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Biogeochemistry of the Hay Mountain Project, Tombstone District, Arizona for Liberty Star Minerals

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Summary & Recommendations

- The Hay Mountain biogeochemical data, when corrected for known sources of variance such as plant species and laboratory, provide a valuable layer of information to guide exploration efforts for buried and blind porphyry Cu-Mo systems in the project area.
- Multi-element, aqua-regia ICP-MS data were provided for 750 vegetation samples form the Hay Mountain project area, of mostly creosote, mesquite, and whitethorn acacia twigs and leaves, and a single specimen of sagebrush.
- Each element was assessed for its data quality and whether known sources of variance caused notable differences in their distribution. These sources of data bias were levelled out using Z-score normalization.
- The three main sources of induced, non-geochemical variance included plant species, laboratory, and batch number. Whereas the three main plant species and two laboratories have adequate spatial and compositional coverage of each sub-group to apply levelling corrections, atypical values in batch number RE11168965 were excluded from output maps for affected elements.
- In addition to levelling between labs and species, the Cu response is further enhanced by correcting for root uptake of Mg, an essential nutrient, resulting in better spatial definition of anomalies and structural trends in the regression residuals of Cu against Mg.
- Some structural trends can be inferred from a combination of the Mo distribution with the orientation of lineaments in Google Earth imagery, which warrant more detailed follow-up in combination with geological and geophysical data.
- Combinations of variables can be used for target identification and search-space reduction through RGB colour-composite grid maps, e.g. Cu-Mo-K. Additional RGB maps of other combinations can be provided upon request.
- A species-classification diagram was constructed based on multivariate discriminant analysis, which highlighted 5 potentially mislabelled entries that required verification, 2 of which were confirmed to be mislabelled.
- It is strongly recommended to use all outputs of this work in combination with all other geospatial data available, including geophysics, surface geology, structural trends, terrain, and field observations, for search-space definition and targeting purposes.

Scope – Work Agreement

Background

Liberty Star has approached Vancouver Geochemistry to provide services in the form of validation and interpretation on their biogeochemical data from the Hay Mountain Project, Tombstone District, Arizona. In particular, the quality of the biogeochemical data is to be assessed regarding its capacity to support the recognition of buried porphyry-copper and related mineralization in the Project area and inform exploration decisions.

Liberty Star's Hay Mountain Project is located in the Tombstone Mining District in southern Arizona. Geochemical and geophysical surveys in the Tombstone district have been interpreted by Liberty Star to indicate a potential center of porphyry copper mineralization in the Hay Mountain project area. Liberty Star believes that porphyry copper mineralization has been emplaced into structures. The exploration concept pursued by Liberty Star in the Hay Mountain project area focuses on the potential for a porphyry copper deposit under the basin-fill deposits. Evidence for this Cu mineralization is the high Cu and molybdenum (Mo) values in mesquite twigs as reported by Newell (1974). Potential in the district is for carbonate-hosted replacement-type porphyry copper mineralization at intermediate to moderate depth, as well as for shallow chalcocite blanket porphyry type mineralization (SRK report, August 2011).

Description of Services

Vancouver Geochemistry was contracted by Liberty Star to provide the following services and deliverables:

- Data Validation: Review of the quality of biogeochemical data provided.
- Exploratory Data Analysis & Interpretation: Data exploration to assess geochemical trends in data space and map space and interpretation of potential indicators for buried copper mineralization. This may include levelling of element data, where appropriate, between sampled vegetation species, sampling seasons or years, or other sources of external influence.
- Report: A written report on the data assessment, including statements on data quality and utility, interpreted maps, and recommendations for the use of the data and data products in furthering exploration efforts on the Hay Mountain Project.
- Transfer of all interpreted data, data products, and any electronic files resulting from the work outlined above.

Work Completed

- Data Compilation & Validation
- Data Levelling: correcting for variance induced by
    a. Tree species
    b. Laboratory
- Biogeochemical Mapping
    a. Thematic maps in KML format (Google Earth)
    b. Grid maps in GeoTIFF format (GIS)
- Interpretation & Targeting
    a. Element associations & correlations
    b. Species classification based on chemical composition
    c. Adjustment for differential element uptake by plant roots
    d. Element combinations in RGB colour-composite maps
- Reporting

Data Compilation & Validation

The provided compilation of the Hay Mountain biogeochemistry (HayMtn_ALSassay_VegAll-Zscores2.xls) was found to contain a few data errors and modifications that hampered a full review of the data quality and distributions. One sample plotted ~10km west of the grid; 4 elements had mixed units within the same column (Ag, Au, Hg in ppm & ppb, and Ti in ppm & pct); and all below-detection data were presented at detection level.

To ensure an unbiased data review, the provided original laboratory data were merged with field data based on their sample numbers (HayMtn_Master_Input.csv). The total data set comprised 771 entries, of which 750 plant samples and 21 QC samples. Metadata preserved in the table include Sample Number, Sample Type, Sampler, Easting, Northing, UTM Zone, Species, ID_Lab, Lab, Batch, and LabDate. All data were imported into ioGAS for validation and exploratory data analysis.

Of the 50 reported elements, 37 are available for all samples as they are reported by both ALS and Acme laboratories, while 13 are exclusively reported by ALS (Be, Ce, Cs, Hf, Li, Nb, Pd, Pt, Rb, Re, Sn, Y & Zr).

Data Precision

Due to the nature of the sample material, metal contents are generally low to very low, and many are near their analytical detection limits. Despite this, 20 out of 50 of the reported elements have acceptable to very good precision (Ba, Ca, Ce, Co, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Rb, S, Sr, Y & Zn). Poor to mixed precision data are reported for 15 elements (Ag, Au, B, Cd, Cr, Cs, Fe, Hg, La, Li, Re, Sb, Se, Ti & Zr), while another 15 are generally at or below detection levels (Al, As, Be, Bi, Ga, Hf, Nb, Sc, Sn, Te, Th, Tl, U, V & W).

Levelling Data

The aim of the biogeochemical survey is to provide element maps that display the geological variance across the survey area to guide exploration for buried and blind porphyry copper / gold / molybdenum deposits as expressed in the chemistry of plant tissues. Three other sources of variance are present within the dataset, which need to be accounted for before proceeding with detailed interpretation, which are 1) the two laboratories: Acme and ALS (Fig. 1); 2) the three (+1) sampled plant species: creosote, mesquite, and whitethorn acacia, plus a single sagebrush (Fig. 2); and lab batch.

