MMI™ REFERENCE SAMPLES FROM THE GEMAS EUROPEAN DATABASE FOR LITHOID COMPARISON & ANALYSIS

INTRODUCTION & BACKGROUND

The Geochemical Mapping of European Agricultural Soils (GEMAS) project (Reimann et al (2014)) included some 2108 soils samples of agricultural (Ap) soils which were analysed for 53 elements after MMI™ extraction. The low-density, high quality and widespread distribution of the samples over the whole of Europe potentially provides for a number of soil samples diagnostic of underlying lithology. The Degree of Geochemical Similarity (LithoID) between soil samples has been previously investigated (Mann et al (2016), Caritat de & Mann, (2018)) and discussed in Technical Bulletin TB30.

This Technical Bulletin describes the suitability and selection of GEMAS Ap samples as references for the LithoID technique.

SAMPLING ANALYSIS & QUALITY CONTROL

The GEMAS project was initiated by EuroGeoSurveys (EGS) geochemistry Group in 2008 and carried out in co-operation with financial support from Eurometaux, the European Association of Metals. Each member geological survey agreed in late 2007 to early 2008 to collect samples according to a jointly agreed field procedure. The sampling density was 1 per 2500 km^2. The whole territory was divided into 50 km x 50 km sampling cells, the countries were free to decide where within a cell to take the samples. Two types of sample were collected the 'Gr' sample from land under permanent grass cover (0-10 cm) and an 'Ap' sample from the ploughing layer of agricultural land at a depth of 0-20 cm. The MMI™ extraction and subsequent ICP-MS analysis were undertaken only on the 'Ap' sample.

Sample analysis was undertaken at the Toronto laboratory of SGS. Extracts were prepared using standard MMI™ protocol; 50 g of sample were mixed with 50 ml of MMI-M solution and shaken for 30 minutes. They were allowed to stand overnight before centrifuging for 10 minutes at 8500 rpm, using a Sorvall Evolution RC (ThermoElemental Corporation). Extracts were analysed using a PerkinElmer NexION 300D ICP mass spectrometer fitted with a Universal Cell, by measuring them against calibration standards prepared in MMI-M matrix solution.

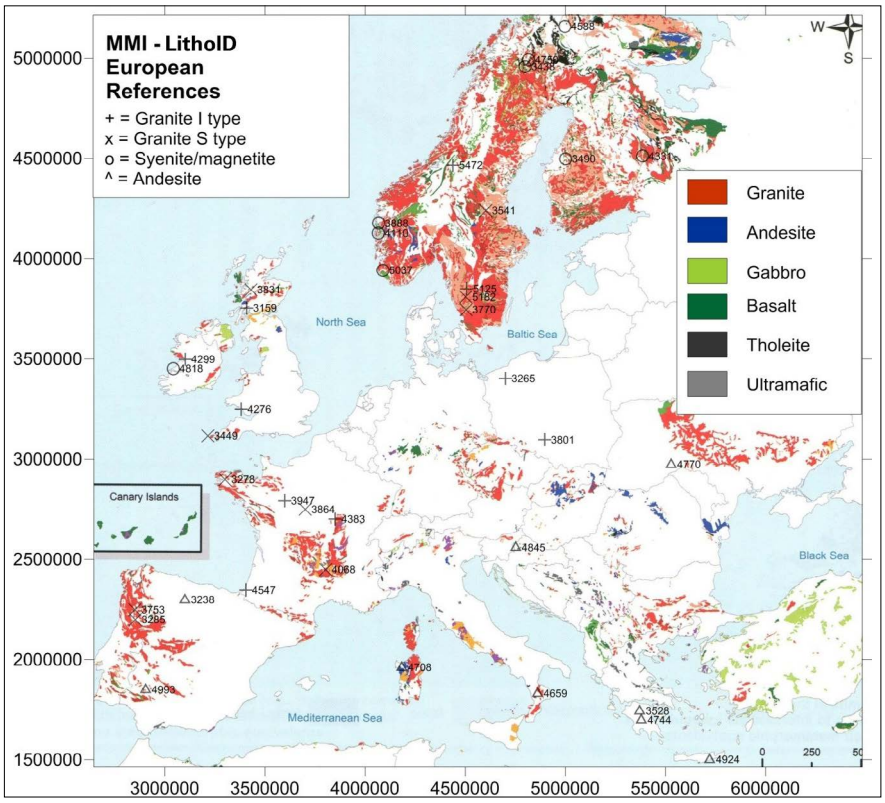

Figure 1: Igneous Geology Map of Jahne (Reimann et al (2014)) with Locations of Reference Soils over Various Acid Felsic and Intermediate Rock Types Superimposed.

