LITHOGEOCHEMISTRY AND MMI-M

INTRODUCTION

The behaviour of many rock-forming elements is dictated by their ionic radius. A plot of ionic radius versus atomic number for a number of cations is shown in Figure 1 below.

In general, ionic radius increases with atomic number (with increasing size of nucleus and electron cloud), and decreases with increasing charge within each period of the periodic table. Thus, the single charged cations Na+, K+, Rb+, Cs+, Tl+ have the largest ionic radii (apart from some anions). Highly charged cations of B, & Al3+ are small (0.2 and 0.51Å respectively). Silicon has a radius of 0.41Å.

IONIC RADIUS, SUBSTITUTION AND GEOCHEMISTRY

Substitution in silicate (and other) mineral lattices is often on the basis of ionic radius. If we re-arrange common cations according to ionic radius, some of the common mutual occurrences in rocks and soils are more easily observed.

For example, Pb(II) and Ag(I), commonly very closely associated in some ores, have very similar (large) ionic radii, 1.26Å and 1.2Å respectively. (It should be noted that ionic radius is not the only factor involved in determining mineralogical associations. Solubility and affinity for sulphur are but two others.) It is also not surprising, on inspection of the above table, to find that thallium (Tl) can be used as a geochemical proxy and indicator for Pb and Ag, as shown in Figure 2.

COMPATIBLE AND INCOMPATIBLE ELEMENTS

Elements common in core magmas such as Fe and Ni have divalent cations with ionic radii in the range 0.6 – 0.8Å. Elements in the periodic table with ionic radii between 0.5 and 1Å are considered "compatible" and substitute or are incorporated into crystallizing silicates in early rock formation. Elements with ionic radii greater than 1 are less commonly substituted, remain behind in residual fluids and are considered "incompatible". These are shown in Table 2.

Also included in the above table are some late-stage crystallizing elements.
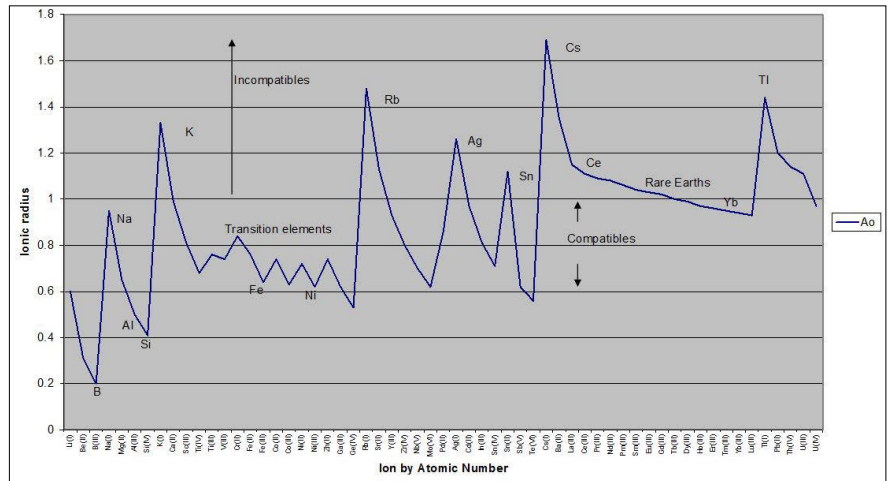

Figure 1: Ionic Radius (after Pauling Expressed in Angstroms or nm x 10) for a Number of Cations Arranged According to Atomic Number
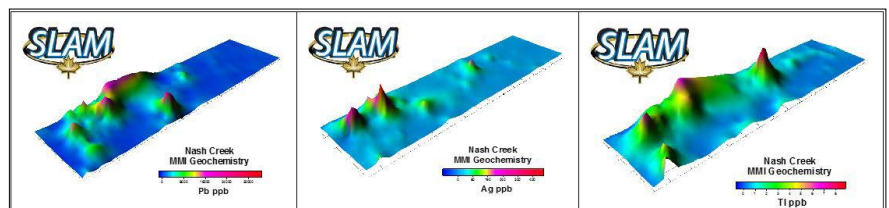

Figure 2: Geochemical Plots for Pb, Ag and Tl for Nash Creek, New Brunswick (Courtesy Slam Exploration Ltd).

