



Government of **Western Australia**
Department of **Mines, Industry Regulation and Safety**

RECORD 2017/11

NW BIOGEOCHEMISTRY AND BEYOND PROJECT

by
MJ Lintern, T Ibrahimi, T Pinchand and A Cornelius
CSIRO



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Perth 2017



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GSWA is releasing the report as part of its Record Series to ensure a wider distribution for the results and the proof-of-concept that biogeochemistry can delineate large-scale mineral system signatures and relate to different areas of bedrock. Although GSWA provided support to the project, the scientific content of the Record, and the drafting of figures, has been the responsibility CSIRO. No editing has been undertaken by GSWA.



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NW Biogeochemistry and Beyond Project

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Executive summary

The principal scientific objective of the North West Biogeochemistry and Beyond Project was to undertake a large regional survey to determine if biogeochemical techniques could be successfully applied to the less explored NW section of the Yilgarn Craton. The NW regional survey data were combined with a previously completed NE survey to cover the entire north Yilgarn - an area of ~ 130000 sq km.

The three secondary scientific objectives for this Project were as follows:

- 1) Analyse over 750 mulga (*Acacia* spp.) foliage samples from the NW Yilgarn; these were collected previously near boreholes and wells that had been sampled for groundwater.
- 2) Statistically compare the effectiveness of biogeochemistry against other techniques e.g. laterite and groundwater from the same area. Data sets to be compared including the geology, groundwater and other geochemical data on the MINEDEX database. The analysis will add value to the outputs of the MERIWA Project M414 on groundwater samples and specifically test whether trees can be used as a substitute - or be complementary to - the groundwater samples. In addition, results will be compared with biogeochemical data sets from outside the NW Yilgarn to test the effectiveness of the method on data already generated from site studies.
- 3) Determine whether biogeochemistry supports the mineral endowment potential of the NW Yilgarn, principally in the Narryer Gneiss Terrane. The Au and U prospectivity of this region in particular has been highlighted recently by a number of exploration companies. If successful, this biogeochemical method of exploration would be particularly useful in the extensive areas of cover in this region.

Major outcomes of the Project were:

- 1) Summary statistics and percentiles were produced for each element in a table to provide immediate information that can be compared with data collected by other future (site) surveys. For example, the 90th percentile for Au is 1.0 ppb and 1% of the data is over 3.1 ppb Au based on 2130 cases.
- 2) For the Yilgarn data set, there is little correlation between the hydrogeochemistry, laterite, GSWA data sets and the biogeochemistry data sets suggesting that one data set cannot act as a surrogate for the others, however, each may be individually useful in identifying areas of interest.
- 3) Standards and duplicates were satisfactory in making the data set robust for statistical analysis.
- 4) The data were classified according to categories and classes. The significance of the t-test statistic was used as a tool to compare classes for different elements; numerous significant differences were recorded between classes for different elements suggesting, for example, that some elements (or combination of them) could be used to discriminate between different regolith and geological units e.g. Narryer Gneiss mulga phyllodes have much higher mean U concentrations than other geological classes.
- 5) The Atlas provides a preliminary interpretation of the geochemical data, how the different classes in the categories relates, and how data between sites and regional data sets compare. Element distribution plots showed the spatial distribution of elements across the north Yilgarn. Some of the regional geochemical features previously identified by the NE Yilgarn data set were not substantiated when the NW data was added to it. For example, the higher Sr values in the eastern part of the NE Yilgarn data set, which were suggested as being related to distance from coast, have a lower mean concentration than those for the NW data set. Consequently, the larger data set vindicates our expanding the geochemical data set to include a broader area as it changes our interpretation and conclusions.
- 6) The prospectivity of the Narryer Terrane was investigated. The Narryer Gneiss in the far NW area of the dataset has significantly higher U than the other geological classes e.g. granite, greenstones, sediments investigated but Au, Ni, Cu and Zn concentrations are similar to other geological classes. Uranium in mulga correctly identified known deposits in the NE data set.
- 7) Three indices (or multiple element combinations) were used in an attempt to identify regions within

the element distribution maps that may be worthy of follow-up. The indices were Au- , Ni- and dust-based. Some areas were identified by the Au index and Ni index but generally there does not seem to be any great advantage in the use of the indices over individual elements themselves.

