



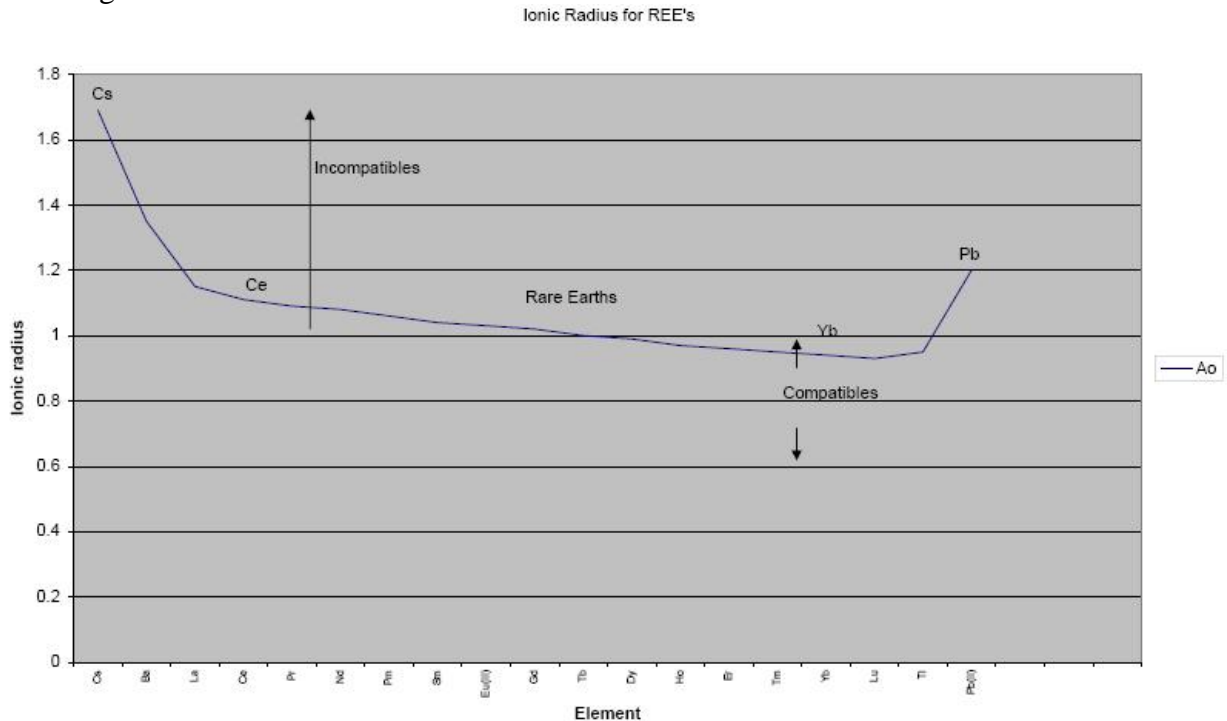
**TECHNICAL BULLETIN – RARE EARTHS AND  
MMI GEOCHEMISTRY**

**DECEMBER 2005**

## Introduction

Rare earth elements appear commonly and strongly in partial digestions from a wide range of “unexpected” mineral deposit styles and geological assemblages – komatiitic nickel sulphides, vein-type Au deposits, and kimberlites for example. Rare earths commonly are thought of as being associated with felsic and granitic rocks and carbonatite mineralization. Soils over these rock types exhibit concentrations of rare earths commonly of the order of hundreds of ppb in MMI digestions.