Potassium (r=1.33Å) forms the basis of many feldspars; calcium (r=0.99 Å) also forms the basis of many plagioclases which fractionate and crystallize late. Magnesium (r=0.65Å) and calcium, both group II elements, effectively illustrate the importance of ionic radius; magnesium being smaller is substituted and occurs in e.g. olivines in early stage mafic rocks which also contain the compatibles

iron (r=0.76Å), and nickel (r=0.72Å). Chromium Cr(II) (r=0.84Å) and titanium Ti(II) (r=0.90Å) are often found in mafic and ultramafic environments. However,

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they are slightly larger than Mg, Ni and Fe, and accordingly are often found within the sequences in ponded flow facies environments and/or layered sills which are a result of some fractionation. Examples occur at The Mount (see Technical Bulletin TB20) and in other Yilgarn Craton komatiite flow environments.

The rare earths (REE), which with the exception of Eu2+ have triply charged cations, also illustrate the importance of ionic radius. Light rare earths, such as La3+ and Ce3+ with crystal ionic radii >1Å are among the "incompatible" elements which do not readily enter into the early rock building minerals. These early lanthanides along with other "incompatibles" such as Cs, Rb, U, Tl, and Th are "left" in high level fractionating fluids, and hence are associates of feldspars in granites, syenites, monzonites and pegmatites i.e. in felsic rock types. The heavier rare earths such as Yb3+ and Lu3+ have ionic radii <1Å and are more easily accommodated in silicate minerals. Accordingly, they are more evenly distributed between mafic and felsic rock types. In particular light to heavy REE ratios provide for useful discrimination between felsic and mafic rock types (see TB18).

Until recently this behaviour was documented for, and thought to be confined to, rocks. With the development of the MMI-M extractant (which is capable of complexing with and extracting a large number of elements from soil samples) these observations can now be extended to soils above weathering rocks. Soils have the advantage that in general their occurrence is not limited as is rock outcrop. Several notes of caution need to be expressed. Soils can be subject to being "impure" both in a lateral and vertical sense. Where a soil occurs near a lithological boundary it will contain elements of both members. For this reason partial extractions such as MMI™, provide sharper, better information for this purpose, than total digestion which will incorporate mechanically transported litho fragments and at best "blur" the boundaries, or at worst fail to discriminate. Classic type soils for reference purposes therefore need to be taken from large well-developed large units (preferably upslope) to eliminate chances of lateral movement and contamination. Where the

Table 1: Ionic Radii for Common Cations Arranged by Size

Element	Å	Anumber	Element	Å	Anumber	Element	Å	Anumber
Cs(I)	1.69	55	Ca(II)	0.99	20	Zn(II)	0.74	30
Rb(I)	1.48	37	Dy(III)	0.99	66	Ni(II)	0.72	28
Tl(I)	1.44	81	Cd(II)	0.97	48	Sn(IV)	0.71	50
Ba(II)	1.35	56	Ho(III)	0.97	67	Nb(V)	0.7	41
K(I)	1.33	19	U(IV)	0.97	92	Ti(IV)	0.68	22
Ag(I)	1.26	47	Er(III)	0.96	68	Mg(II)	0.65	12
Pb(II)	1.2	82	Na(I)	0.95	11	Fe(III)	0.64	26
La(III)	1.15	57	Tm(III)	0.95	69	Co(III)	0.63	27
Th(IV)	1.14	90	Yb(III)	0.94	70	Ni(III)	0.62	28
Sr(II)	1.13	38	Y(III)	0.93	39	Ga(III)	0.62	31
Sn(II)	1.12	50	Lu(III)	0.93	71	Mo(VI)	0.62	42
Ce(III)	1.11	58	Pd(II)	0.86	46	Sb(V)	0.62	51
U(III)	1.11	92	Cr(II)	0.84	24	Li(I)	0.6	3
Pr(III)	1.09	59	Sc(III)	0.81	21	Te(VI)	0.56	52
Nd(III)	1.08	60	In(III)	0.81	49	Ge(IV)	0.53	32
Pm(III)	1.06	61	Zr(IV)	0.8	40	Al(III)	0.5	13
Sm(III)	1.04	62	Ti(III)	0.76	22	Si(IV)	0.41	14
Eu(III)	1.03	63	Fe(II)	0.76	26	Be(II)	0.31	4
Gd(III)	1.02	64	V(III)	0.74	23	B(III)	0.2	5
Tb(III)	1	65	Co(II)	0.74	27			