- 8) A correlation matrix table showed which elements in the phylloides were associated to one another. The results were not unexpected e.g. the REE, Ca-Sr and Fe-Ga-Th-Ti were correlated.
- 9) The robust principal component analysis does not add significantly to the interpretation of the element distributions. Principal component (PC) 1 was influenced by REE, PC2 by dust, PC3 by Mo, P and Rb and PC4 by alkaline earth elements as evidenced by positive loadings.
- 10) Individual site studies demonstrated the importance of the larger regional data set as geochemical data is put into deposit-related context.

The data set generated for the North Yilgarn and compilation of the site studies into other data sets will be a powerful tool for explorers that use biogeochemistry when searching for mineral deposits. Exploration companies will be able to compare data generated within their own projects to these data and investigate whether their leases are worthy of further investigation. A regional survey has not been done before with one plant genus in Australia on this scale. Correct interpretation of biogeochemical data from prospects has been difficult before since this data has not been available. This project is part of a long-term strategy to investigate the use of biogeochemistry to mineral exploration at different scales including prospect, district, regional and national scales.

1 Introduction

1.1 Background

Biogeochemistry is a low cost mineral exploration technique whereby plant samples are analysed for their elemental contents. Biogeochemistry is attracting increasing interest in Australia as it is perceived as a new method of exploring for mineral deposits, and in particular those hidden beneath transported regolith such as sand dunes, colluvium or alluvial sediments (Anand et al., 2014). Deep-rooted plants are a geochemical sample medium capable of integrating the geochemical signal of a large volume of the regolith (Figure 1). Using these techniques, the mineral prospectivity and geology of extensive areas of buried bedrock can leave traces of critical elements to reveal their sub-surface presence at the surface. It may help drill targeting by better defining areas of interest with greater confidence and supplement other techniques such as soil or stream sediment sampling which may be less effective in these areas. Biogeochemistry has been effective at detecting mineralisation targets and has been used extensively in Canada (Dunn, 1986; Dunn, 2007), and Russia (Malyuga, 1963; Kovalevsky, 1987), and trialled in Australia (Cole, 1965; Brooks et al., 1995; Lintern et al., 1997; Lintern, 2007; Anand et al., 2007; Reid et al., 2008; Reid et al., 2009) but remains largely untested in a regional sense except for a few cases in Canada (Dunn, 1981).

This Project addresses the agenda of the UNCOVER Initiative being developed by the Australian Academy of Science, Australian industry, State and Federal governmental bodies; specifically, it will assist Theme 4 which is to characterise and detect distal footprints of mineralisation. Biogeochemistry is part of a longer term CSIRO Discovering Australia's Mineral Resources scientific strategy that is investigating the use of sampling media and techniques for mineral exploration through cover at different scales including prospect, district, regional and national. The strategy has been partly developed to test the potential of biogeochemistry (and other techniques) as a robust addition to the mineral explorer's toolbox, and to provide clear information to industry demands as to if, where, how and why tree sampling should be used.

