RARE EARTHS AND MMI^{TM} – CHONDRITE PLOTS, LREE/HREE RATIOS

INTRODUCTION

The rare earth elements (REE's) provide some interesting and often diagnostic geochemical behaviour between different rock types. This arises because they have a very similar electronic structure which is manifest in large, slightly declining ionic radii as atomic weights incrementally increase (the lanthanide contraction). As a result the rare earths are in general incompatible with mafic melt material, and lighter rare earths (LREE) are more incompatible than heavy rare earths (HREE).

Europium which has the capacity for a bivalent cation is a special case and is concentrated in plagioclase, often appearing as a "Europium Anomaly" on chondrite plots. The rare earth compositions of chondrites, a class of primitive meteorites are used to normalise and simplify rare earth patterns from different rock types. SGS Technical report 1114 by Nicholas Turner (Dec 2014) gives an excellent introduction to the analysis of rare earths by ICPMS and the use of chondrite plots to normalize and present the findings graphically. Figure 1 shows on a chondrite plot how the rare earths behave in two basalts of different origin.

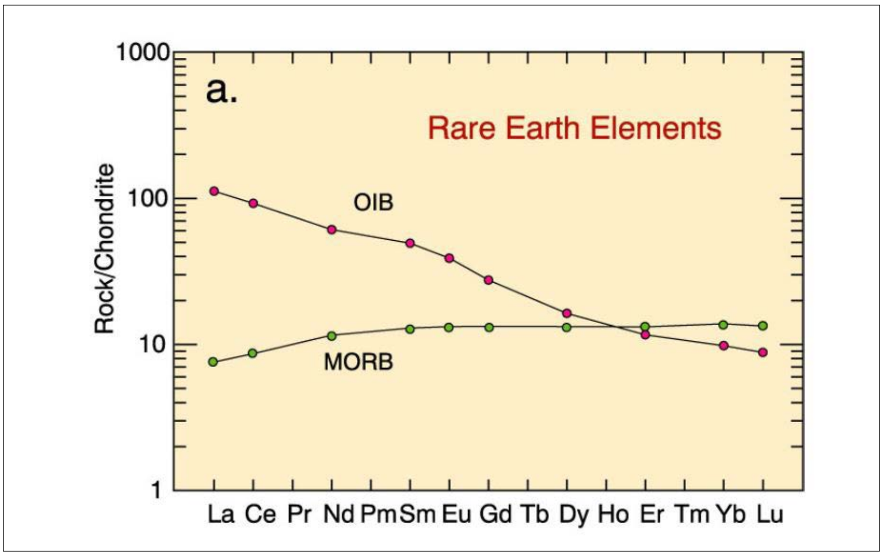

Figure 1: Rare Earth Chondrite Pattern for an Alkaline Ocean Island Basalt (OIB) Versus a Tholeiitic Mid Ocean Ridge Basalt (MORB)

Alkaline OIB's are favoured by deeper melting and lower % of partial melting over tholeiitic or flood basalts and retain their higher rare earth content; partial melting clearly depletes the rare earths in the melt, resulting in a melt for MORB which is closer to chondritic in composition (the chondrite composition plots as a horizontal line from 1 on the y axis of the above diagram). In general felsic and intermediate rock types also have slopes declining from Light Rare Earth Elements (LREE) to Heavy Rare Earth Elements (HREE) similar to the OIB curve above, whilst mafic and ultramafic rock types have slopes similar to the MORB curve. This technical bulletin examines the rare earth compositions in soils after MMI^{TM} extraction and analysis by ICPMS.

CHONDRITE PLOTS FOR RARE EARTHS IN SOILS AFTER MMI™ EXTRACTION

Eleven of the rare earth elements are routinely analysed by ICPMS after MMI™ extraction of soils. Turner (2014) provides the following denominator values for these elements for chondrite normalisation:

Ce	Dy	Er	Eu	Gd	La	Nd	Pr	Sm	Tb	Yb
0.813	0.325	0.213	0.0722	0.259	0.315	0.597	0.1	0.192	0.049	0.209

These normalisation factors were applied to the rare earth ppb values for nine different MMI™ reference samples (see TB30 and TB33) from Western Australian and North American reference data sets.