Table 2: Properties of Some Elements Relating to Ionic Radius

Compatible Elements	Late Crystallizing Elements	Incompatible Elements
Ni, Fe, Mg (Cr, Ti) Heavy REE's e.g. Yb, Lu	K, Ca,	Cs, Rb, Sr, U, Th, Pb Light REE's e.g. La, Ce

Table 3: Locations used for Soils over Classic Rock Types

Sample Number	Rock Type	Location	Comments
BB01	Granite	Bullabulling	Bali Dome
KA01	Basalt	Kambalda	Red Hill
KA02	Ultramafic sheet flow Ums	Kambalda	Eastern Goldfields
KA03	Ultramafic Sheet Flow Ums	Spargoville	Eastern Goldfields
LL05	Felsic	Widgiemooltha	
WC01	Chert	Widgiemooltha	Widgie Chert
KD238	Ultramafic channel flow Umc	Kooldesak	West Edge, Yilgarn Craton
KD222	Banded Iron BIF	Kooldesak	
LM206	Ultramafic channel flow Umc	Coolgardie	Eastern Goldfields
LM209	Gabbro	Coolgardie	

Table 4: Elements Considered "Less Useable" for Lithogeochemistry

Elements often below LDL	Elements often above instrument limits	Commodity Elements	Regolith dominated elements
Bi, Mo, Sb, Sn, Te, Tl	Al, Ca	Ag, Au, Cu, Pb, Zn	Ca, Mn?