The results were examined and elements (Bi, Hg, In, Pd, Pt, Sn, Ta and Te) with >50% of results <Lower Limit of Detection (LLD) were removed; any remaining values <LLD were replaced with 0.5*LLD. This resulted in the following 45 elements being included in this study: Ag, Al, As, Au, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Sm, Sr, Tb, Th, Ti, Tl, U, W, Y, Yb, Zn and Zr.

METHODOLOGY

As mentioned in Technical Bulletin TB30 there are seven key steps in calculating the LithoID Spearman coefficient of similarity between two samples:

1. Arrange elements in alphabetical order in MMI™ file, remove any with >50% of values <LLD.

2. Replace any remaining element values <LLD with 0.5*LLD

3. Calculate rankings

4. Select a reference sample

5. Calculate Spearman r_{sp} values vs reference

6. Plot distribution of sample r_{sp} vs reference sample(s)

7. Prepare XY scatter diagram of rankings any two samples

Initially the rankings of all 2108 samples for the 46 elements were calculated according to the steps above. In selecting samples for reference purposes, the geological maps prepared by Jahne (Reimann et al, 2014) and the Wiki geological map of Europe (**HTTPS://EN.WIKIPEDIA.ORG/WIKI/GEOLOGY_OF_EUROPE**) were used to identify primary reference sites.

In addition to the geological maps, ppm/ppb elemental values of the soil samples, site visits (in some cases) and Google Earth were used to further verify sites as suitable. The LithoID methodology was then applied to identify up to 10 further closely related sites for each primary reference, so that a statistically significant final list in excess of 100 reference sites was established. Similar due diligence was applied to these additional reference samples, and any not conforming or deemed inappropriate were removed from reference considerations.
The efficacy (or otherwise) of this methodology will be made evident later in this document.

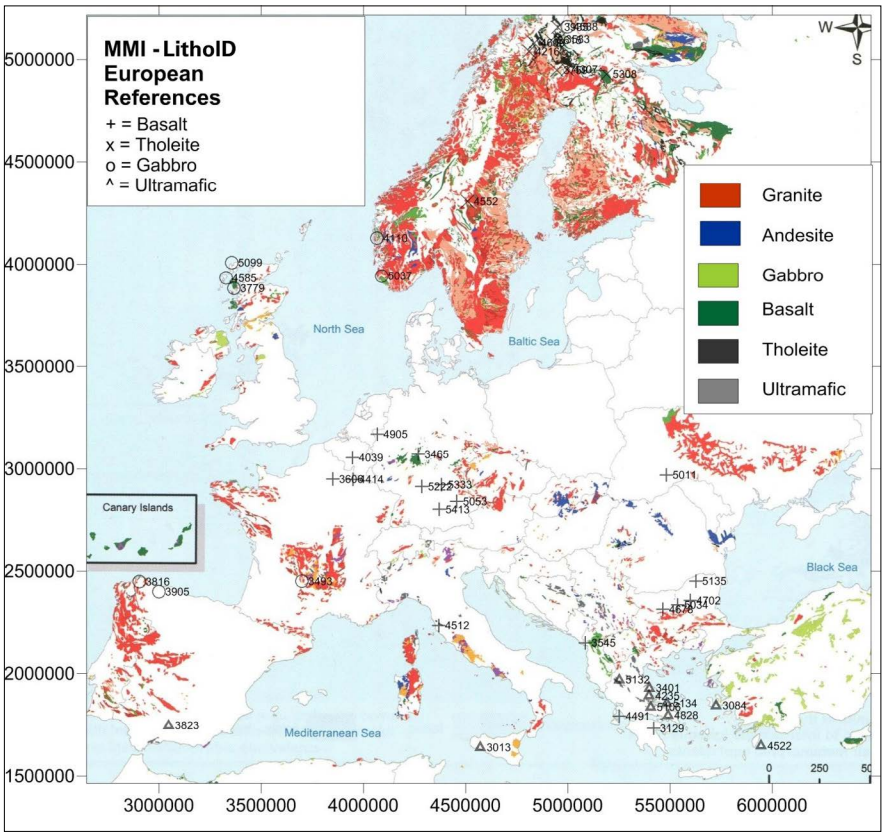

Figure 2: Locations of GEMAS Soils over Various Mafic and Ultramafic Lithology Types (After Jahne (Reimann et al, 2014))