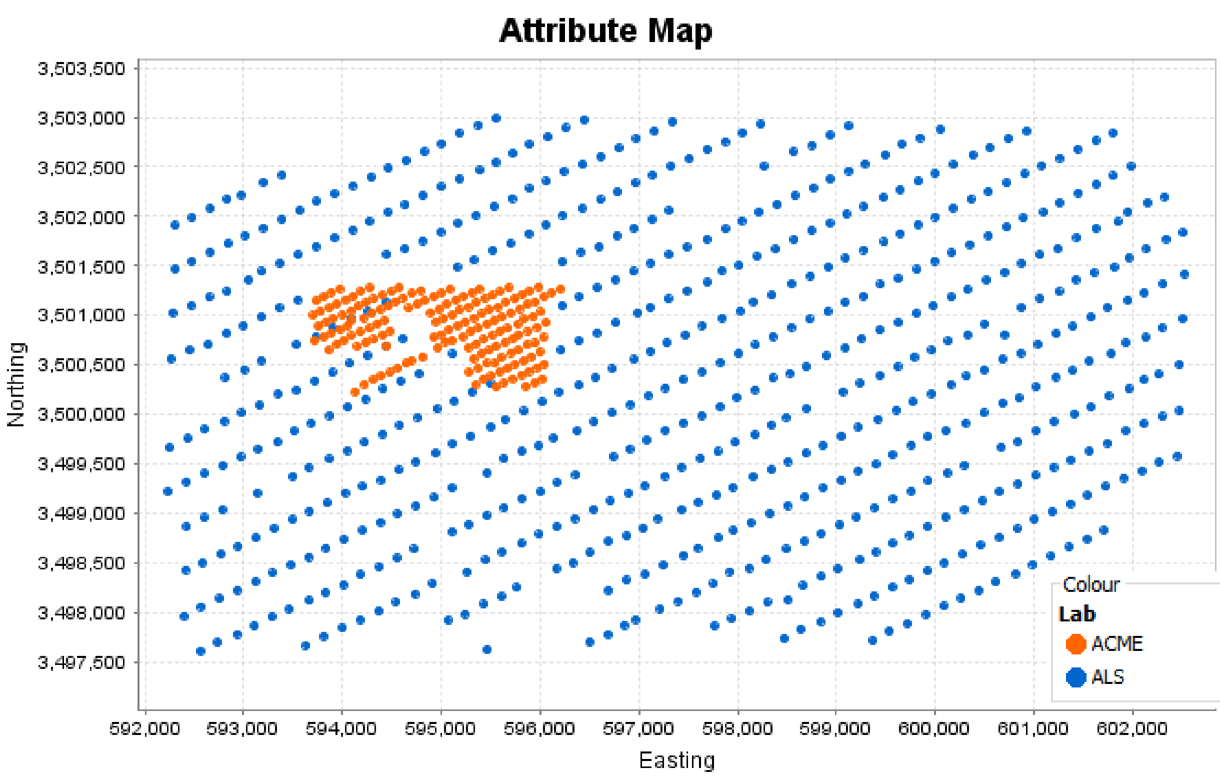

Figure 1 - Attribute map of the Hay Mountain biogeochemical survey area, coloured by Laboratory (orange = Acme, blue = ALS)

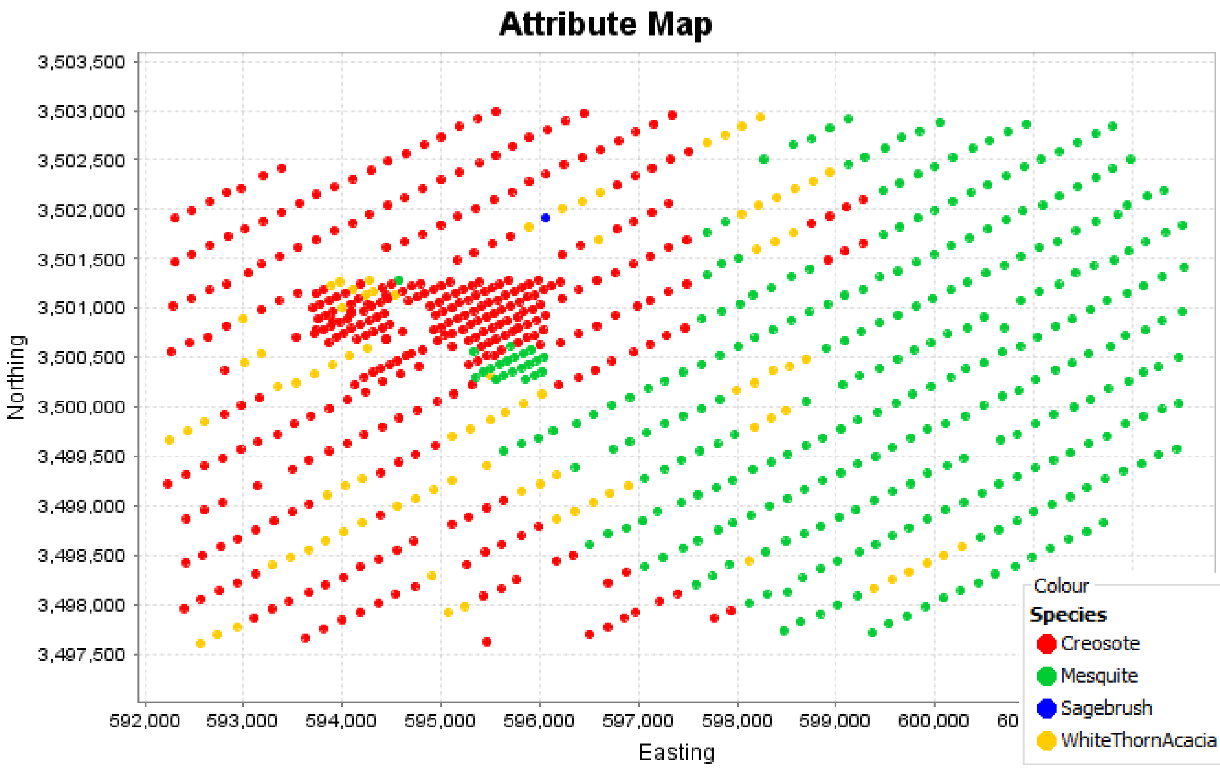

Figure 2 - Attribute map of the Hay Mountain biogeochemical survey area, coloured by sampled plant species (red = creosote, green = mesquite, yellow = whitethorn acacia, and blue = sagebrush)

Several techniques are available for levelling of disparate populations to make them more comparable. Simple translations, which use either the mean or the median ratio within each group, can be used when populations have similar dynamic ranges and distributions (kurtosis) around the central value. However, when standard deviations differ strongly between groups, a Z-score transformation may be more appropriate. Although the results may be more abstract as they involve negative and positive numbers (number of standard deviations away from the mean), the data distributions are more comparable, while outliers within each group are still respected.

Nineteen elements showed strong differences in element contents between the sampled plant species and required levelling (Ag, Ba, Ca, Cd, Co, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Re, S, Sr, & Zn). The skewed distributions were normalized by a log-10 transformation before calculating the Z-score for each group (Fig. 3). As sagebrush was only represented by a single sample, it was omitted from the levelled results.

After correcting for species variance, 8 elements showed major differences between the laboratories (Ag, Ca, Cu, K, Mg, Mn, Na & P). These elements were levelled by lab using a linear Z-score transformation (Fig. 4). Three elements did not require levelling between species, but did between labs (La, Sb & Se), which were levelled by Z-score calculations of the log-transformed data. No levelling was required for Au, Ce, Cr, Cs, Fe, Hg, Pd, Pt, W & Y.