Table 1 shows the reference samples, their locations and the LREE/HREE ratio defined as (Ce+La)/(Er+Yb).

Table 1: MMI™ Reference Samples used to Obtain Chondrite Plots and LREE/HREE Ratios

Sample	Location	Geology	Class	Code	LREE/HREE
PJ04	W.A., Watheroo	Granite	Acid felsic	1	102.0661
PJ16	W.A., Warriedar	Mafic	Mafic/ultramafic	3	8.108108
KAL04	W.A., Bonnie Vale Rd	Ultramafic Aku	Mafic/ultramafic	3	1.616162
KAL31	W.A., Mandilla	Felsic	Int.felsic/sed	2	10
NS 13-2	Canada, Nova Scotia	I type granite	Acid felsic	1	7.506007
NB 12-1	Canada, New Brunswick	Tonalite	Intermediate	2	7.650602
NS 11-1	Canada, Nova Scotia	Tholeite	Mafic/ultramafic	3	2.076503
BC 13-1	Canada, British Columbia	Olivine Basalt	Mafic/ultramafic	3	10.95238
NS 16-1	U.S.A. Nevada	Miocene Basalt	Mafic/ultramafic	3	0.02459

The chondrite normalised plots for these soils are shown in Figure 2.

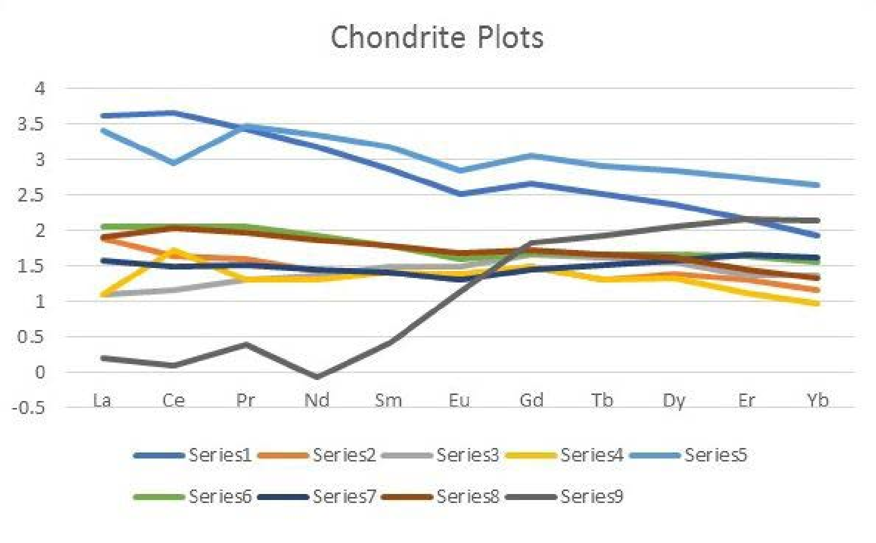

Figure 2: Chondrite Plots for MMI™ Analysis of Soils Over Various Reference Samples. Series 1=WA Yilgarn Granite, Series 2=WA Yilgarn Mafic, Series 3=Yilgarn Komatiite Ultramafic, Series 4= WA Yilgarn Intermediate Felsic, Series 5=Nova Scotia I-Type Granite, Series 6=New Brunswick Tonalite, Series 7=Nova Scotia Tholeite, Series 8=British Columbia Olivine Basalt, Series 9=Nevada Alkaline Hasalt. Note Y-Axis is Logarithmic Scale

Firstly it is noticeable that the chondrite plots of these soils after MMI^{TM} extraction are similar to the chondrite plots for rocks after total digestion i.e. that soils over certain mafic rocks have near horizontal chondrite plots, while soils over more differentiated rocks such as granite and intermediates have slopes which decline from LREE to HREE. The curve for series 9, the soil over alkaline basalt from Nevada has a very different pattern – it has a positive slope from LREE to HREE i.e. HREE values are higher. This has also been noted from whole rock analyses in this area; rhyolites, not just mafic rock types show this behaviour. This may be as a result of the presence of garnet. The partition coefficient into garnet for Er is 18 and Yb is 30, whereas Ce and La are both 0.05 meaning this mineral if in equilibrium with a partial melt will cause the HREE/LREE ratio to steeply increase in the residuum.