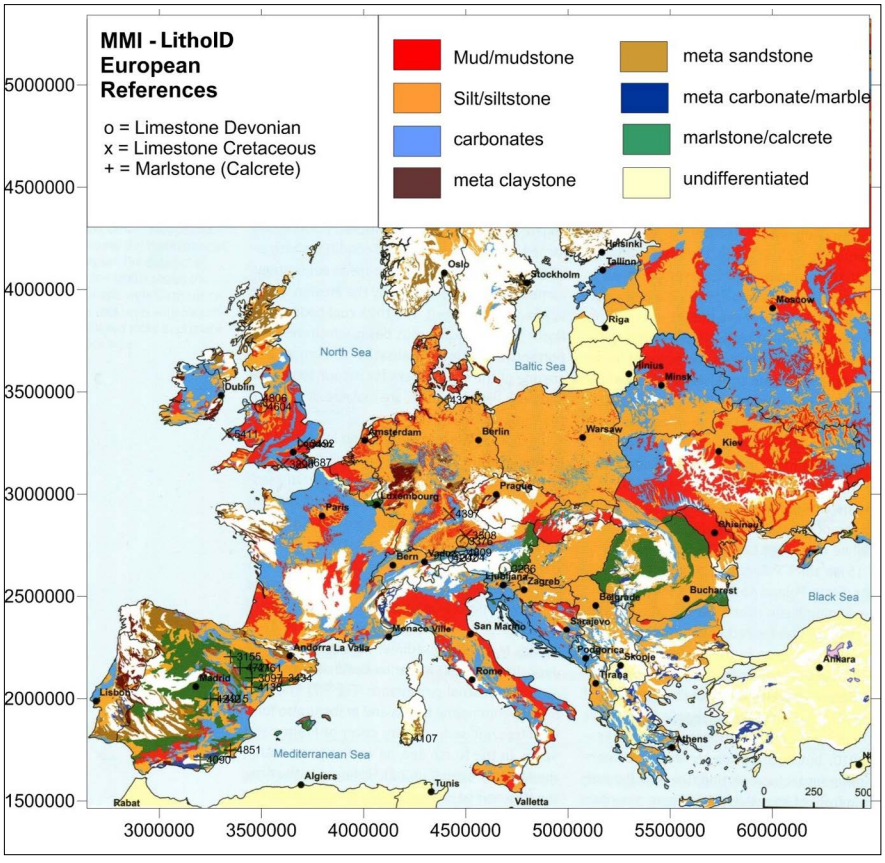

Figure 3: Locations for Carbonate Related GEMAS MMI™ Reference Sites Superimposed onto Map of Surface Sediments of Europe (After Jahne (Reimann et al, 2014))

REFERENCE SITES/TYPES

1. Greenock Granite I type #3159

Soil sample #3159 is from a typical I-type granite location at Greenock in the Palaeozoic-Precambrian belt of Scotland. Greenock is at the south-western end of the Grampians some 40km north of Glasgow. Sample #3159 contains 450ppm Al and 5290ppb Ce. The locations for #3159 and closely related sites 3265, 3801, 3947, 4276, 4299, 4383, 4547, 5125, and 5472 are shown on Figure 1.

2. Penzance Granite S-type granite #3449

GEMAS soil sample #3449 is from the Penzance on the south west tip of England. The sample is over Cornubian S-type granite which contains 18ppb Sn, and high concentrations of Cs, and Nb. The concentrations of rare earths in this sample is lower than for I-type granites, in this case e.g. Ce=118ppb. Related sites 3278, 3285, 3541, 3753, 3770, 3831, 3864, 4068, and 5182 are shown on Figure 1, along with the location for #3449.