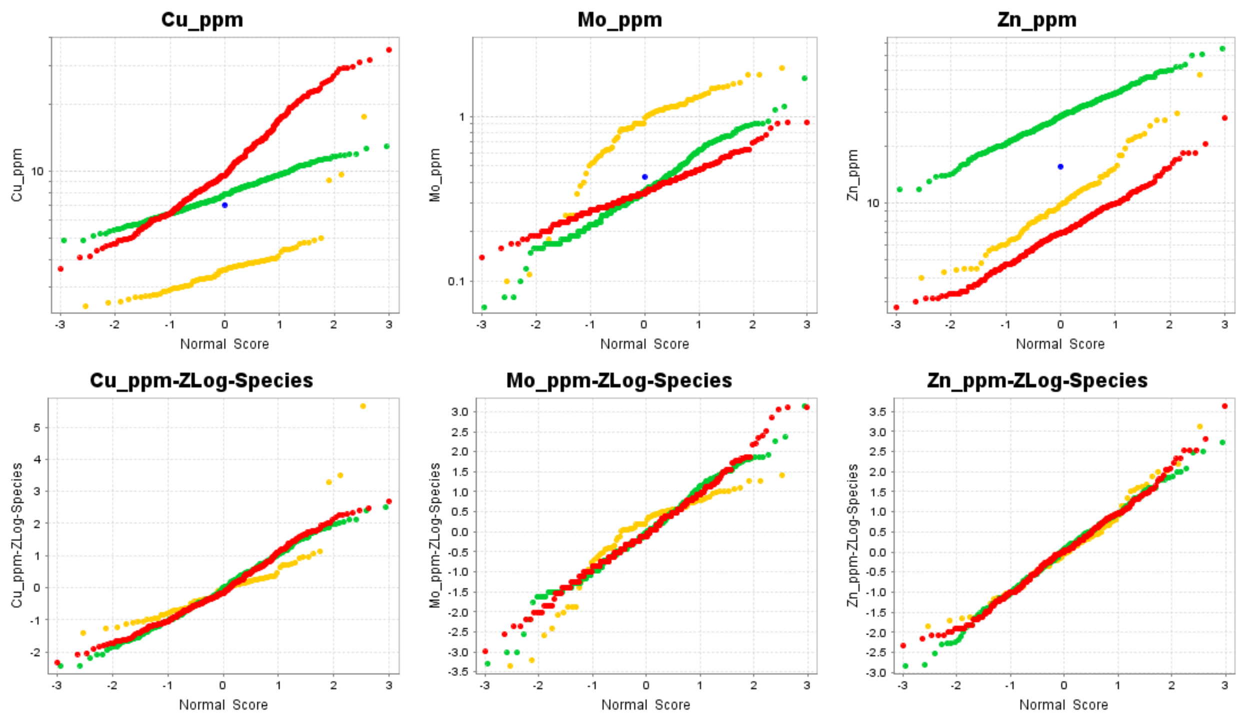

Figure 3 - Split normal probability plots for Cu, Mo & Zn, coloured by species. Above: raw data, logarithmic axes. Below: levelled data by species, using the Z-score of the log-transformed data. Note that while the main body of the data overlaps, outliers are preserved after levelling.

Some elements (Ce, Cr, Fe, Hg, La & Y) displayed a strong linear anomaly in the southeast of the map, related to Acme batch number RE11168965, which was excluded from these elements' maps. The small number of samples in this batch (n=10) precludes meaningful levelling for removal of this bias.

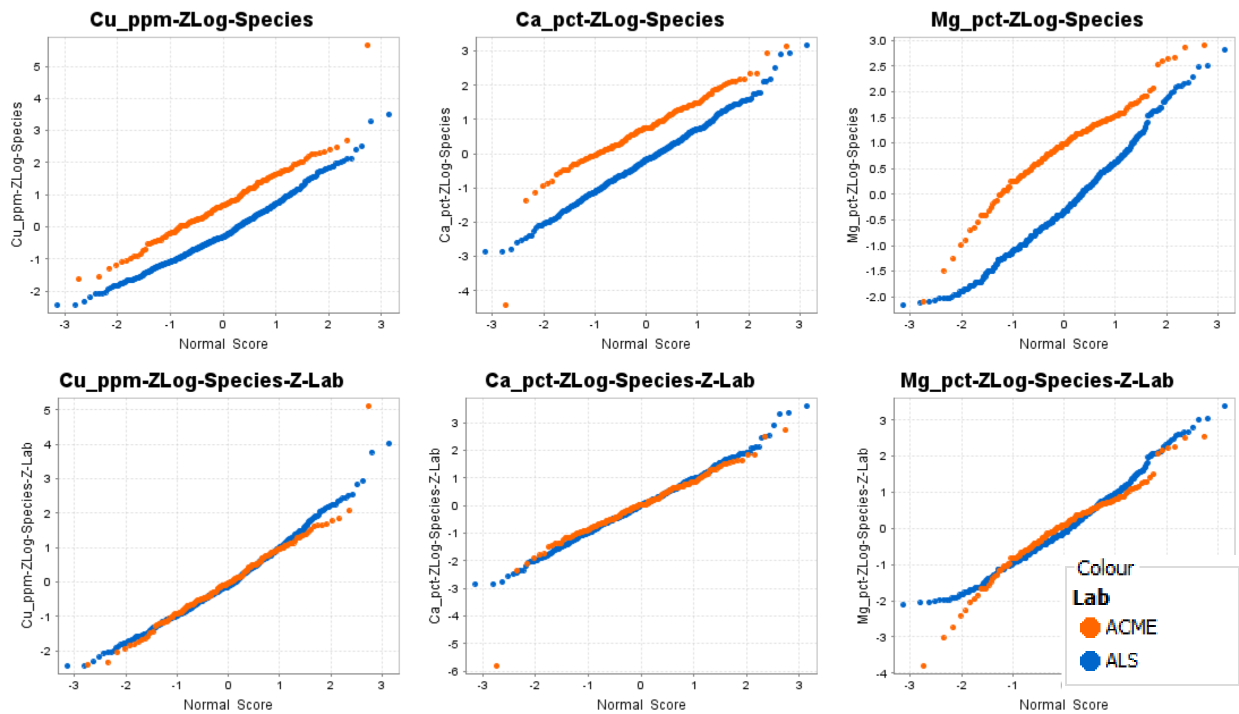

Figure 4 - Split normal probability plots for Cu, Ca & Mg, coloured by laboratory. Above: levelled data by species. Below: levelled data by species and laboratory.

Biogeochemical Maps

All validated and (where appropriate) levelled results were plotted on maps for spatial interpretation and targeting. Two types of maps were created for export: thematic variable maps, which scale each variable by size and colour at each sample point; and interpolated grid maps that provide a continuous representation of each element for the entire survey area, which serves to interpret spatial continuity of observed trends. All map outputs are provided in ZIP files as separate digital appendices to this report.

Thematic Variable Maps

The thematic variable maps of all outputs were exported as KML files that can be plotted in Google Earth for interpretation in relation to surface features in aerial imagery (Fig. 5).