LREE TO HREE RATIOS

A simple way to express the slopes of the chondrite patterns quantitatively is to calculate LREE to HREE ratios. In the case of the soils after MMI^{TM} extraction this is best determined by the simple ratio (Ce+La)/(Er+Yb) (not normalised). This ratio is shown for the chosen reference samples in Table 1. The LREE/HREE ratio ranges from over 100 in a soil over granite lithology, to around 1 for soils over Western Australian ultramafic rocks, and to less than 0.03 for the Nevada alkaline basalt with positive chondrite plot slope. It (LREE/HREE) has the scope to be diagnostic of underlying rock type. Additionally it provides a simple quantitative index which can be plotted spatially.

LREE/HREE FOR WESTERN AUSTRALIA

The quartile classed post map for LREE/HREE for outlet sediment samples from Western Australia from the National Geochemical Survey of Australia (NGSA) program is shown in Figure 3.

Figure 3 shows that many of the upper quartile values for LREE/HREE for Western Australia plot in the south-west of the state, in the SW part of the Archaean Yilgarn Craton. This part of the Craton is dominated by granitoid rocks; the high LREE/HREE ratios reflect soils over rocks which have a greater degree of differentiation (away from basalt). The eastern part of the Yilgarn Craton, east of longitude 1200 E

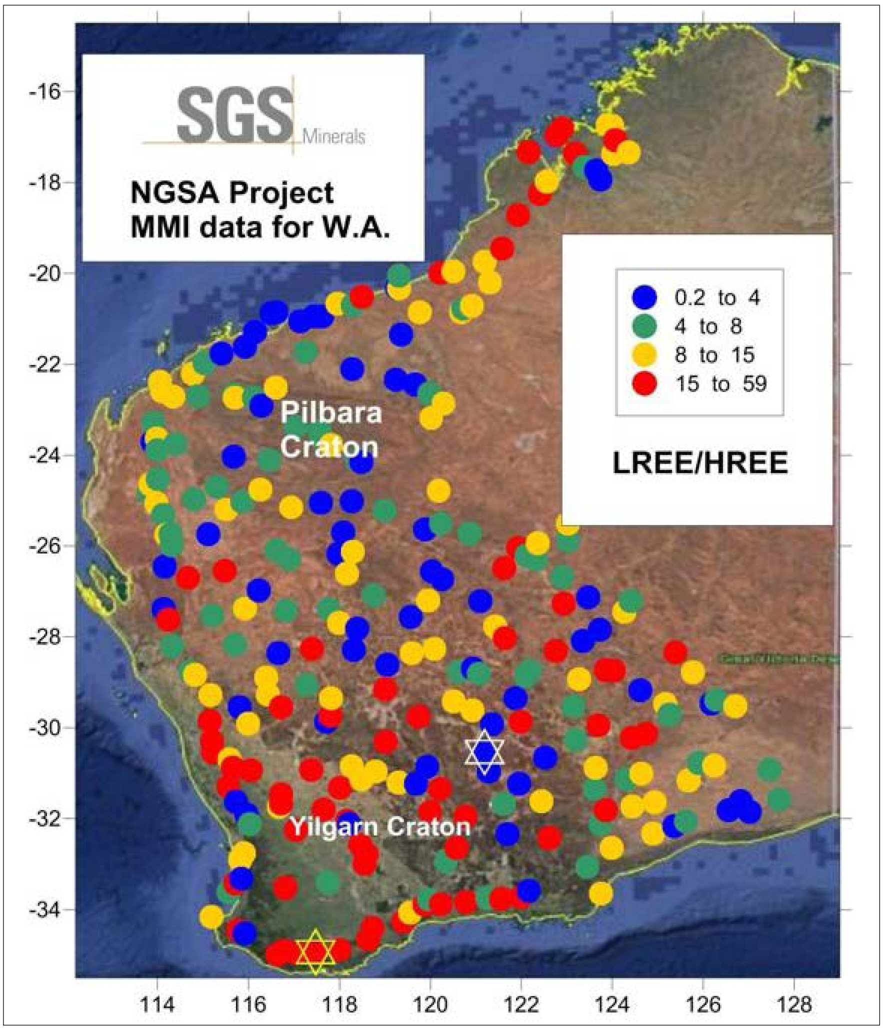

Figure 3: LREE/HREE Ratios Plotted by Quartile for Samples from the NGSA Sampling Program