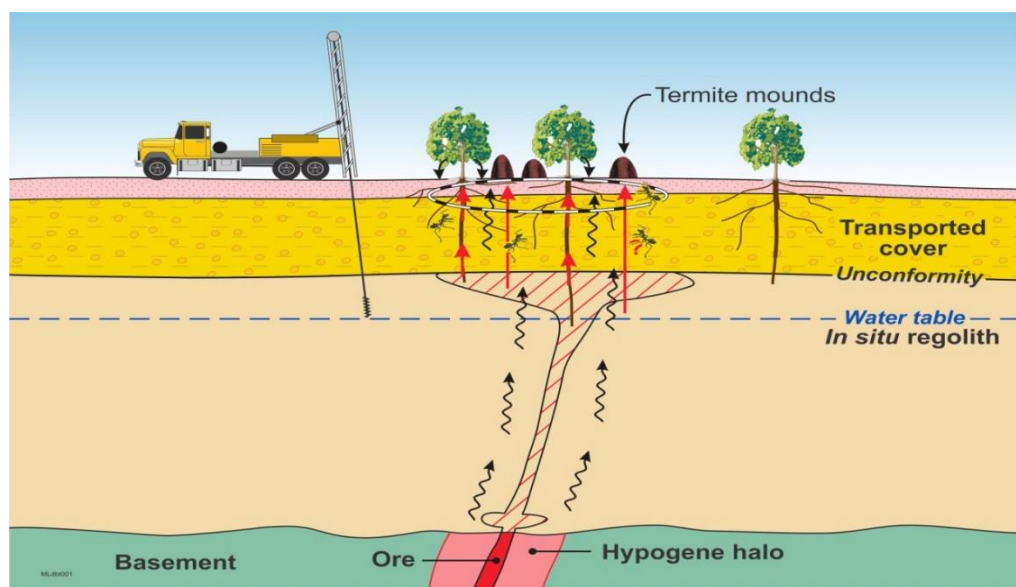


Figure 1 Use of biota, and in particular trees, to bring metals to the surface from deeply buried ore deposits to facilitate exploration. In remote areas, bores or drill holes are often absent and so in the initial phases of exploration, the geochemist may have to rely solely on less proven exploration techniques. Alternatively, pattern drilling of geophysical targets has to be employed which is a relatively more expensive option. (Modified from Anand et al., 2009; 2014.)

CSIRO has been at the forefront of biogeochemical science for mineral exploration in Australia. However,

many exploration companies have independently undertaken biogeochemical surveys without full knowledge and application of the techniques involved. The risk here is that if ambiguous results are received from biogeochemical surveys (undertaken on an ad hoc basis and with little scientific direction and rigour), it may discourage mineral explorers from the outset. With the increasing interests shown in biogeochemical surveys, this Project came at an opportune time since there is a particularly urgent need to engage with the mineral exploration industry to ensure that the new biogeochemical science is being interpreted and applied correctly and appropriately in different settings and scales.

1.2 Previous studies

This project followed on from three earlier MERIWA biogeochemistry and hydrogeochemistry projects M402, M407 and M414 and (Gray et al., 2009, Reid et al., 2010 and Gray et al., 2014). Sample area for this project was selected on bore and well availability where groundwater samples were taken for M414. The groundwater chemistry of the Yilgarn Craton is complicated by variably acid and saline nature of the southern parts (Figure 2). The NE Yilgarn biogeochemical and groundwater study area is outlined in Figure 2. In order to have consistent groundwater characteristics (which may be important for plant uptake), with relatively fresh and pH neutral groundwater occur. The area is dominated by mulga in this region.

One of the initial concept for the NE Yilgarn project (M414) was to develop an early stage exploration method to locate regional prospective areas by using low density (>5 km sample spacing) sampling in a reasonably well explored area such as the northeast Yilgarn Craton. Robust use of any technique for regional exploration requires consistent and reliable sampling, quality analytical data and streamlined interpretation procedures. Previous work has demonstrated that mulga biogeochemistry may potentially locate buried Au and VMS deposits at the site scale (Anand et al., 2007).