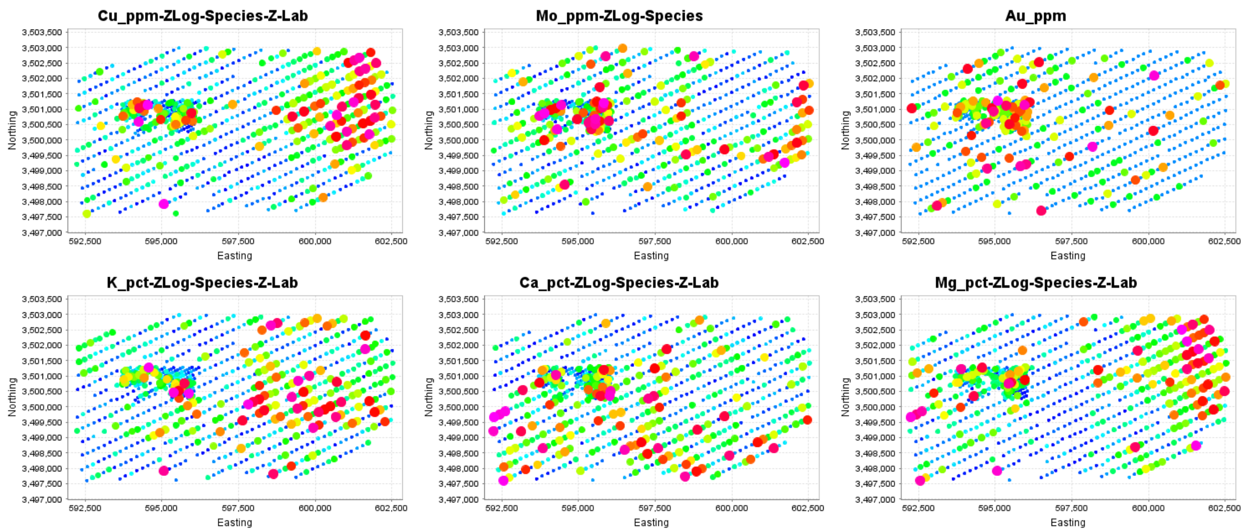

Figure 5 - Thematic variable maps of (levelled) Cu, Mo, Au, K, Ca & Mg, coloured and sized by relative element content.

Grid Maps

Grid maps were produced using an inverse distance-weighted interpolation, with a 50m cell size (1/4 of the average sample spacing), a 6-cell search radius, 3-cell smoothing, progressive colour ramp, and north-illuminated shading (Fig. 6). All grid maps were exported in geotiff format for use in any GIS software package.

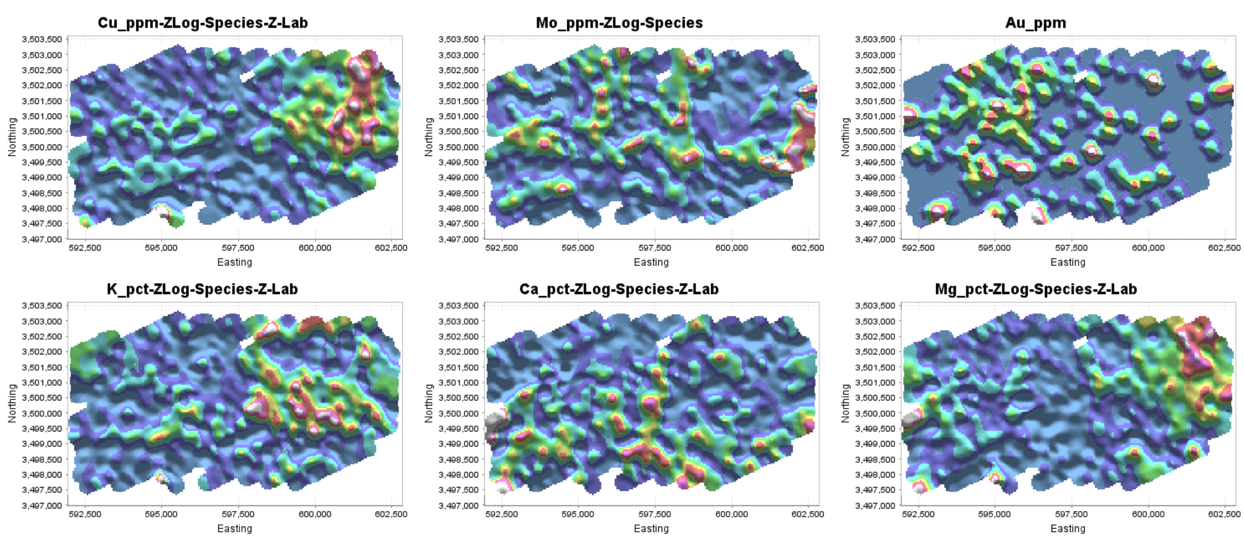

Figure 6 – Interpolated grid maps of (levelled) Cu, Mo, Au, K, Ca & Mg; 50m cell size.

Species Identification & Classification

Discriminant analysis is a supervised, multivariate technique that aims to define group membership based on its composition. With the input of 15 elements (Ba, Ca, Co, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr & Zn), discriminant-projection analysis provided distinct groupings of the 3 main plant species based on their geochemical composition. The output variables, DP1 and DP2, were used to construct a species-classification diagram (Fig. 12). While most samples plot within their respective clusters (fields on the diagram), 5 outliers were identified that require verification of plant species, as they may indicate mislabelled entries, if not chemical outliers. Two of the five outliers could be confirmed to be different species, the remaining three (115024, 115121, and 309029) were excluded from interpolated and thematic maps.