contains many samples with LREE/HREE in the lowest (blue) quartile, reflecting soils over mafic and ultramafic rocks. These have low gradient slopes on chondrite plots. To the north, the Archaean Pilbara Craton displays few catchments with upper quartile (red) LREE/HREE values consistent with the paucity of granite in that Craton.

The highest LREE/HREE of 59 (yellow star) is from a granite dominated salt lake catchment north-west of Albany near the south coast, and the lowest 0.23 (white star) is from a mafic/ultramafic dominated catchment NW of Kalgoorlie.

LREE/HREE FOR NORTH AMERICA

The LREE/HREE ratios for 162 samples taken from various parts of the United States of America and Canada are shown in Figure 4.

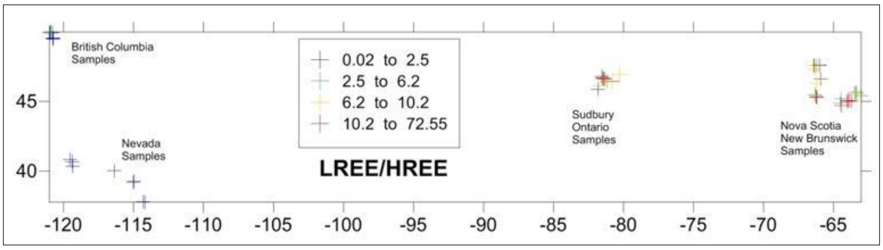

Figure 4: LREE/HREE Ratios Plotted by Quartile for North American MMI^{TM} Reference Samples

Samples were taken in triplicate, so that each cross on Figure 4 represents three samples. Additionally the scale of the diagram is such that that in some cases each cross may represent more than 3 samples. It is evident that upper quartile (red) crosses occur in British Columbia, Ontario (Sudbury area), Nova Scotia and New Brunswick sampling areas where granitoid terrain occurs. The highest value for LREE/HREE, 72.55 occurs in a sample from the Bay of Fundy, New Brunswick. The Nevada area has no samples with upper quartile values, but a number in the lowest quartile, including that, 0.02 with the lowest LREE/HREE ratio. This is from a sample in the Cortez Mountains, and likely attributable to garnet in the samples.

LREE/HREE FOR EUROPE

The LREE/HREE ratios for 2108 MMI^{TM}-analysed samples taken from agricultural soil samples from the GEMAS (Geochemistry of European Agricultural Soils) project are shown in Figure 5.