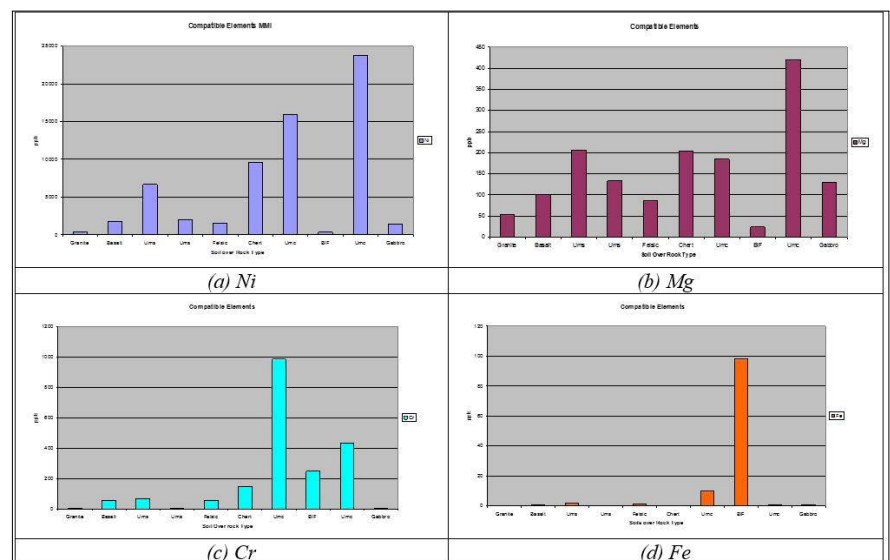

(a) Ni

(b) Mg

(c) Cr

(d) Fe

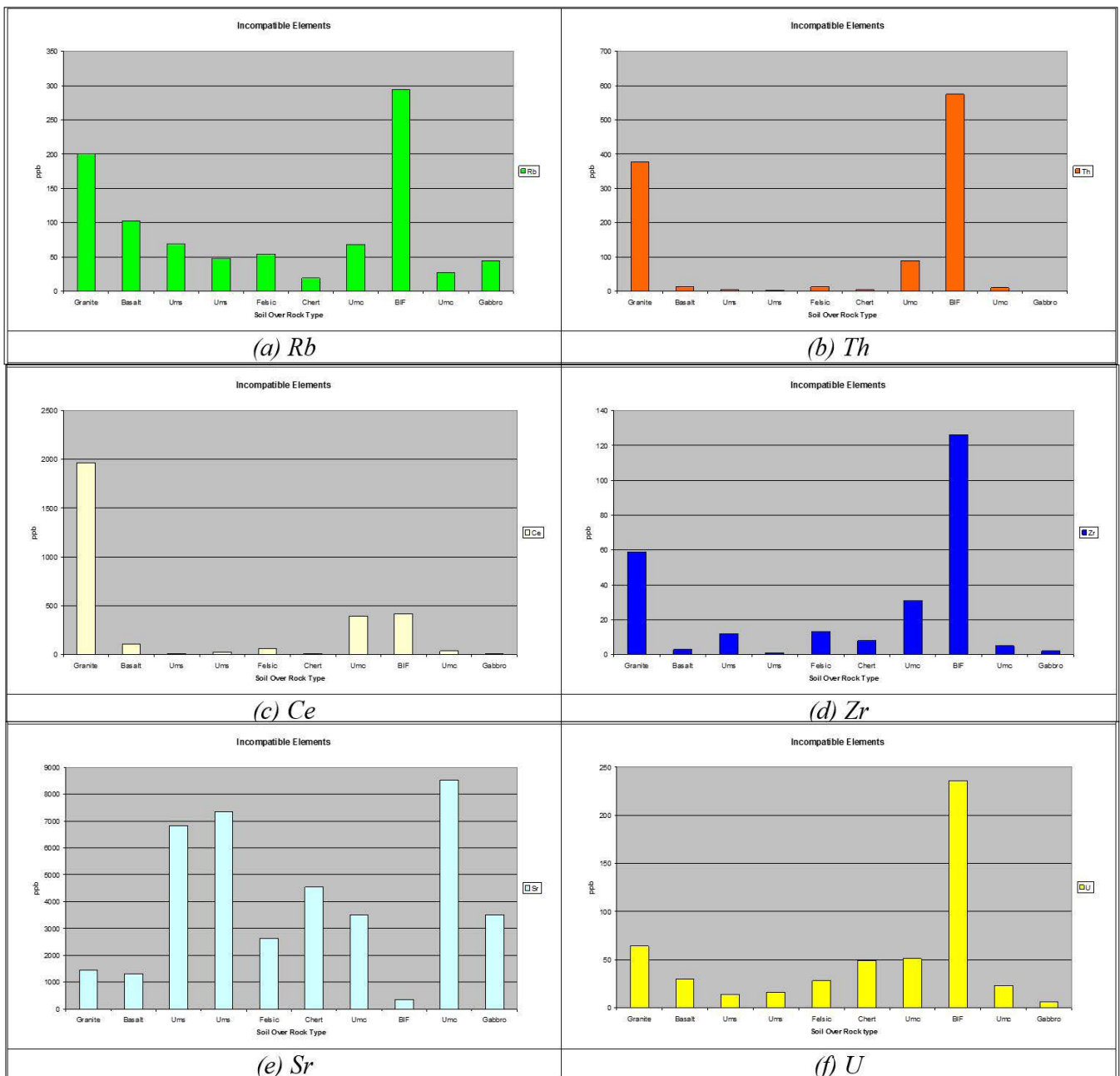**Figure 3: Plots for Compatible Elements in Soils over Various Rock Types**

Figure 3: Plots for Imcompatible Elements in Soils over Various Rock Types

defining lithology is beneath exotic cover, the effects of the exotic cover need to be assessed and factored into interpretation viz. is the signal from the bedrock or overburden or both? Again, for classic rock types and reference samples, exotic cover needs to be absent or have minimal influence. Type samples should not be complicated by sampling in the vicinity of mineralization, faults or shear zones. This is new science and is evolving. It will prove to be only as useful as the intelligence of the interpretation.

CHOOSING DIAGNOSTIC ELEMENTS

Choosing the elements from the forty-plus elements available from an MMI-M extraction which will provide the most useful diagnostic lithogeochemical information involves a number of factors. Firstly, the element must be represented above the ICPMS detection limit for a number of rock types. Secondly it must be below the upper analytical limit of the ICPMS for most rock types. Thirdly it must report at different levels in soils for various rock types. Lastly the reasons for reporting those different levels should

ideally have some basis in hard rock geochemistry to allow for meaningful interpretation. In order to assess which elements best satisfy those criteria, a number of soil samples over classic rock types were taken, or retrieved from archive. All were from the Archaean Yilgarn Craton of Western Australia. Soils were obtained from roadside locations; their details are listed in Table 3.