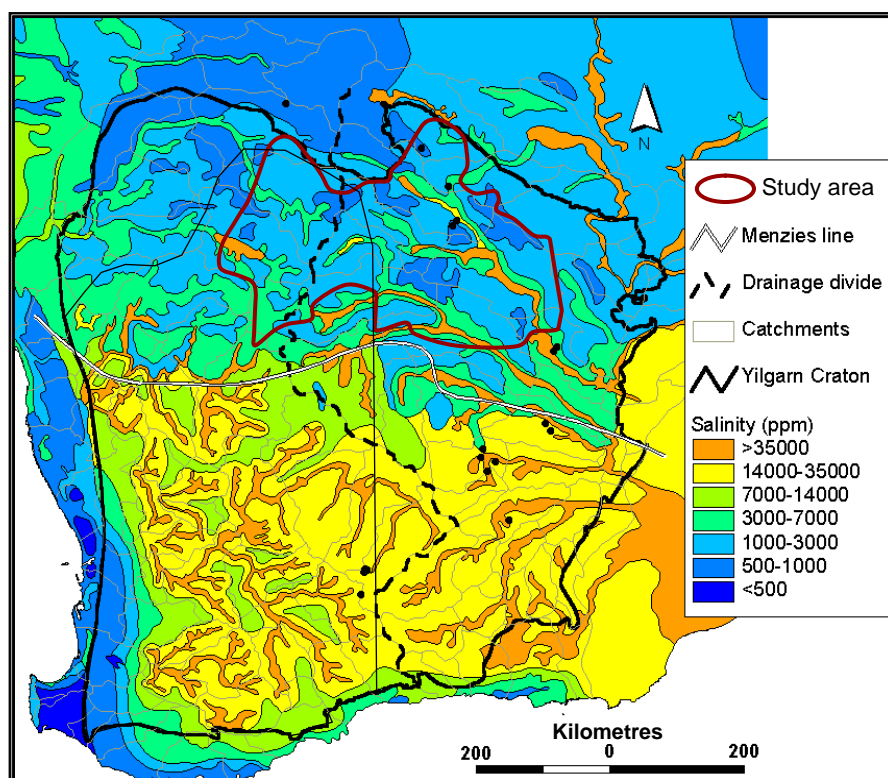


Figure 2 Modelled groundwater salinities in the Yilgarn Craton (Commander, 1989), with the study area of the northeast Yilgarn biogeochemistry project overlaid (Reid et al., 2010).

The NE Yilgarn hosts extensive Fe-rich lateritic materials (e.g. lateritic residuum, ferruginous saprolite, and ferruginous lag). Most of these materials develop in situ and may contain enrichments of metals e.g. Au, Cu, and Ni that broadly reflect the bedrock on which they develop. Weathering and landscape processes,

including lateral dispersion, serve to distribute this material (and their contained metals) from their source to adjacent areas of transported regolith and effectively increase the size of the anomalous area to provide a larger footprint to aid exploration.

Two major regional surveys of surface material have been conducted in the NE and NW Yilgarn region: a geochemical laterite survey was conducted over part of the NE Yilgarn (MERIWA Project M371, Cornelius et al., 2008) and a regolith material compilation conducted by GSWA in part of the NE Yilgarn over several map sheets on the WACHEM database. The WACHEM database is a compilation of multi-element geochemistry of rocks unconsolidated surface material (regolith) and drill core collected by the Geological Survey of Western Australia (GSWA) including data compiled by Hallberg (2008). Samples have been analysed for a range of major element oxides, trace elements, rare earth elements (REE), and isotopes by a variety of analytical approaches at commercial, government and university laboratories. The majority of samples in the north Yilgarn study area are confined to 1:250000 map sheets with surveys undertaken by GSWA themselves but there are, in addition, other sundry samples of regolith material. There are potential issues with comparing the data from these three sets of data with the biogeochemical data sets. These are as follows:

- 1) The coverage of the regolith data only partly covers the biogeochemical surveys.
- 2) The Yilgarn Atlas data was collected at a lower density to the biogeochemical data (Figure 3).
- 3) The GSWA surveys contain a variety of laterite material that was sampled including weathered rock, duricrust and soil. Some of these materials (gossan) may naturally contain higher concentrations of elements than others (aeolian sand) but have been grouped into the one data set.
- 4) The GSWA database contains many samples that were collected at a much higher density (Figure 4). Samples will need to be selected to compare with the corresponding biogeochemical sample.
- 5) Unlike the CSIRO groundwaters, the samples from the Yilgarn Atlas and the GSWA data sets were not collected from the same location and so are not directly comparable with one another.

In view of these limitations, there is probably minimal benefit in undertaking a complex statistical comparison between the biogeochemical data set and those from the GSWA and the Yilgarn Atlas. Nevertheless, a geochemical comparison will be made between nearest neighbour samples.