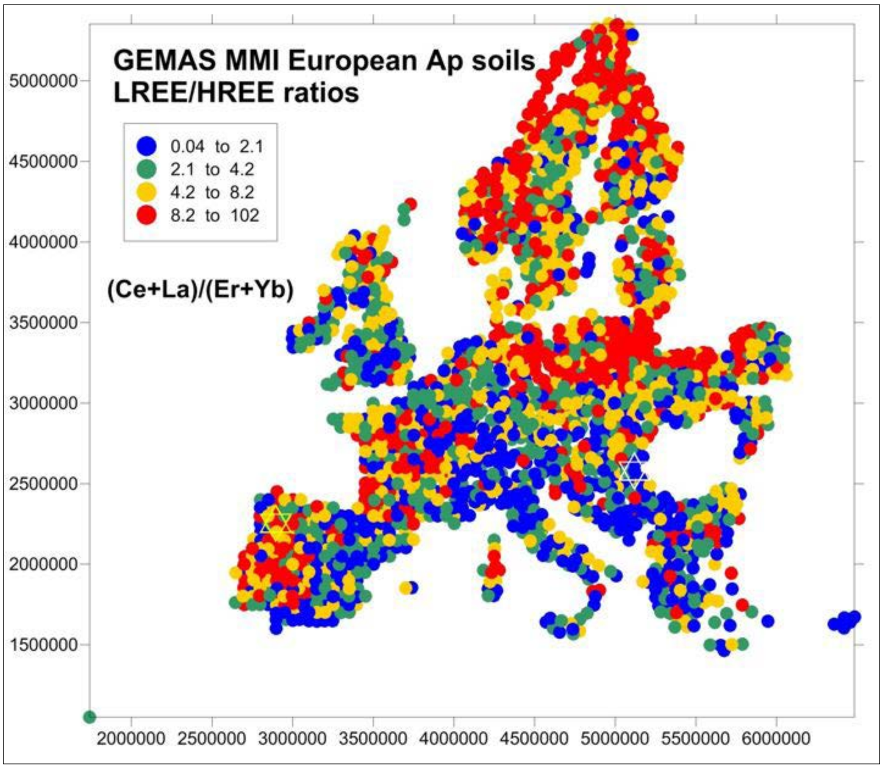

Figure 5: LREE to HREE Ratios in Quartiles for Europe using MMI^{TM} Analysis of Soils from the GEMAS Data Set.

The red dots on Figure 5, the upper quartile values for LREE/HREE, are prevalent in areas of granitoid rocks for Scandinavia, Scotland, Poland and Northern Ukraine, Central France and the island of Sardinia. Conversely the blue dots, lowest quartile for LREE/HREE, coincide with areas from Italy, the Balkans and Greek Islands which include large areas of mafic and ultramafic rocks, including ophiolites. In the case of the United Kingdom they coincide with areas of Jurassic and Cretaceous limestone which show characteristics (high Ni, Mg and low REE content) of the contemporaneous ophiolite activity.

The highest value of LREE/HREE of 101.97 is from a sample in NW Spain, whilst the lowest, 0.045 is from a sample in Serbia.

Not surprisingly there is a similarity between the LREE/HREE distribution and that for Ce, as shown in Figure 6.

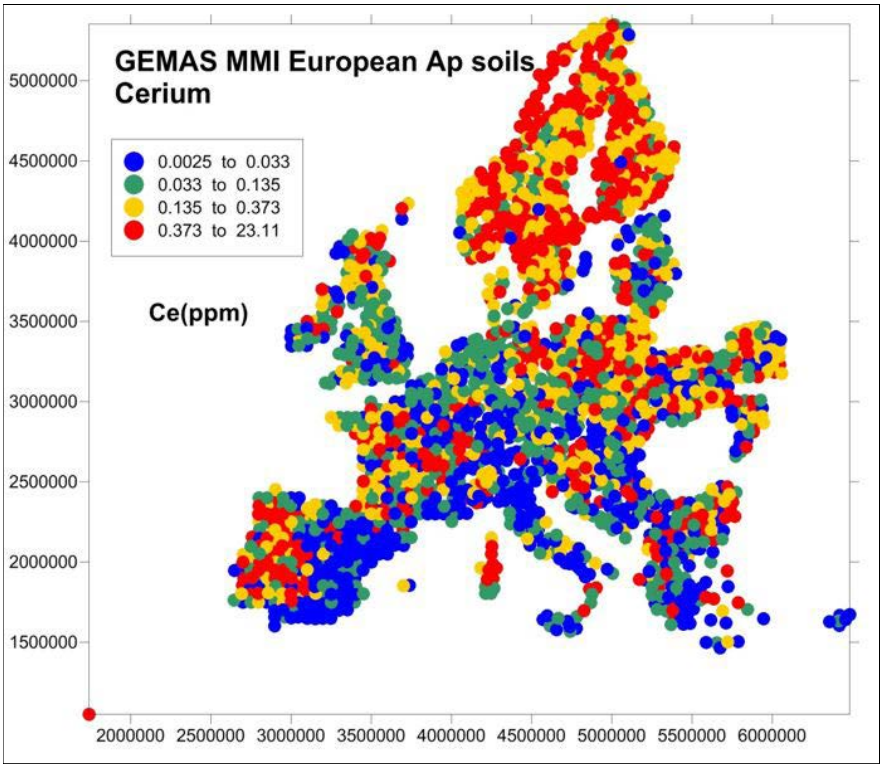

Figure 6: Quartile Plot for Ce after MMI^{TM} Extraction and Analysis of European Agricultural Samples from the GEMAS Project

The similarity between plots 5 and 6 is unsurprising because all rare earth elements are incompatible, and LREE more so than the HREE as predicated in the introduction.