The elements analyzed after MMI-M extraction of these soils were: Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Er, Fe, Gd, La, Li, Mg, Mo, Nb, Nd, Ni, Pb, Pd, Pr, Rb, Sc, Sm, Sn, Ti, U, W, Yb, Zn, and Zr. A number of elements were found to

be "less useable" for lithogeochemistry due to the range of their analytical values, regolith factors and/or association with specific mineralization events. These are shown in Table 4.

BEHAVIOUR OF COMPATIBLE ELEMENTS

The values of four of the compatible elements Ni, Cr, Mg and Fe in soils over the classic rock types are shown in Figure 3.

Two of these, Ni and Cr display the characteristics expected from their concentrations in rocks as shown in Figure 3(a) and 3(c), that is higher concentrations in ultramafic and mafic soils than in soils over felsics and granites. The other two, Mg and Fe, as shown in Figure 3(b) and 3(d) do not. Mg is found in a range of rock types. Fe is useful in highlighting iron rich sediments e.g. Banded Iron Formation. Whilst iron is associated with regolith events, it is converted to the relatively immobile Fe(III) ion in duricrust soils which does not swamp or mask source. It is apparent that it is the Fe(II) ion which provides useful lithological information from soil extractions.

INCOMPATIBLE ELEMENTS

Concentrations of six of the incompatible elements Rb, Th, Ce, Zr, Sr and U in soils over the classic rock locations are shown in Figure 4.

The first four, Rb, Th, Ce and Zr are diagnostic of felsic and granites; Th, Ce and Zr have low values in soils over mafic and ultramafic rocks whilst Rb has an above-background and usefully variable distribution over a number of soil/rock types. Sr as a diagnostic element is not suitable – it again probably suffers from involvement in secondary duricrust viz calcrete formation. Uranium is often found to be in high concentrations in soils over sediments and particularly granitoids i.e. soils derived from crustal origins.

LIGHT TO HEAVY RARE EARTH RATIOS

For comparing light to heavy rare earth ratios, we will use Ce and Yb. Plots of this ratio for soils over various rock types are shown in Figure 5.
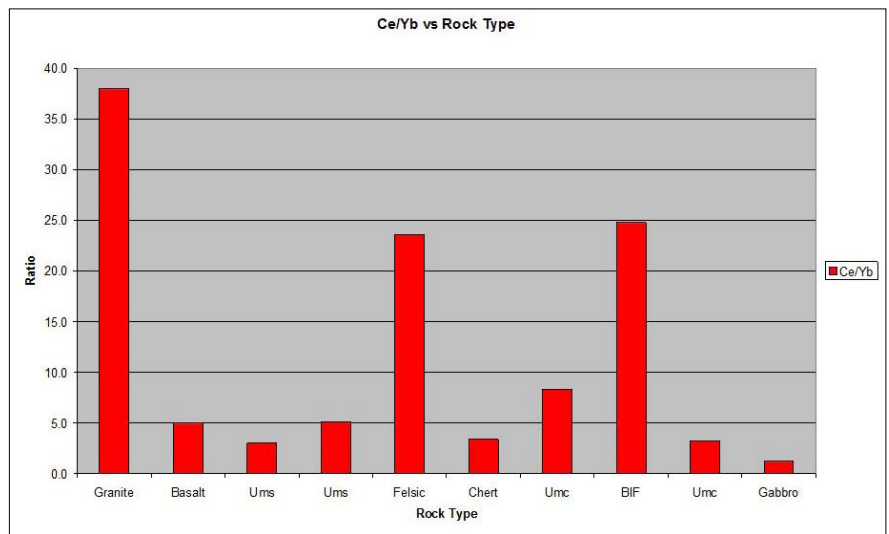