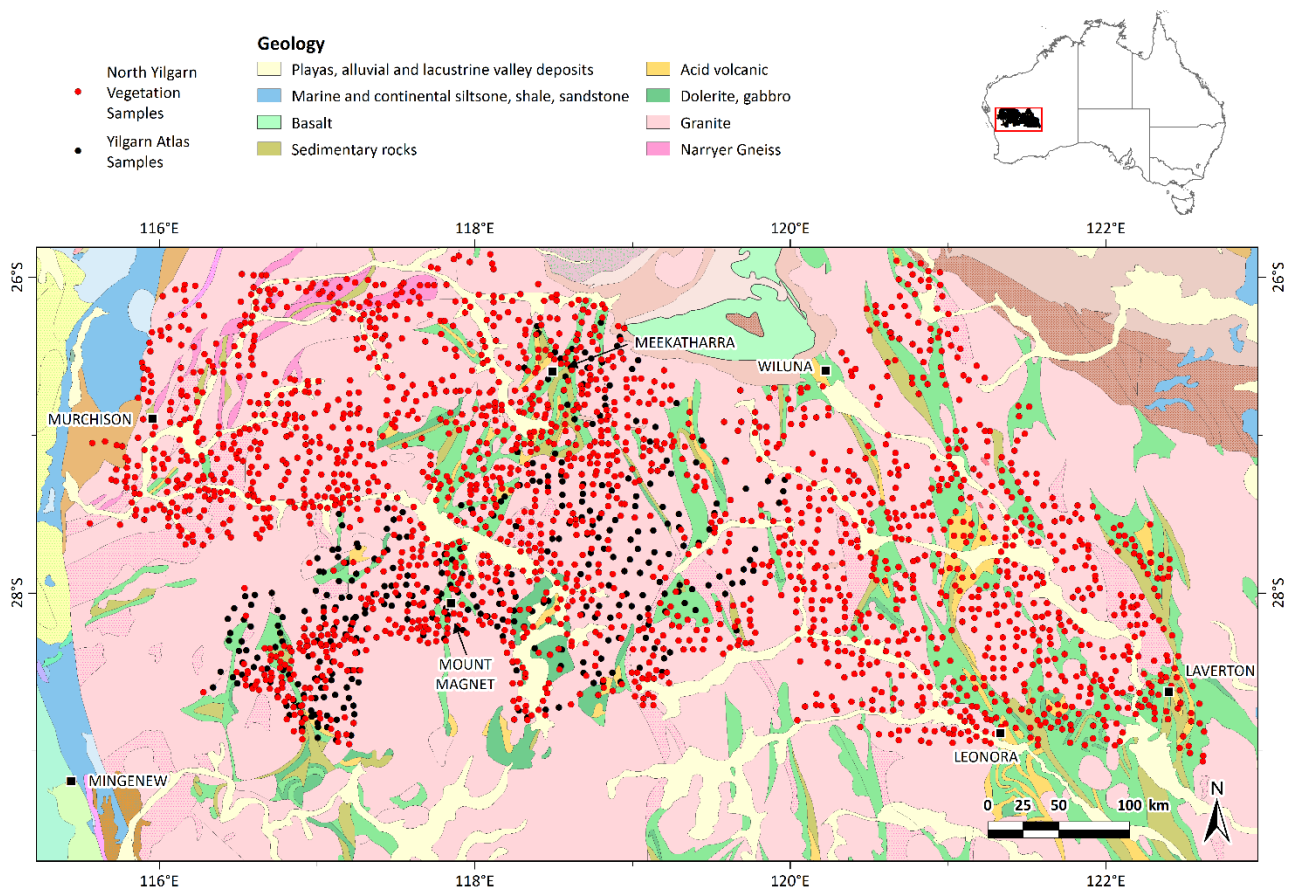


Figure 3 The NE and NW biogeochemical survey locations are combined (red symbols) in this figure and compared with the Yilgarn Atlas laterite sample locations (black symbols) located within the confines of the biogeochemistry data. Note the lower density and coverage of the Yilgarn Atlas samples compared with the vegetation samples. Geological data sourced from GSWA website.