3. Hesse Basalt #3465

Soil sample #3465 is from the Hesse state of Germany, and is located some 80 km north-east of Frankfurt. This sample contains just 28ppm Al and 72ppb Ce. Related sites 3606, 4039, 4414, 4905, 5053, 5222, 5333, and 5413 are shown along with this sample on Figure 2. The relationship of the primary reference sample and the secondary sites to the mapped basalt of Jahne is evident.

4. Lapland Tholeite #3935

Tholeites or tholeiitic basalts are Fe rich, Mg poor mafic rocks substantially different to basalts of the calc-alkaline series. As shown on Figure 2 they are prevalent in northern Sweden and Finland. Sample #3935 is from Lapland and contains 149ppm Fe, 10ppm Mg and 546ppb Ce after MMI™ extraction. Related sites 3583, 3615, 3759, 3795,

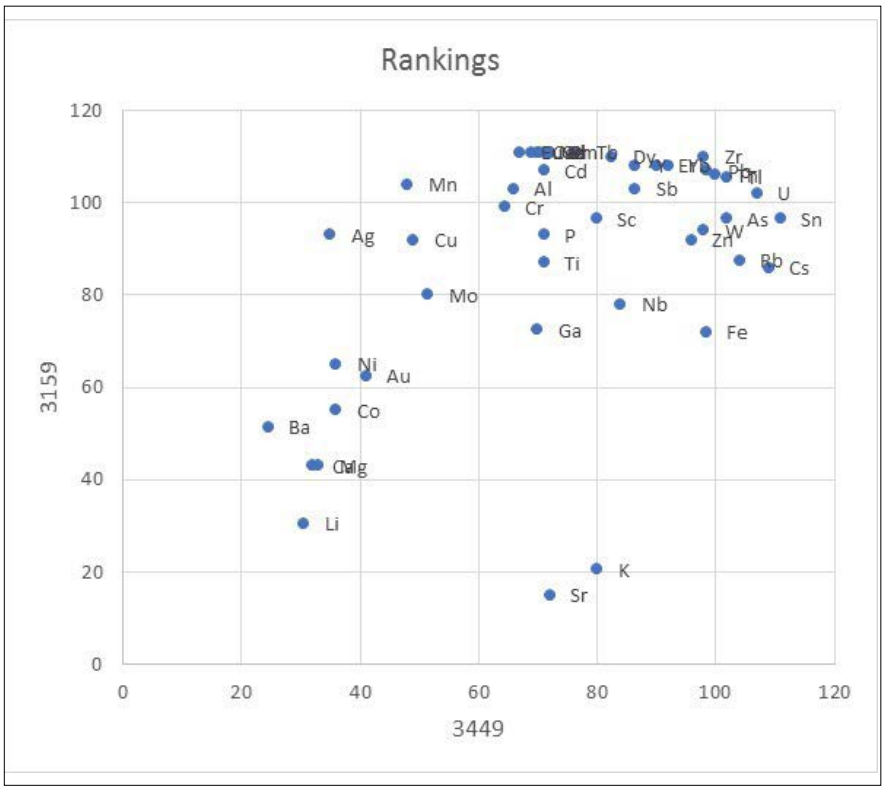

Figure 4: Comparison of Rankings for I Type (#3159) and S-Type (#3449) Granites.