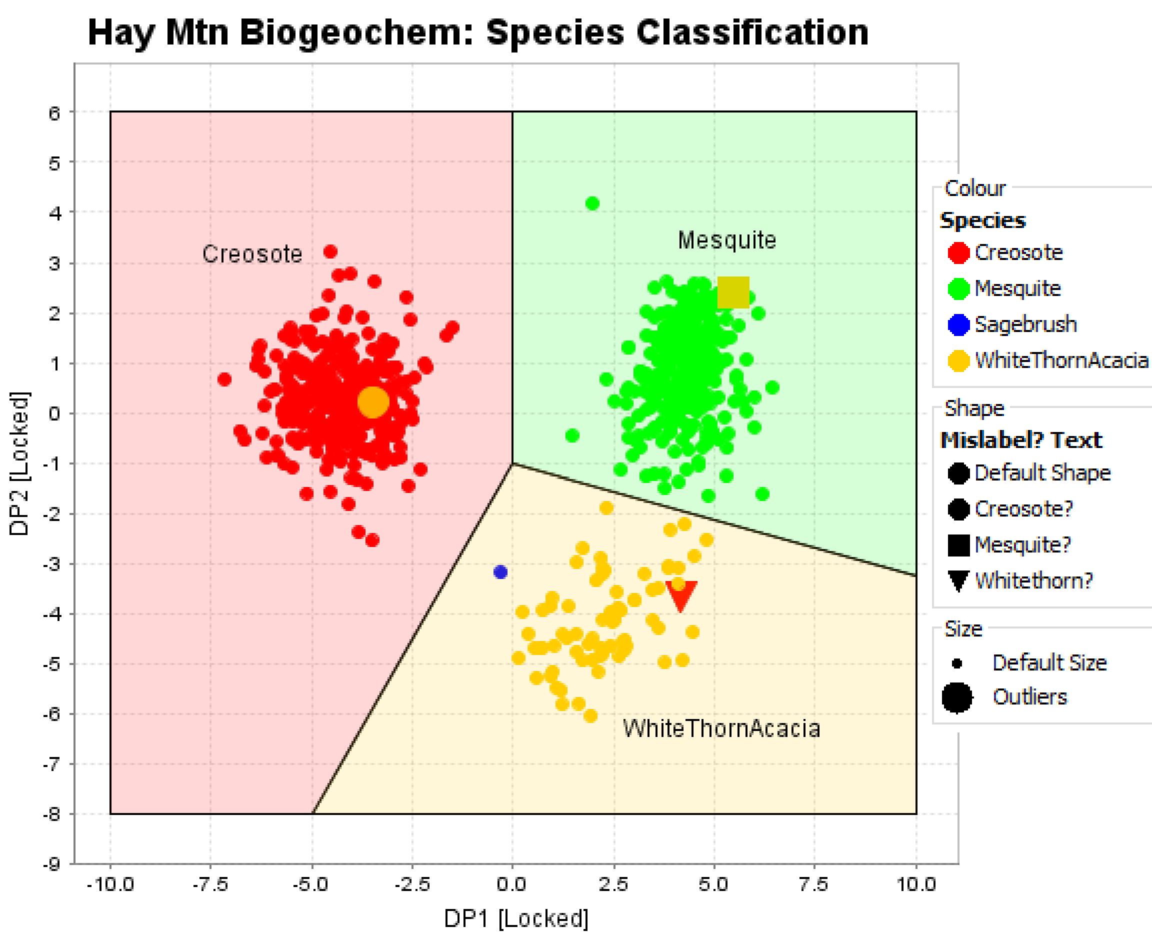

Figure 7 - Species-discrimination diagram for the Hay Mountain biogeochemical data, based on disriminant-projection analysis of 15 elements (Ba, Ca, Co, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr & Zn), coloured by species, with large symbols for outliers, with symbol shapes for suggested correction (possibly swapped samples or mislabelled entries).

The attributes of Fig. 7 were plotted on a grid map of levelled Cu data, for spatial reference and to assess whether any spurious data could be explained from a potential mislabelling (Fig. 8). Sample 309029 stands out as a single-point anomaly at the southern edge of the map but was confirmed to be a whitethorn specimen. While mislabelling has been ruled out, the erratic composition might be the result of a sample swap at the lab and it is recommended to treat this single-point anomaly with due cause.

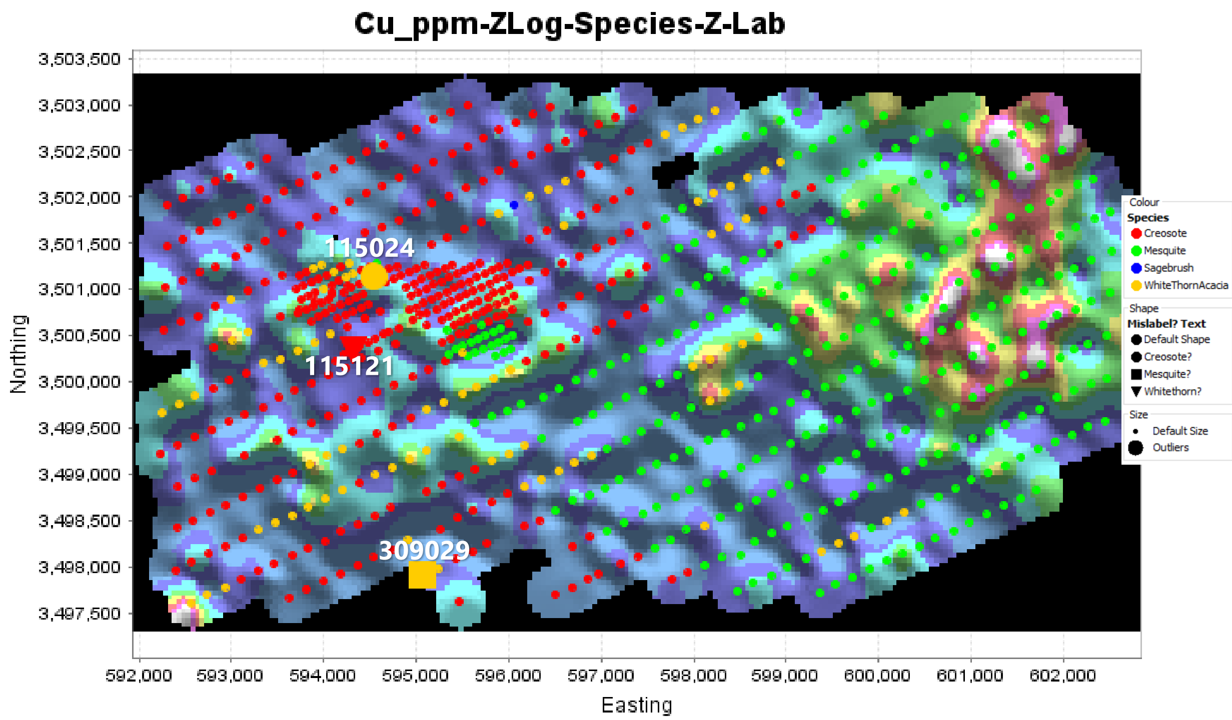

Figure 8 - Attribute map coloured by labelled plant species projected onto a grid map of the levelled Cu data. Suspect mislabels represented as large symbols and identified by sample number.

Interpretation & Targeting

Beyond the obvious sources of variance, plant species and laboratory, some others should be considered before we assume that any high metal content or anomalous value can be directly ascribed to buried mineralization. Other potential sources of variance include the soil conditions (e.g. Eh, pH, groundwater levels), soil provenance, physiography, structural geology, plant physiology, surface contamination, etcetera. Some observations will be highlighted below, but it is recommended to critically evaluate all output maps in their environmental context before prioritizing or using the data for target definition.

Physiography

Plotting the levelled Cu data in Google Earth shows a few clustered anomalies in the densely sampled western part of the grid ("Target Area 1 & 15"), and a broad zone of elevated Cu contents over the eastern part ("Target Area 51"), which coincides with an area of reddish, Fe-oxide rich soil that may represent colluvium derived from the hills to the north (Fig. 9). Lighter colours in the image could represent phyllic or argillic alteration of the rocks to the north, which requires field verification. The extent and location of the broad anomalous area suggests either significant lateral dispersal or a change in soil conditions or provenance.