The rare earths are in fact, not rare: they are more correctly referred to as the Lanthanides, although the term “Rare Earths” is widely used and accepted. That term probably arose because their very similar chemistry delayed their separation and discovery as 14 discrete elements. Cerium is more common in the earth’s crust than copper, and even the least abundant “rare earth” is more common than elements such as As and Cd, commonly used as pathfinders in geochemistry. The chemistry of the Lanthanides is dominated by the trivalent oxidation state except for Ce which has a tetravalent state as well, and for Eu which has a divalent ion. The Lanthanides have characteristically relatively insoluble sesqui-oxides, but importantly good mobility in weathering profiles and ability to be complexed e.g. in partial extractions. The trivalent cations are large (e.g.  $\text{Ce}^{+++}$  ionic radius  $1.11 \text{ \AA}$  c.f.  $\text{Fe}^{+++}=0.64 \text{ \AA}$  and  $\text{Al}^{+++}=0.50 \text{ \AA}$ ) and possibilities for substitution in silicate crystal lattices is probably limited. The so-called Lanthanide contraction (shown in Figure 1) is the very small reduction in ionic radius which occurs from light to heavy rare earths from  $\text{La}^{+++}=1.15 \text{ \AA}$  to  $\text{Lu}^{+++}=0.93 \text{ \AA}$  is as a result of imperfect shielding of each 4f electron, similar outer electron shells and steadily increasing atomic number.



It has been used, usually in a “chondrite normalised” form, to investigate the history and origin of magmas and crustal rocks. The light rare earths are among the “incompatible” elements such as Cs, Rb, U, Th, K, Ti, Li and Be which do not readily enter into the early rock building minerals. Cerium, the most abundant rare earth, occurs principally as the minerals bastnasite, a carbonate, and allanite and monazite, both silicates. All are accessory minerals in granites, grano-diorites, monzonites and syenites. Allanite also occurs in some limestone skarns and pegmatites, whilst monazite is of course also a detrital mineral in mineral sand deposits where it sometimes constitutes an ore for Ce and other rare earths (and Th). Typical contents of Ce in various rocks of the crust are (data source Bernard Gunn, [www.geokem.com](http://www.geokem.com)):

Table 1. Typical Ce contents of Oceanic Crust (ppm).

N-type Morb	EPR Ferro-Basalt	Mauna Kea Hawaiiite	Island Phonolite
0.5-1.5	5-21	44-67	100-330

Investigations of several komatiite-type NiS deposits from Western Australia (e.g. Nepean, Miitel North) have shown similar high concentrations of Ce, Nd and other rare earths from MMI digestions of soils in close proximity to sulphide ore, even when felsic rock types are absent or laterally displaced by some distance. Comparison with whole fresh-rock geochemistry and geological models suggests that in these cases the rare earths are probably derived from felsic plumes incorporated into the basal part of the massive sulphides. As such the rare earths from partial digestions of soils can be a very good vector to ore – at the very least they are an accurate indicator of where the base of the adcumulate ultramafic has undergone thermal erosion.

Kimberlites, whilst having some similarities with ultramafics, also appear to contain concentrations of rare earths along with high Ni and Fe as would be expected from magmas with deep seated origins. It is also possible that in the ejection process, reaction occurs between the ejecting magma and the crustal rocks through which it is being ejected and rare earths are incorporated or at least “mobilized” around the reaction front. Irrespective of these two possibilities, a “reaction rim” of rare earths is a very important, consistent and recognizable feature of kimberlite pipes. This can, and is easily detected in soil geochemistry e.g. with MMI.

Similar observations have been made on a limited number of vein-type gold deposits. Partial (MMI) digestions often show high values for rare earths such as Ce, Nd, La, Yb coincident with the high Au and Ag signals from soils above the mineralized part of the vein system. Again, comparison with the hard rock geochemistry shows that the rare earths are present in the mineralized part of the vein system, and probably indicative of the source of sulphur. Whilst the exact reasons are not yet clearly known, it appears that rare earth elements have a geochemical mobility which is both conducive to excellent vertical migration (and spatial discrimination), and compatibility with weak extractions and ICPMS analysis. Accordingly, they may play a very useful role in exploration for a wider range of mineral deposit types than previously recognized.

In country rocks it may well be that the limited opportunities for substitution result in the Lanthanides along with other “incompatibles” such as Cs, Rb, U, Th, K, Ti, Li, Be being “left” in high level fractionating fluids, and thence an associate of feldspar in granites, syenites, monzonites and pegmatites i.e. in felsic rock types. It is this context that certain Lanthanides may prove to be useful as diagnostic of certain rock types, and certain alteration zones, and have potentially wide application in mineral exploration. In this document several examples will be mentioned –Nickel Exploration, Diamond (Kimberlite) Exploration, “Inferred Geology” using Ni and Ce as indicators of basic Archaean geology, and La, Nd, and Ce as indicators of various porphyry alteration zones.