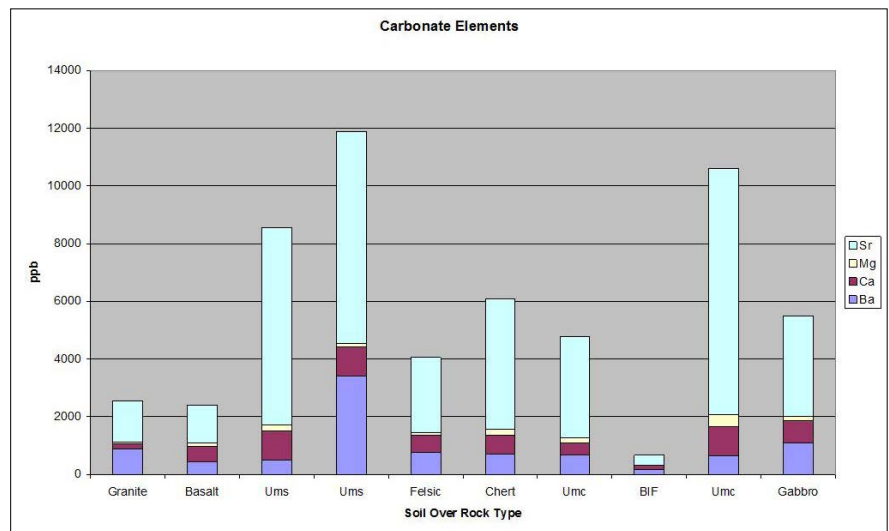**Figure 5: Ce/Yb Ratios for Soils over Various Rock Types**

Figure 6: Alkali Earth Elements in MMI-M Extraction of Soils over Various Rock Types

Table 5: Elements Useful for Classifying Soils over Various Rock Types

Rock Type	"High" values	"Low" values
Granite	Rb, Th, Ce, Zr, Ce/Yb	Fe
Basalt		Ce, Ce/Yb, Ni
Ultramafic (Ums)	Ni	Ce, Ce/Yb
Felsic	Ce, Ce/Yb	
Chert, sediments	As	
Ultramafic (Umc)	Ni, Cr, Mg	Ce, Ce/Yb
BIF	Rb, Th, Ce, Zr, Ti, Fe	Sr
Gabbro		Ce, Ce/Yb, Ni
Limestone	Ca, Ba, Sr	Ni

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.

This is a very useful and diagnostic tool as it is independent of the total amount of contained/available rare earth. This behaviour in soils mimics that of Ce/Yb ratios in hard rock geochemistry.

ALKALI EARTHS (CA, SR, BA)

Despite the alkali earths being subject to regolith processes, they may be useful for identifying limestones and other carbonate-rich sediments.

As shown in the Figure 6, the alkali earths pick out the ultramafic rocks on the basis of high soil pH and the presence of secondary carbonate in the profile. This includes Sr which is "incompatible" and theoretically should be more common in soils above felsics, granites and BIF. However, the carbonate soils of ultramafics (Umc and Ums), can be distinguished from soils over limestone sediments by the fact that they also contain high Ni – a compatible element. Soils above limestone sediments in most situations will have low Ni.

DIAGNOSTIC ELEMENTS FOR CLASSIFYING ROCK TYPES

The following elements (in Table 5) appear to have the best positive (or negative) characteristics necessary for identifying substrate lithology from soil analysis after MMI-M extraction.

COMPATIBILITY PLOT

Yb being a heavy rare earth element has a more constant (and measurable) concentration in soils over most rock types than for example cerium, a light rare earth element. The Ce/Yb ratio has already been noted as a useful discriminator, and it eliminates any variations caused by "availability' of rare earths at the time of crystallization. If this ratio is plotted versus a compatible element such as Ni, a very useful diagrammatic separation of rock types can be made.

Note that there is very good separation of the rock types – ultramafics along the x axis and felsics and granites on the
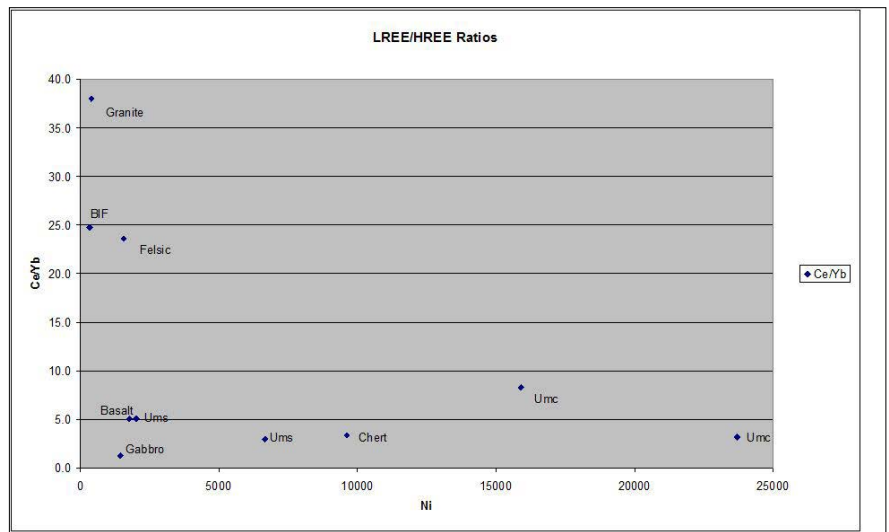