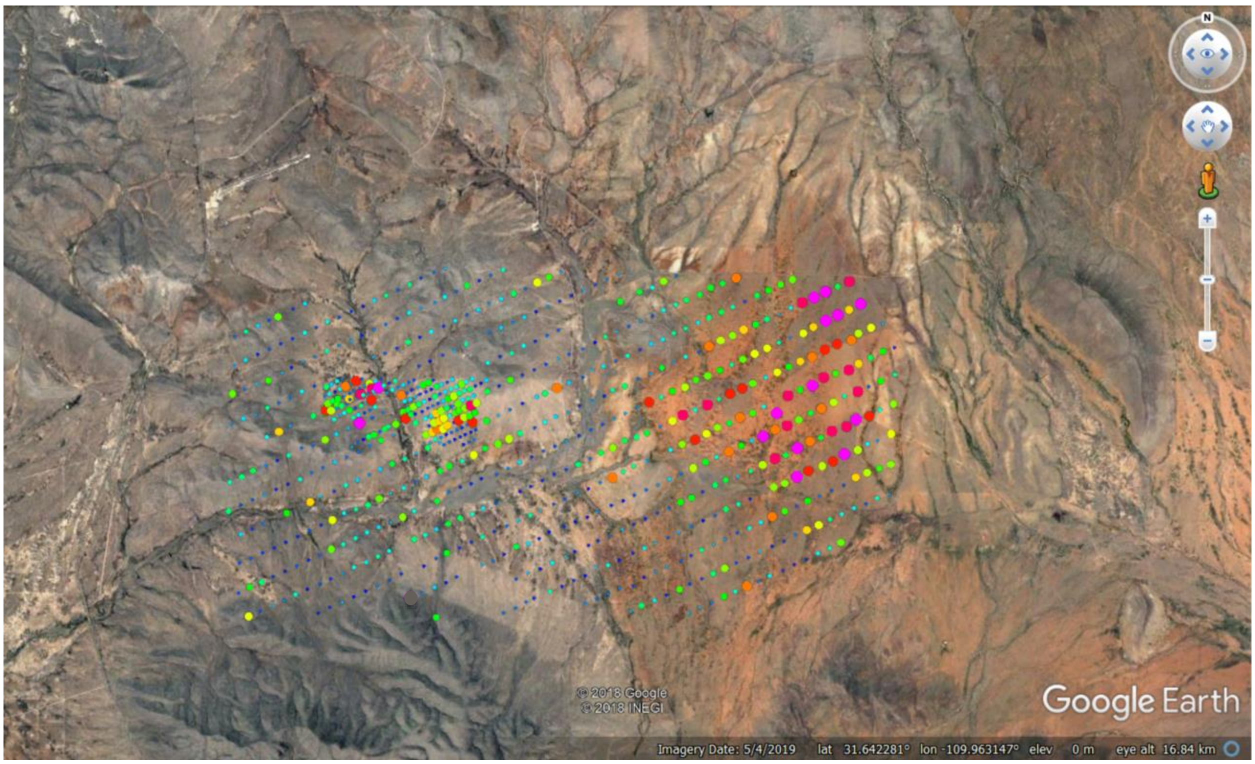

Figure 9 - Levelled Cu data plotted on satellite background imagery in Google Earth, showing elevated Cu contents in small clusters in the western part, and over a broad zone in the eastern part of the project area.

Molybdenum

The spatial distribution of molybdenum is distinct from any other metals, as observed in thematic and grid maps (Fig. 5 & 6). Whereas a simple, divalent Mo^{2+} ion would not be very mobile in oxidizing, neutral to alkaline conditions (much like Cu and Zn), it tends to form an oxy-anionic complex, MoO_4^{2-}, which is quite mobile under most natural groundwater conditions (Fig. 10; Smedley & Kinniburgh, 2017). Cations such as Cu^{2+} and Zn^{2+} adsorb onto negatively charged mineral surfaces or organic molecules at higher pH, while oxyanions remain in solution.

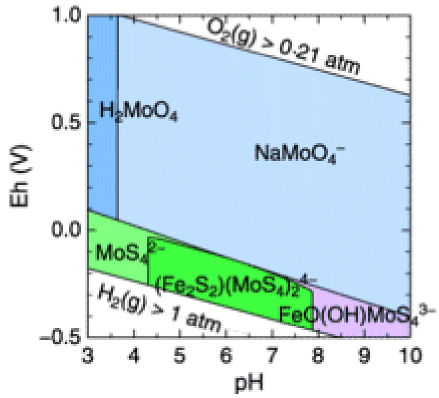

Figure 10 - Pourbaix diagram for Mo in equilibrium with Fe, Na, and S, displaying a wide range of Mo mobility in its oxy-anionic form (from Smedley & Kinniburgh, 2017).

Plotted against Google Earth satellite imagery, it appears that the levelled Mo data reflect underlying E-W and N-S structural geologic trends, expressed at the surface as creek beds (Fig. 11). The relative mobility of Mo in groundwater with respect to other metals would support this interpretation, while at the same time corroborating the presence of elevated Mo in the subsurface, potentially in porphyry-related mineralization.

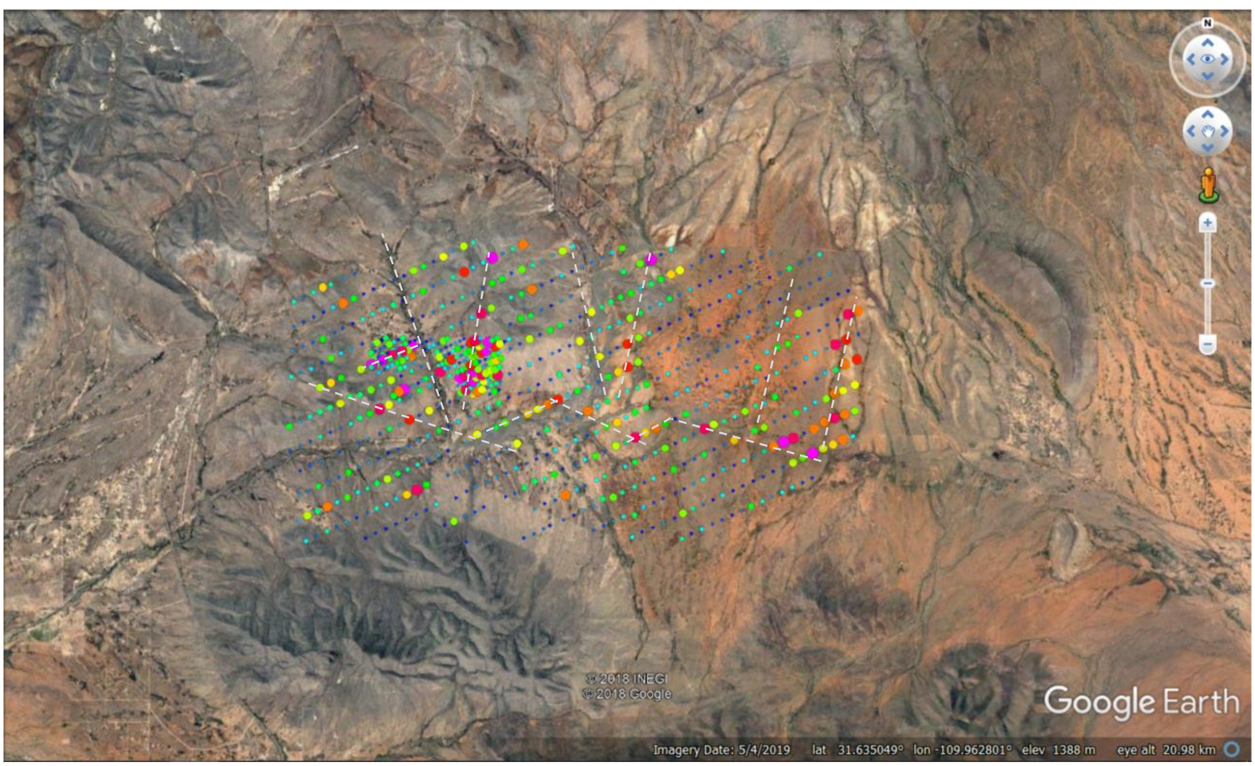

Figure 11 - Levelled Mo data plotted on satellite background imagery in Google Earth, showing alignment with creek beds that may reflect underlying bed-rock structures (dashed lines).

Plant Physiology

The root uptake of elements from the soil and groundwater is somewhat controlled by the plant itself but is not entirely selective to particular elements beyond their ionic charge. When a plant requires essential nutrients such as Mg and Ca for cell turgor and chlorophyll production, it will actively take up divalent ions through its roots and distribute these among its tissues depending on their function (Österås, 2004). While it needs Mg for chlorophyll production, other metals may be harmful to its interior biology and are expelled into disposable bark and leaf tissue, where they may function as a pest deterrent for their toxicity.

