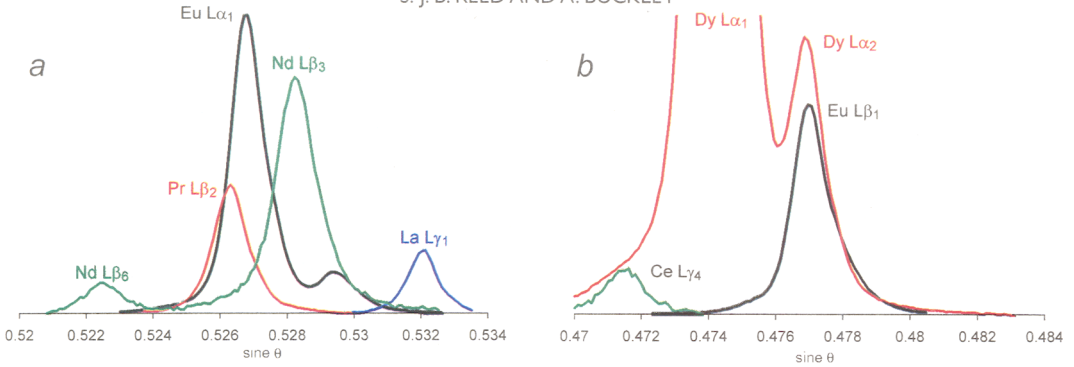


FIG 4. Eu peaks and interfering peaks from other *REE*, with chondritic relative abundances: (a) $\text{Eu-L}\alpha_1$, (b) $\text{Eu-L}\beta_1$.

others, owing to the optimisation of background offsets.

High-order lines

Interferences from higher-order reflections are possible in addition to those caused by first-order lines. Some of the second-order *L* lines of *HREE* lie in the same wavelength range as first-order *LREE* lines, but only minor lines are involved in such cases, and the second-order reflections are of relatively low intensity. For example, $\text{Yb-L}\gamma_4$ and $\text{Lu-L}\gamma_2$ second-order lines interfere with $\text{Nd-L}\alpha_1$ (first order), but the intensity is in the region of 10^3 times lower (for equal concentrations) and can be reduced at least another factor of 10 by using pulse-height analysis.

Of greater potential importance are high-order interferences from non-*REE* elements, which may be present in higher relative concentrations. Possible candidates include third-order *K* lines of Y, Zr and Nb, but these have excitation energies of 17 to 19 keV and are only weakly

excited by electrons of normal energy. The strongest interfering line of this type is $\text{Y-K}\alpha_1$ (third order), which could affect the background measurement for $\text{Ho-L}\beta_1$, but only on the high-angle side, which is not used (because of other interferences) in the conditions given in Table 1. Interferences from second-order *L* lines of elements above Lu in atomic number are generally small and most of the elements concerned do not commonly coexist with *REE*. A case of possible significance is $\text{Th-L}\alpha_1$ (second order) interfering with $\text{Dy-L}\alpha_1$ (first order).

Conclusions

Computer synthesis of X-ray spectra using the ‘Virtual WDS’ program enables the influence of the abundances of *REE* and other elements present to be taken into account in the choice of background measurement positions. Also, the magnitude of inter-element line overlaps can be estimated as a guide to whether or not corrections

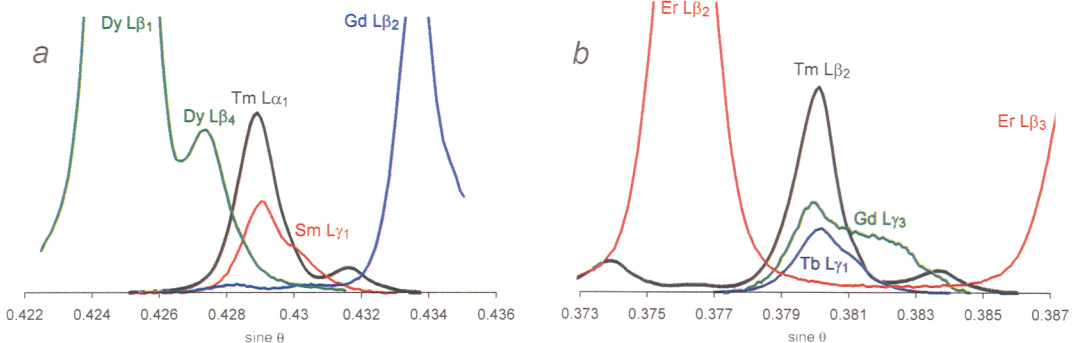


FIG. 5. Tm peaks with interferences: (a) $\text{Tm-L}\alpha_1$, (b) $\text{Tm-L}\beta_1$.