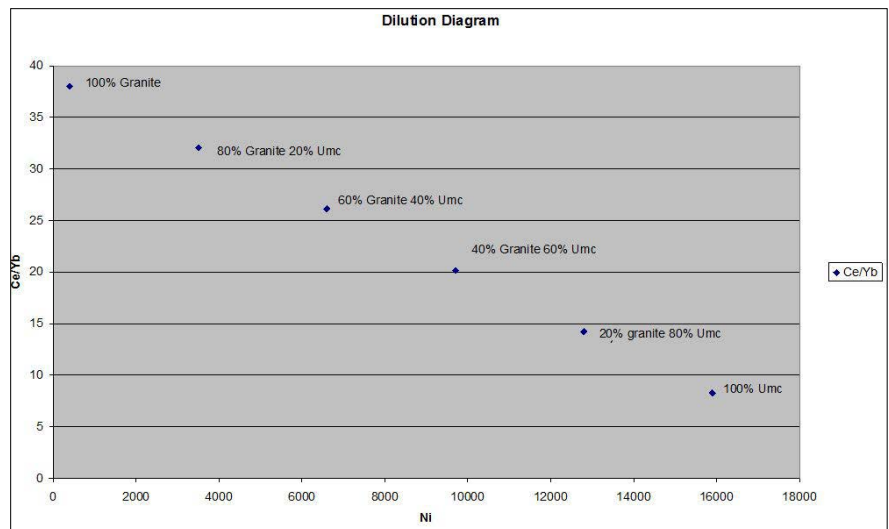**Figure 7: Ce/Yb Ratios for Various Rock Types**

Figure 8: Theoretical Ce/Yb Versus Ni Plot for Various Admixtures of an Ultramafic and Granite

vertical. Mafic rocks have low values of both Ce/Yb and Ni.

DILUTION DIAGRAMS

The soils taken for the type classifications have been deliberately taken from the vicinity of large outcrops, and never down-slope (to avoid contamination). That this has been reasonably successful is illustrated by the fact that the Ce/Yb values and the Ni values on the above plot are close to the vertical and horizontal axes respectively. This fact can now be used to investigate soils where a mixture of two end members exists. It is illustrated by the (theoretical) example of the mixing of the granite (BB01) and Umc (KD238) samples from the above suite. The EXCEL calculated Ni and Ce/Yb values for various

mixtures are shown in Figure 8.

SUMMARY AND CONCLUSIONS

The ionic radii of elements is often the fundamental factor behind discrimination of lithology. Many of the elements which provide useful information can be analyzed by ICPMS, and as shown in this document most are amenable to ICPMS after MMI-M extraction of soils. It is difficult to suggest a single universal element package useful for all geological terrain types, but a minimum package which could be used to discriminate granitoids, felsics, sediments, mafics and ultramafics might include: Ni, Ce, Fe, Mg, Ti, Yb. As shown in TB18 the first two are the most important.

Lithological discrimination of this kind is of most obvious use to the exploration geologist. However, the production of baseline geochemical maps of bio-available elements, as is provided by this kind of geochemistry should not be limited to resource exploration. Geochemical maps, and the inferred geology maps which their combined geochemistry construct, can also be used for environmental and agricultural purposes. A map of bio-available K, Ca, Mg and Fe in the Margaret River Wine District was used to indicate the soils most suitable for the growth of vines (and large marri trees). The capability of the MMI-M extraction to provide information of interest on elements such as As, Cr, Cd and Pb will also mean that valuable baseline data (and maps) at potentially polluted sites can be provided very quickly and simply.

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