**Light to Heavy Rare Earth Ratios**

As shown on Figure 1 above, there is not a great deal of difference in ionic radius between one rare earth and the next. For many years it was thought that the very similar chemical configuration of the Lanthanides would result in very constant ratios for light e.g. La, or Ce versus heavy e.g. Yb, or Lu elements in the sequence in a variety of rock types (the ratio Ce/Yb is often used because of the greater absolute abundance of these two elements). However the differences in the ionic radii across the series result in subtle differences in the behaviour of the rare earths during cooling and precipitation from magmas. As shown in Figure 1, the heavy rare earths are more compatible than the light rare earths due to their decreased ionic radius. In fact, the light to heavy rare earth ratios in rocks provide a very good method for identifying and categorizing magmatic history. Soil up until recently have not been studied for similar behaviour. Figure 1 below shows the Ni and Ce values obtained from MMI digestion of soils across a BIF/Felsic and ultramafics, part of a komatiite sequence at Kooldesak, on the western edge of the Yilgarn Craton.

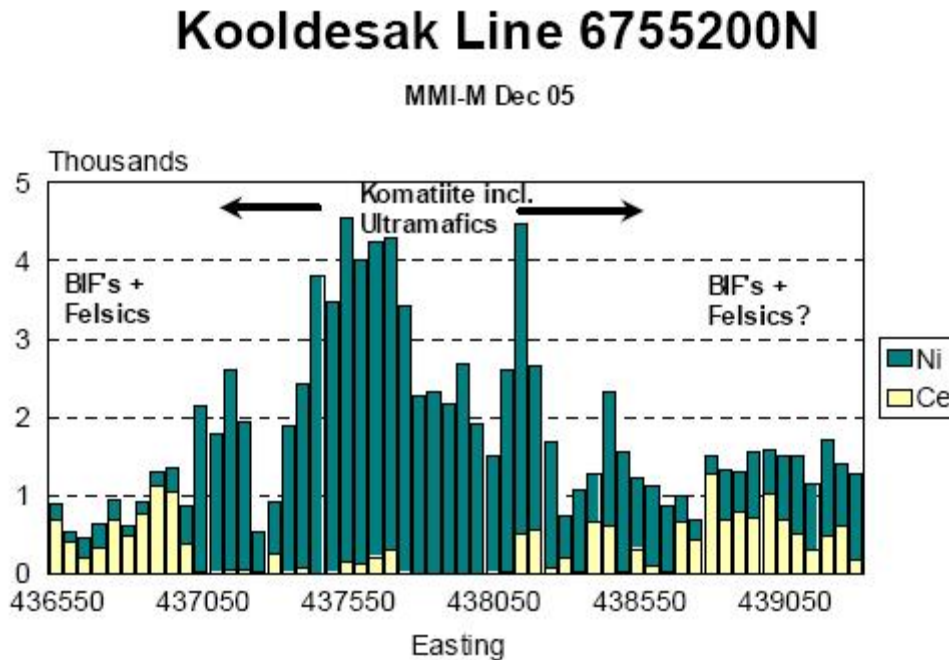
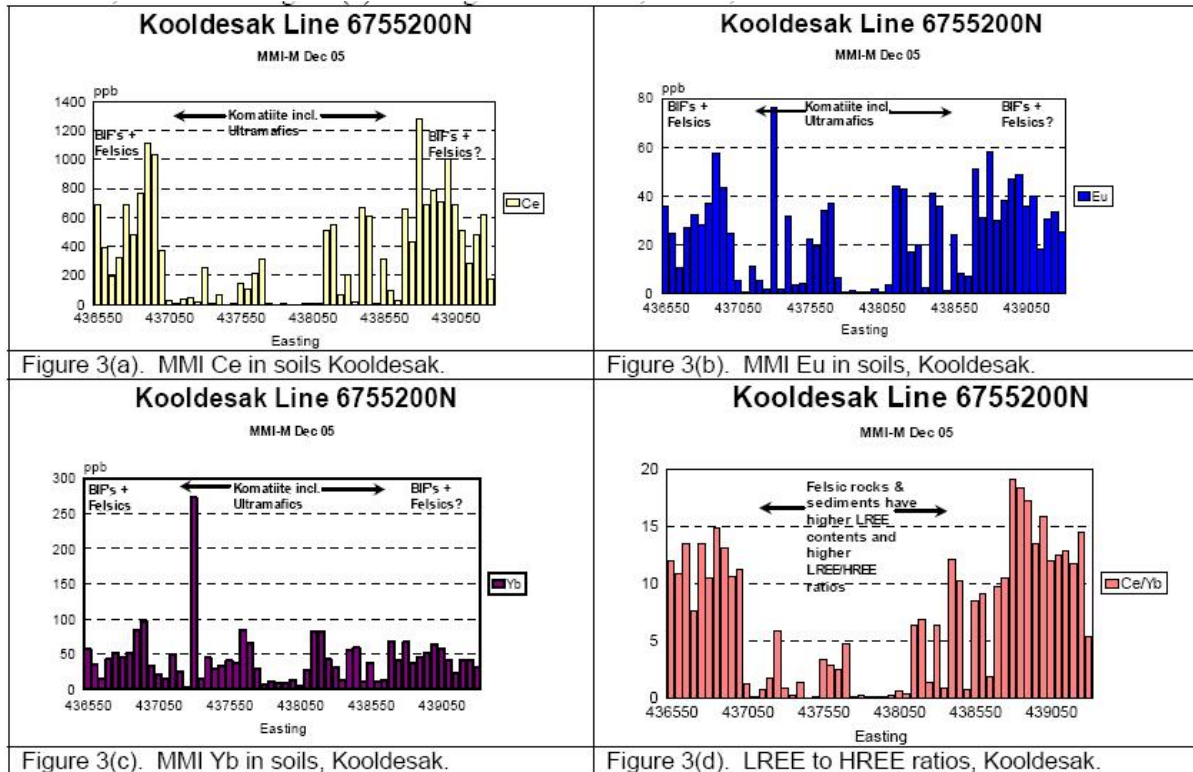