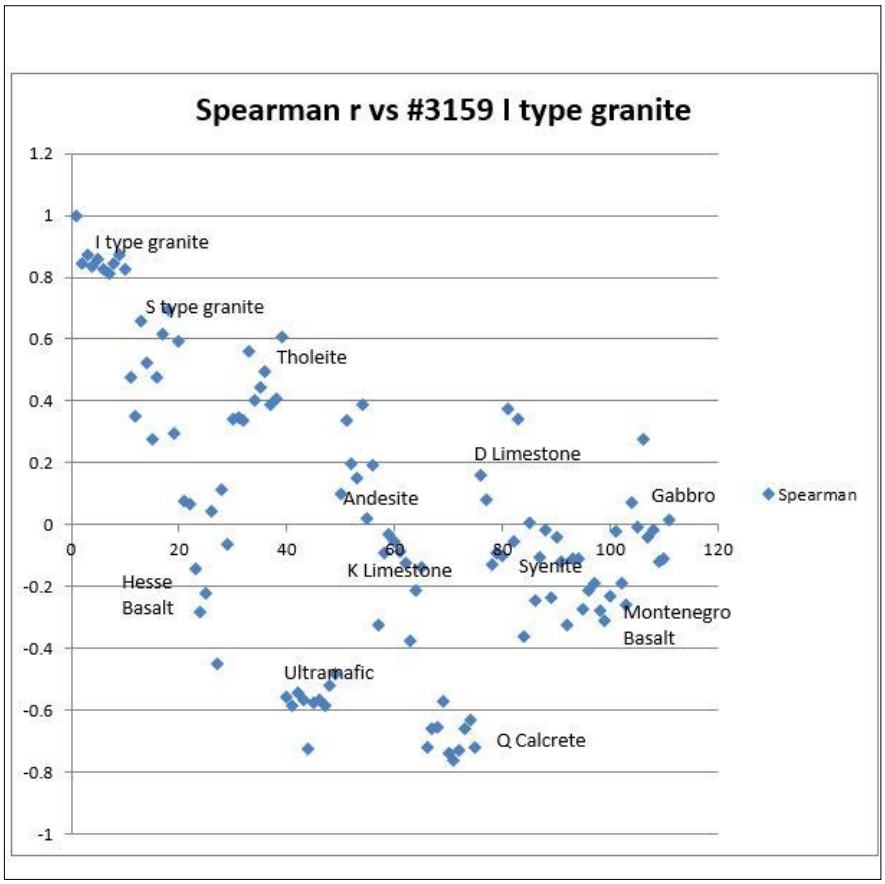

Figure 5: Frequency Diagram for all 111 Reference Samples Against the I-Type Granite Reference #3159

4216, 4307, 4552, 4609, and 5308 are also shown on Figure 2.

5. Rhodes Ultramafic #4522

The island of Rhodes, immediately south of the west coast of Turkey is comprised almost entirely of ultramafic rock. Soil sample #4522 contains 229ppm Mg, 8490ppb Ni and 10ppb Ce. Related sites 3013, 3084, 3401, 3823, 4235, 4828, 5106, 5132, and 5134 are shown along with #4522 on Figure 2.

6. Sardinian Andesite #4708

The north western corner of the island of Sardinia in the Mediterranean is comprised of andesite. Soil sample #4708 which overlies it contains 132ppm Mg, 2220ppb Ni and 272ppb Ce. The locations of sample site #4708 and related sites 3238, 3528, 4659, 4744, 4770, 4845, 4924, and 4993 are shown on Figure 1.

7. Dover Limestone #3687

The Dover limestone sample #3687 overlies cretaceous chalk 20km north-west of Dover in south-east England. The soil sample contains after MMI™ extraction, 1020ppm Ca, 37ppm Mg, 568ppb Ni and 54ppb Ce. The location, along with related sites 3492, 3508, 3898, 4321, 4397, and 5411 is plotted on Figure 3.

8. Madrid Calcrete Q #4242

The Madrid calcrete reference site #4242 lies over quaternary marlstone (i.e. pedogenic carbonate); the sample was taken 95km south-east of Madrid and contains 1880ppm Ca, 46ppm Mg, 596ppb Ni and 12ppb Ce. Related sites 3097, 3155, 3434, 4090, 4138, 4721, 4761, 4851, and 4915 are shown along with #4242 on Figure 3.

9. Innsbruck Limestone D #3404

Sample #3404 is from 19km east of Innsbruck in Austria, an area underlain by Devonian limestone. Along with related sites 3266, 3376, 4107, 4202, 4604, 4806, and 4809 it is plotted on