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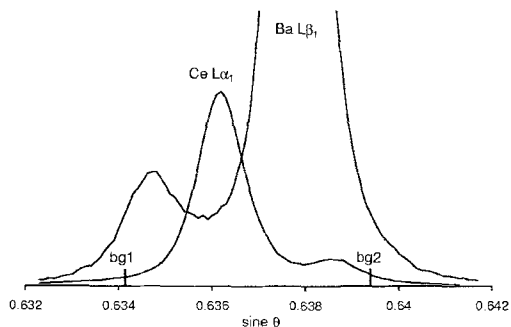


FIG. 6. Ce- La_1 with interfering Ba- $L\beta_1$ peak (Ba/Ce = 10); subtraction of background as measured at positions bg1 and bg2 automatically allows for Ba- $L\beta_1$ interference.

are needed. Further, predicted peak intensities allow a suitable counting strategy to be devised, taking account of the widely varying chondrite-

normalised REE abundance patterns occurring in natural minerals. (For details of 'Virtual WDS', see <http://www.esc.cam.ac.uk/astaff/buckley/vwds1.html>).

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TABLE 2. Interference factors (for definition, see text) using different analysis conditions (see Table 1); most significant cases indicated by bold font. Values given are for a particular instrument and not necessarily quantitatively correct for other instruments

Elem.	Opt.	Interference factors										
La	1	Sb -0.0005	Te -0.0002	I -0.0006	Cs	0.020						
Ce	1	Te -0.0016	I -0.0030	Ba	0.0070							
	2	Cs	0.0022									
Pr	1	V -0.0007	Cs -0.0016	Ba -0.0032	La	0.0011						
	2	V -0.0057	Cs	0.0012								
Nd	1	I -0.0034	Cs -0.0043	Ba -0.0014								
Sm	1	Ba -0.0006	Ce	0.0032	Pr	-0.0075						
Eu	1	Cr -0.0002	Mn -0.078	Ba -0.0063	La -0.0013	Ce -0.0009	Pr	0.14	Nd	0.0096		
	2	Mn	0.0063	Ba -0.017	La -0.0044	Ce	0.0001	Pr	0.15	Nd	0.0078	
	3	Cr -0.0004	Mn	-0.13	La	0.0005	Ce -0.0015	Pr	0.14	Nd	0.011	
	4	Mn	0.030	Fe	-0.20	Ce	0.0001	Pr	0.0003	Nd -0.0003	Dy	0.26
	5	Mn	0.0079	Fe	0.010	Ce -0.013	Pr -0.0026	Sm -0.0013	Dy	0.21	Yb -0.010	
Gd	1	Cr -0.0032	La	0.0056	Ce	0.039	Nd	0.0019				
	2	Nd -0.0011	Sm -0.0034	Ho	1.2	Lu	-0.022					
Tb	1	La	0.0006	Ce -0.0037	Pr	-0.011	Sm	-0.012				
Dy	1	Mn	0.37	Fe -0.013	Ce -0.0049	Pr -0.0003	Sm -0.0008	Eu	-0.059	Yb	-0.0035	
	2	Mn	0.37	Ce -0.0079	Sm -0.0013	Eu	0.0024	Yb	-0.0056			
	3	Sm	0.0003	Eu	0.0043	Gd	0.0022	Tb -0.0024	Tm	0.0016	Yb -0.0016	
Ho	1	Ni	0.042	Eu	0.0049	Gd -0.0038	Dy -0.0050	Yb -0.0042	Lu	-0.0089	Re -0.0046	
Er	1	Fe -0.0052	Co	0.27	Nd -0.0049	Eu -0.0086	Gd -0.0075	Hf	0.013			
	2	Fe -0.0088	Co	0.27	Hf	0.013						
Tm	1	Fe -0.0016	Sm	0.081	Gd -0.0007	Tb -0.0037	Dy	0.011	Ta	0.027		
Yb	1	Ni	-1.15	Sm -0.0089	Eu -0.031	Dy	0.0026	Ho -0.029	W	0.0052		
	2	Ni	0.017	Sm	0.0021	Gd -0.0012	Ho -0.011	W	0.0051	Re -0.0008		
Lu	1	Co	0.46	Ni -0.0011	Sm -0.0020	Eu -0.0003	Gd -0.0011	Dy	0.079	Ho	0.089	
		Er	-0.0027	Yb -0.0016	Re	0.0006						

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