Scatter plots of divalent metals against Mg shows some correlation with Cu, Zn, and Mn (Fig. 12). These correlations may reflect geological control such as a mafic soil protolith or may indeed relate to differential root uptake. Either of these processes can be adjusted for by calculating the robust regression residuals ("RResid") of Cu, Zn, and Mn against Mg.

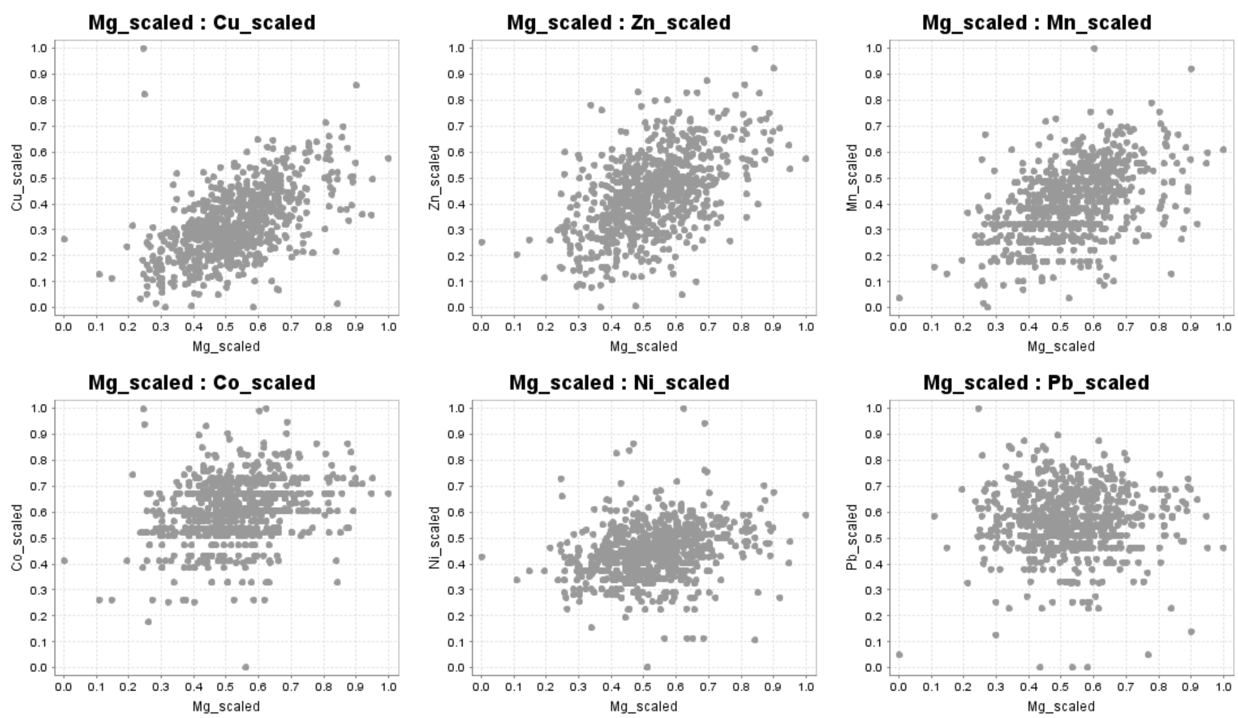

Figure 12 - Scatter plots of Cu, Zn, Mn, Co, Ni, and Pb against Mg (levelled and scaled), display moderate correlations of Cu, Zn, and Mn with Mg.

The regression residuals of Cu against Mg produce enhanced anomalies in the west, and reduce the extent of the eastern anomalous area, providing greater confidence that these new patterns reflect elevated metal endowment in the underlying strata (Fig. 13).

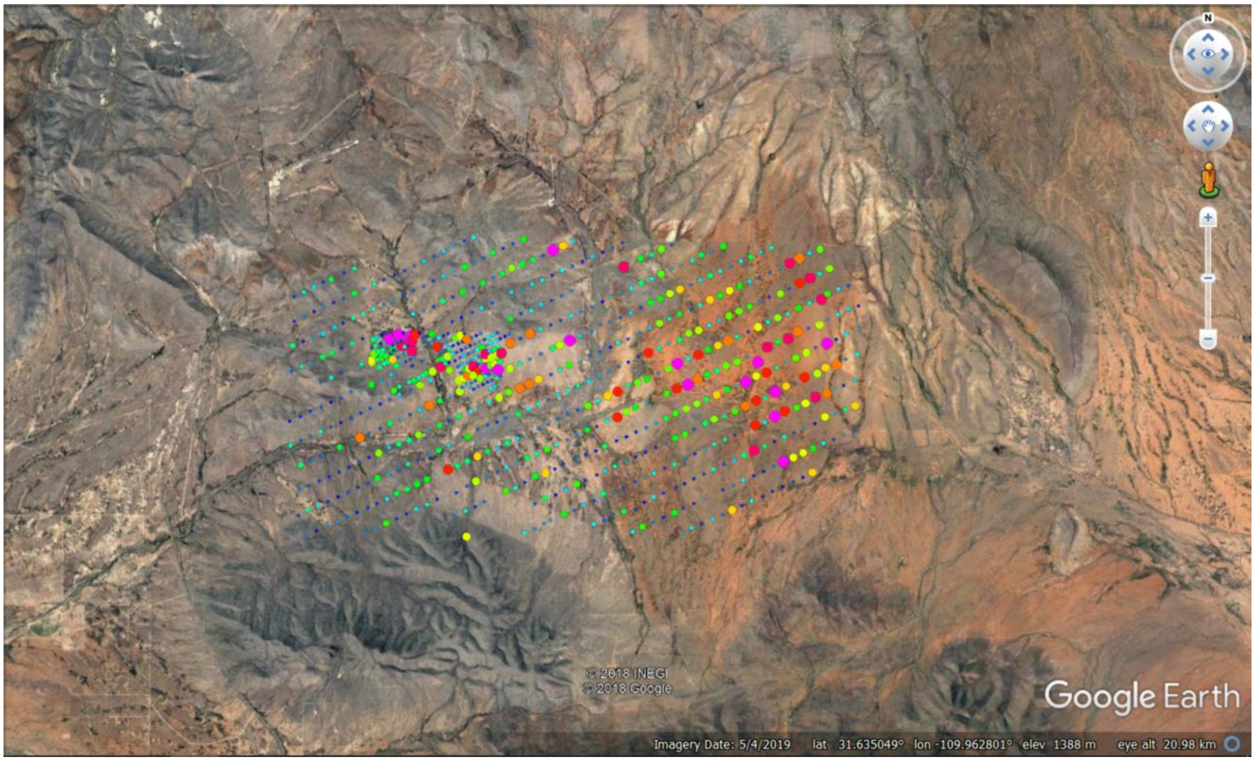

Figure 13 - Regression residuals of Cu against Mg plotted on satellite background imagery in Google Earth, shwoing enhanced anomalies to the west and more restricted anomalous areas to the east.