Figure 2. Ni and Ce concentrations in soils after MMI-M extraction.

The ultramafics in the komatiitic central section of the transect can be readily identified by the  $Ni > 2000$ ppb soil samples. Clearly Ce is lower in this (central) section and higher in the adjacent BIF/Felsic terrain. In Figure 3 (a-c), the histograms for other rare earths Eu and Yb are shown along with Ce, as well as a figure (d) showing various ratios, Ce/Yb, Yb/Eu and Ce/Eu.



The heavier rare earth Yb, shows a much lower contrast in absolute concentrations between the ultramafic and felsic/sediment samples (n.b. there is one exceptional very high value). This same phenomenon is observed in hard rock geochemistry - ytterbium is considered “conservative” and cerium “non-conservative”. Thus the Ce/Yb ratio also shows a marked change between the komatiite lavas and felsics/sediments. This could be important and useful, particularly for applying this geochemistry to areas with cover, where absolute concentrations will not be directly relevant. The anomalous soil sample is very interesting; it also contains very high Fe, Eu, Cr, Sc, Al, U and Ti and is skeletal soil over a uniquely mapped sediment. Soil samples demonstrably komatiitic, either sheet flow ultramafic or mafic (MMI  $Ni > 1500$ ) were selected from the above data set; likewise soil samples demonstrably derived from BIF and containing high Fe (MMI  $Fe > 15$ ppm) were selected from the above data. Table 2 below shows relevant data for the rare earths Ce and Yb for these two data sets.

Table 2. MMI Ce and Yb data for komatiite and BIF samples.