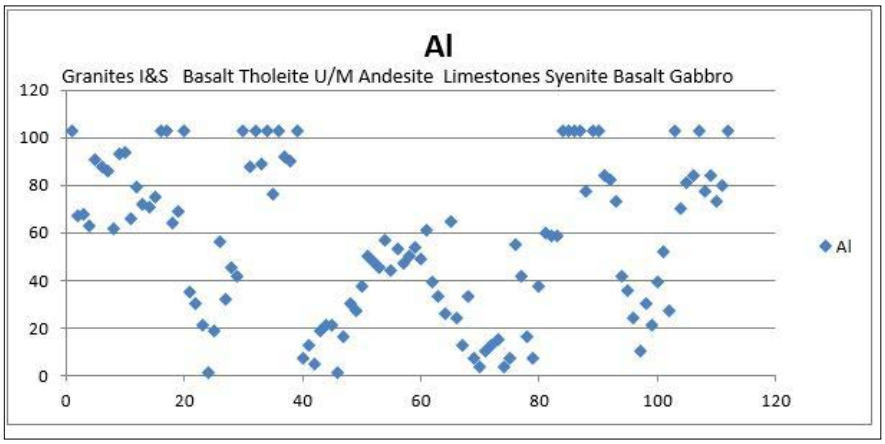

Figure 6: Rankings for Al (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Rankings for aluminium are in well formed "groups" according to reference rock type**
- **Granites, tholeites and syenites have highest rankings for Al**
- **Basalts, ultramafics and limestones have lowest rankings for Al**
- **Ga is a Group III element which behaves similarly to Al and is diagnostic**

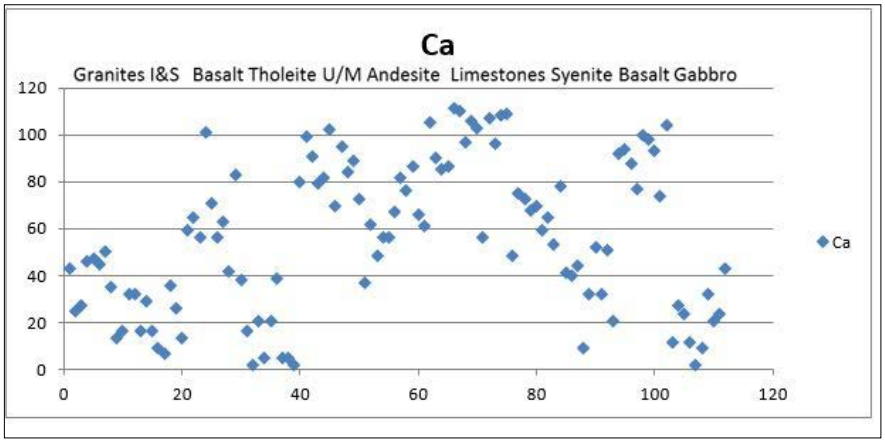

Figure 7: Rankings for Ca (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Rankings for Ca are in less well-formed "groups" than for Al**
- **Limestones have highest rankings for Ca**
- **Tholeites and gabbros have lowest rankings for Ca**

Figure 3. The sample contains 460ppm Ca, 55ppm Mg, 1220ppb Ni and 120ppb Ce.

10. Kiruna Syenite/magnetite #4750

Syenite is an intrusive, igneous, intermediate rock, with which magnetite and ilmenite are often associated. It is an important lithology in the vicinity of Kiruna, Sweden. Sample #4750 is from 64km south-east of Kiruna and after MMI™ extraction was found to contain 2200ppm Fe, 896 ppb Ti and 62ppb Ce. Related sites are 3438, 3490, 3888, 4110, 4197, 4331, 4588, 4818, and 5037; these are plotted on Figure 1 along with the location for #4750.

11. Montenegro Basalt #3545

The map of Jahne (Reimann et al, 2014) shows extensive outcrop of basalt on the west side of the Balkan Peninsula in Montenegro. The sample location, 12km south-east of Bar is 7km from the Adriatic Coast. The sample contains 1090ppm Ca, 14ppm Fe and 44ppb Ce after MMI™ extraction. Related sites 3129, 4491, 4512, 4678, 4702, 5011, 5034, and 5135 along with #3545 are shown on Figure 2.

12. Skye gabbro #4585

Sample #4585 is from the north-west of the Isle of Skye, north-west Scotland; this location is underlain by gabbro. The sample contains 60ppm Ca, 288ppm Fe, 103ppm Mg and 60ppm Ca. Its location along with related sites 3493, 3779, 3816, 3905, 4110, 4588, 5037, and 5099 is shown on Figure 2.

In summary for the 12 Lithology types, 111 soil reference samples have been selected.

RESULTS

There are a number of ways in which the GEMAS reference samples can be compared and contrasted. XY graphs of the rankings between any two samples are instructive. To facilitate this, rankings of just the 111 reference samples were calculated in a separate spreadsheet.