INFLUENCE OF LREE/HREE ON LithoID

Technical Bulletins TB30, TB31 and TB33 relate to LithoID (Degree of Geochemical Similarity) methodology and its ability to discriminate between soils over different rock types. The eleven rare earth elements play an important part in LithoID methodology. In particular the relative ratios and rankings of the rare earth elements are likely to be important, as shown by the ranking diagram for two different basalts in Figure 7.

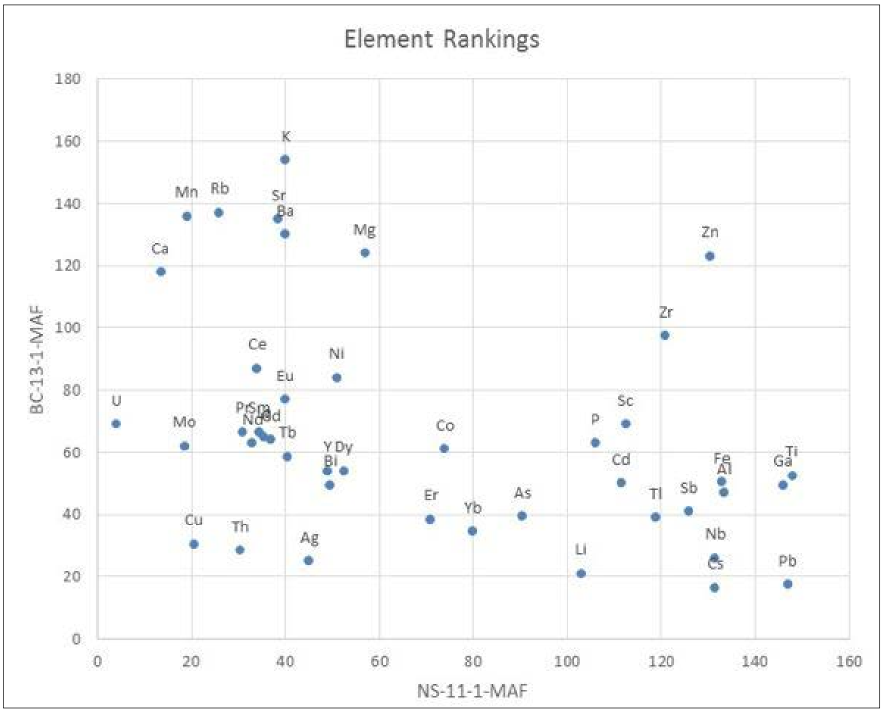

Figure 7: Ranking Diagram for Soil over an Olivine (Alkaline) Basalt BC-13-1 Compared to Soil over Tholeiitic Basalt NS-11-1 (from Technical Bulletin TB33).

The Spearman rsp=-0.40 for NS-11-1 and BC-13-1. This and the ranking diagram Figure 7 suggest BC-13-1 is a very different "basalt" to NS-11-1. Not many elements are close to the 1:1 diagonal. In particular the tholeiitic basalt NS-11-1 has HREE's Er and Yb ranked much higher (70-80) than the LREE's which are ranked less than 40. By contrast the alkaline basalt BC-13-1 has the LREE's e.g. Ce ranked higher (>80) than HREE's (Er and Yb<40). This disparity provides for significant deviation from the 1:1 diagonal derived from within the rare earth element suite; these factors suggest that the relative ratios of LREE and HREE are an important contributing determinant in the effectiveness of LithoID methodology in discriminating soils over different rock types.

REFERENCE

Turner N., (2014). Data analysis of rare earth elements (REE) using chondrite plots. SGS Technical Report 1114, Dec 2014.

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