Factor	Komatiite soils	BIF + FeOx Soils
<b>Ce mean</b>	<b>94.8</b>	<b>819.4</b>
S.Dev. (n)	161 (23)	327 (27)
<b>Yb mean</b>	<b>34.9</b>	<b>67.4</b>
S.Dev. (n)	24.8 (23)	47 (27)
<b>Ce/Yb ratio</b>	<b>1.6</b>	<b>14</b>
S.Dev. (n)	2.03 (23)	3.8 (27)

These figures are compelling. For the komatiite group the Ce/Yb ratio is close to one - some of these soils had a Ce/Yb ratio of less than unity, i.e. Yb greater than Ce. The BIF group had only one soil with a ratio of less than ten. These soils show similar behaviour to that observed in rocks – not surprising in one sense since the soils are derived from them, but also comforting to know that at least in this instance, no major perturbations have been introduced in the creation of the soil imprint. Experimental evidence also shows that light rare earths such as Ce move towards the high temperature aqueous (residual) phase much more readily than HREE when equilibrated with rock material. It is no surprise to find LREE enriched in late stage felsics, granites and sediments.

### Application to a range of Rock Types

Soils over ten different rock types at “classic” or definitive locations in the Yilgarn Craton have been analyzed for the rare earths. The Ce/Yb ratios for these samples are shown in the graph in Figure 4.

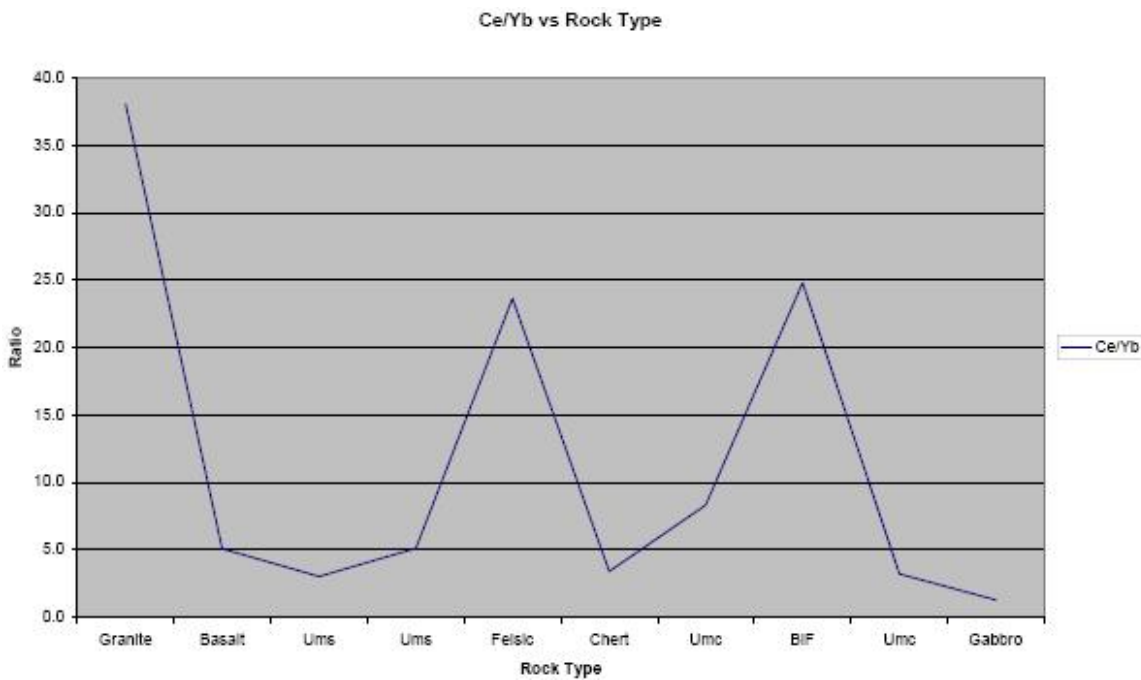


Figure 4. Ce/Yb ratios for soils over various rock types.

Soils over granite, BIF and felsic rocks have Ce/Yb ratios over 20 (and they also have very high Ce). Mafic and ultramafic rocks have ratios less than 5.

**Potential Uses**

Nickel Applications

Diamond Applications

Gold Applications

Geological Mapping Applications