RGB Colour Composite Maps

The spatial distributions of variables can be summarized in red-green-blue colour-composite maps that display the combined distribution of 3 variables at a time. Continuous scaling of the interpolated values provides spatial trends of the element combinations (Fig. 14), whereas discrete percentile cut-offs help to constrain the search space for targeting purposes (Fig. 15). The examples below use combination of the Cu-Mg regression residuals in red, Mo in green, and K in blue, highlighting structural trends where Mo and K are more mobile than Cu in green and cyan (= green + blue); areas of Cu + Ag anomalism in pink (= red + blue); and potential targets where all three variables are anomalous in white.

Many other combinations of elements and derivative variables can be displayed in RGB maps, which can be provided at any point upon request.

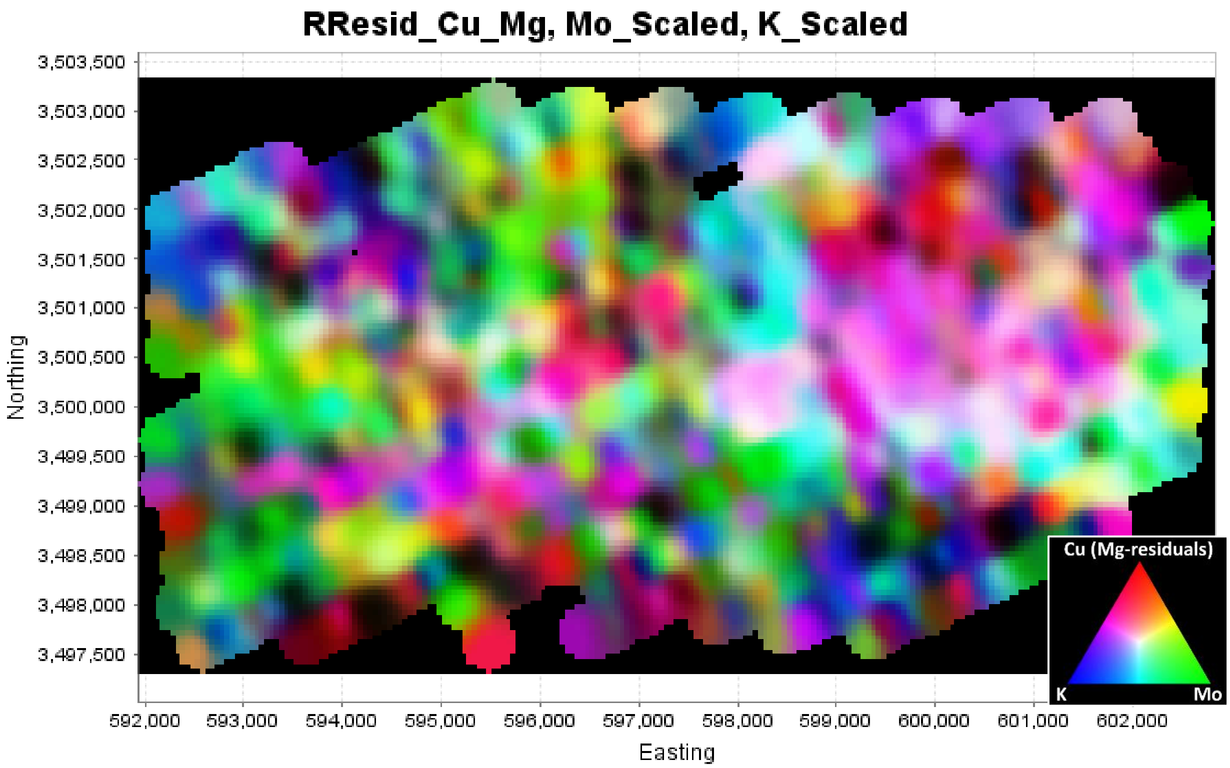

Figure 14 - Interpolated RGB colour-composite grid map of Cu-Mg residuals (red), Mo (green) and K (blue), with continuous scaling and 50m cell size.

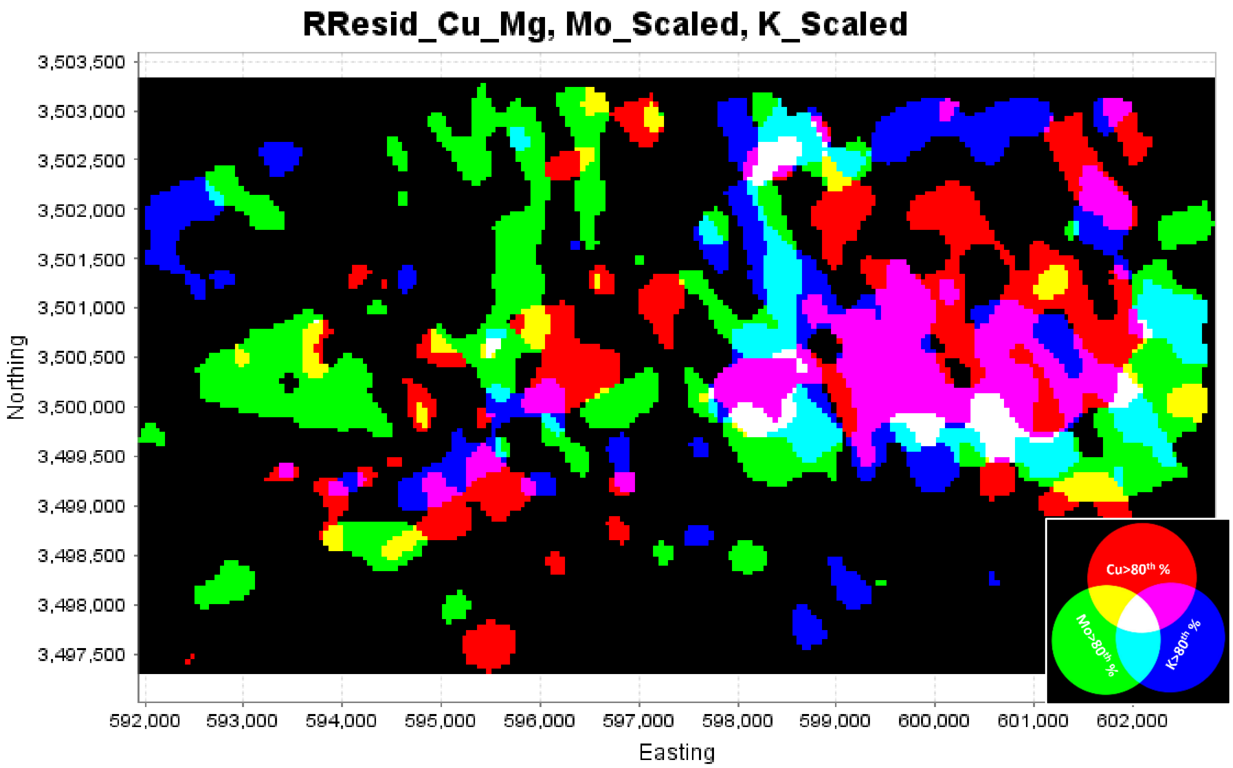

Figure 15 - Interpolated RGB colour-composite grid map of Cu-Mg residuals (red), Mo (green) and K (blue), with discrete 80th-percentile cut-off and 50m cell size.

References

- Österås, A.H., 2004. Interactions between calcium and heavy metals in Norway spruce. PhD Thesis. Stockholm University.

- Smedley, P.L. & D. Kinniburgh, 2017. Molybdenum in natural waters: A review of occurrence, distributions and controls. Applied Geochemistry 84, p 387-432