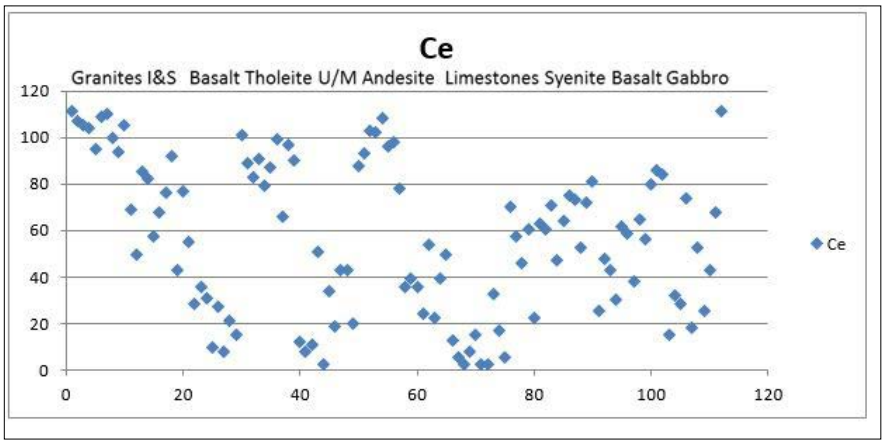

Figure 8: Rankings for Ce (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Ce rankings are in less well formed "groups" than are rankings for Al & Ca**
- **Granites, tholeites and andesites have highest rankings for Ce**
- **Ultrramafics and limestones have lowest Ce rankings**
- **Other rare earth elements behave similarly to Ce**

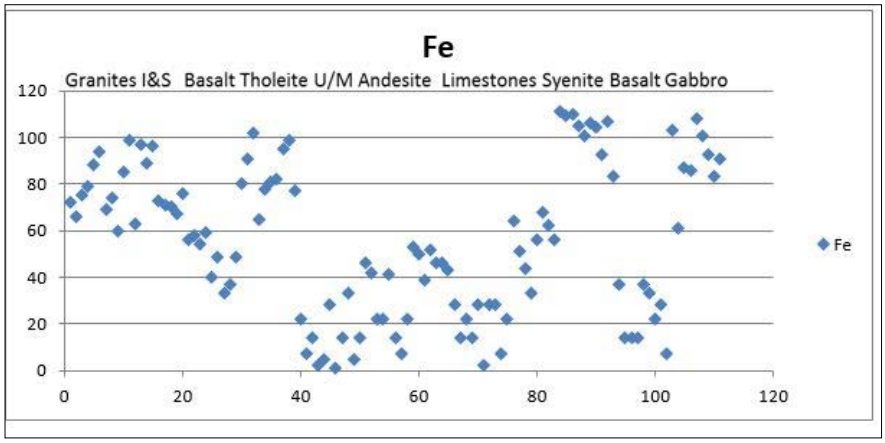

Figure 9: Rankings for Fe (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Highest rankings for Fe are for syenites and gabbros**
- **Ultramafics and limestones have lowest rankings for Fe**

In Figure 4, the rankings of reference samples #3159 and #3449 for I type and S type granites are displayed.

The Spearman LithoID r_{sp} for these two samples is 0.47 i.e. they are related but not that closely. I type granites are thought to be derived from igneous parent material, S-type from sedimentary material. This graph shows that #3449 (S-type) has higher rankings for K, and Sr than does #3159. Interestingly Cs and Sn are ranked highly in both suggesting these elements are not great discriminators between granite types. The I- type granite (#3159) has higher rankings for Ag, Ba, Co, Mn and Ni. The rare earths have similar high rankings for both samples, and are a source of similarity rather than difference.

A second way in which all of the reference samples can be compared is to select one of their number as a "super-reference" and compare all other reference samples to it. In Figure 5 the LithoID r_{sp} values for all references are compared to the I-type granite #3159 "super-reference".

Figure 5 is quite instructive. It shows (a) most reference groups are tightly "clumped" and (b) that diagnostic differences exist between the groups. This is supportive of the methodology used to select additional references from each primary reference sample, and to establish a statistically significant reference set. This diagram could be repeated for any one of the reference samples as a "super-reference".

A third method of comparing reference samples is to examine the rankings for selected individual elements. To facilitate this comparison, the lithology order for the reference groups in the spreadsheet has been appended to the top of the graphs in Figures 6, 7, 8, 9, 10 and 11 which compare the rankings for Al, Ca, Ce, Fe, Ni and Ti for the 12 reference groups.

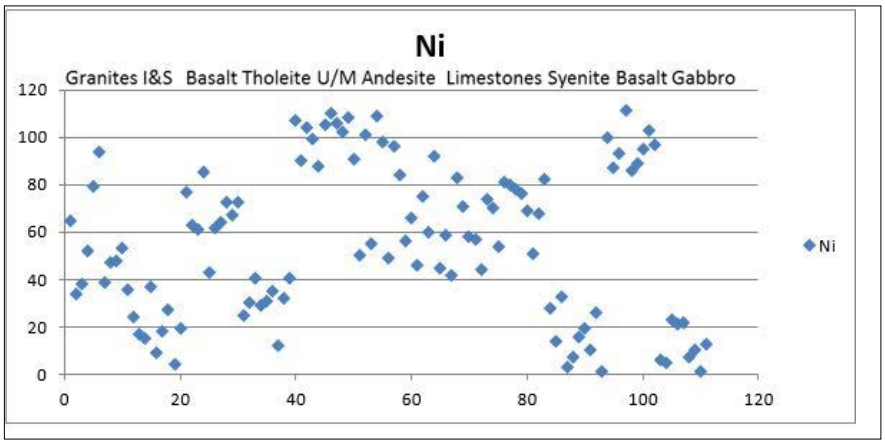

Figure 10: Rankings for Ni (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Ni displays well-formed diagnostic groups, by rock-type**
- **Ultramafics, andesites and basalts have high rankings**
- **S-type granites, syenites and gabbros have low rankings**

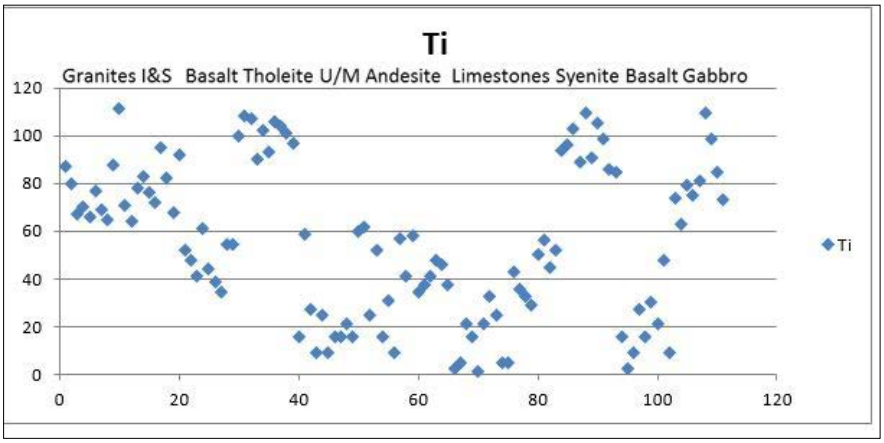

Figure 11: Rankings for Ti (y-axis) for the 111 Reference Samples Across 12 GEMAS Reference Groups.

- **Ti shows a number of tight diagnostic groups depending on rock type**
- **Tholeites and syenites have high rankings for Ti**
- **Ultramafics, limestones and basalt have low rankings for Ti**

DISCUSSION

Investigation of the rankings of selected elements suggests that to varying degrees a large number of elements play a part in LithoID – assessing the similarities (or differences) between soil samples. If not for a statistical treatment such as LithoID it would be an extremely difficult task to assess the individual contributions of 45 elements to the overall geochemistry of these reference soil samples. It is that complexity, and variability which comes with a 45 element comparison which underlines the value of multi-element analysis and the LithoID methodology to elucidate the diagnostic geochemistry of soils.

CONCLUSION

The 45 elements selected for study here viz. Ag, Al, As, Au, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Sm, Sr, Tb, Th, Ti, Tl, U, W, Y, Yb, Zn, Zr are well represented in, and diagnostic of, 12 lithology types. Accordingly they would provide a sound basis for comparison of unknown samples with an MMI™ reference set, whether that is confined to European samples, or a reference set comprising/ including samples from other continents.

REFERENCES

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