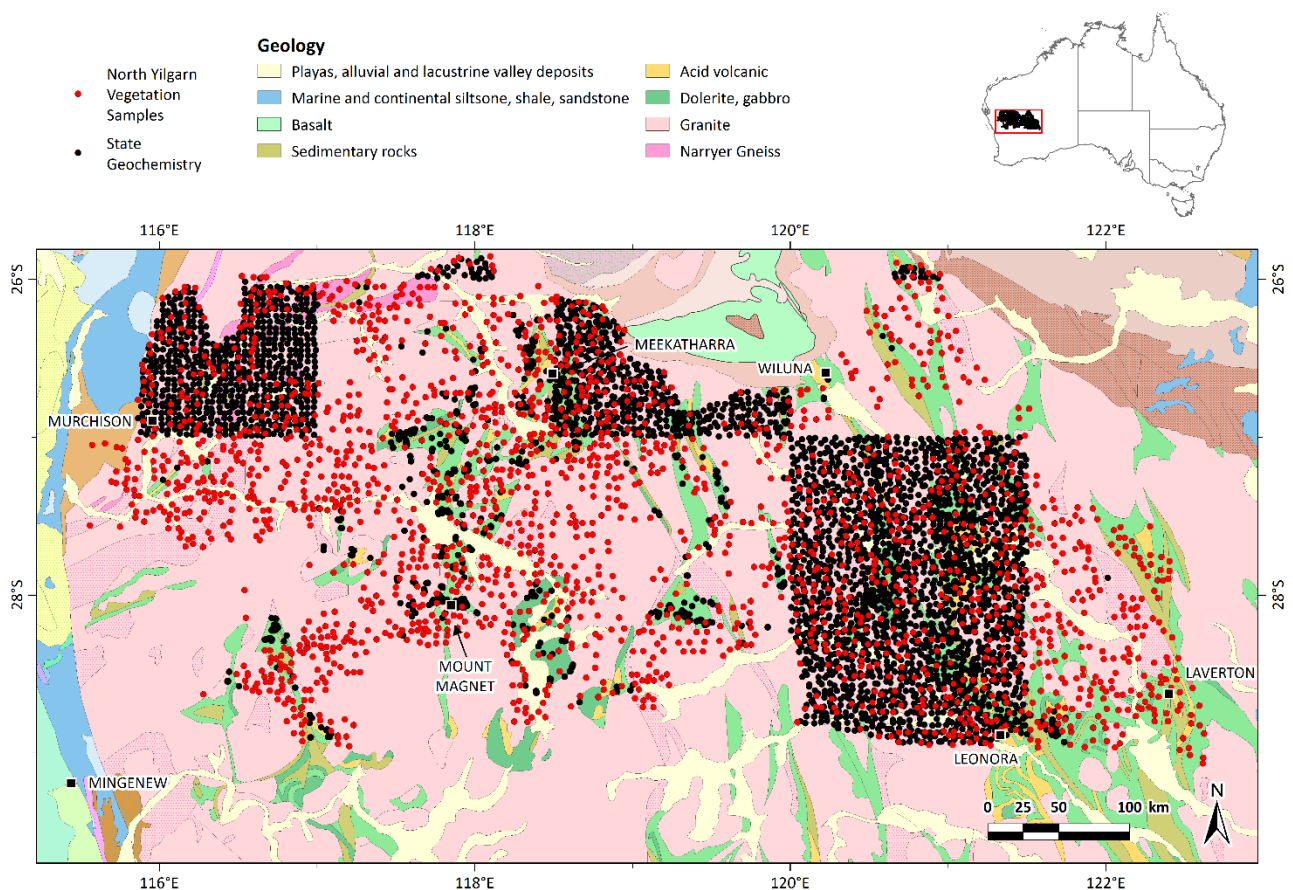


Figure 4: The NE and NW surveys are combined (red symbols) in this figure and compared with data located on GSWA GeoView (black symbols) that fall within the “envelope” of the biogeochemistry samples. The high density GSWA regolith samples are mostly limited to four 1:250,000 map sheets and some sundry samples outside these areas (WACHEM Geochemistry Database, 2014).

Summary of the MERIWA M407 NE biogeochemical survey and site studies

The regional data from the NE Yilgarn Biogeochemical Project (M407) were important in regional biogeochemical sampling for Western Australia but the results have never been compared with other surveys. Thus, the samples taken from the NW Yilgarn will be directly compared with these. Results from NE Yilgarn survey showed:

- Recognition of lithological geochemical signatures over the region, discerning greenstones from granites using novel geochemical indices and multivariate statistics.
- Uranium is the best secondary U deposit indicator in plants in this region, and is successful for detecting most known prospects at this scale.
- The detection of Au prospects across the region was possible using straight element maps, but was improved by the use of a Au mineral exploration index (AuMin1) combining several elements (Figure 5).
- Nickel prospects were identified at the regional scale where the samples were close to the prospects (within 1-2 km) or possibly where the cover thickness was less thick.
- The Leinster and Murrin Murrin areas are strongly highlighted using Ni, Co, Cr and Fe data. The footprints for these two sites were extended up to 20 km or more.
- Detection of VMS style deposits is hampered by Zn and Cu being essential plant nutrients and bearing little relationship to deposits regionally but more to individual plant health.

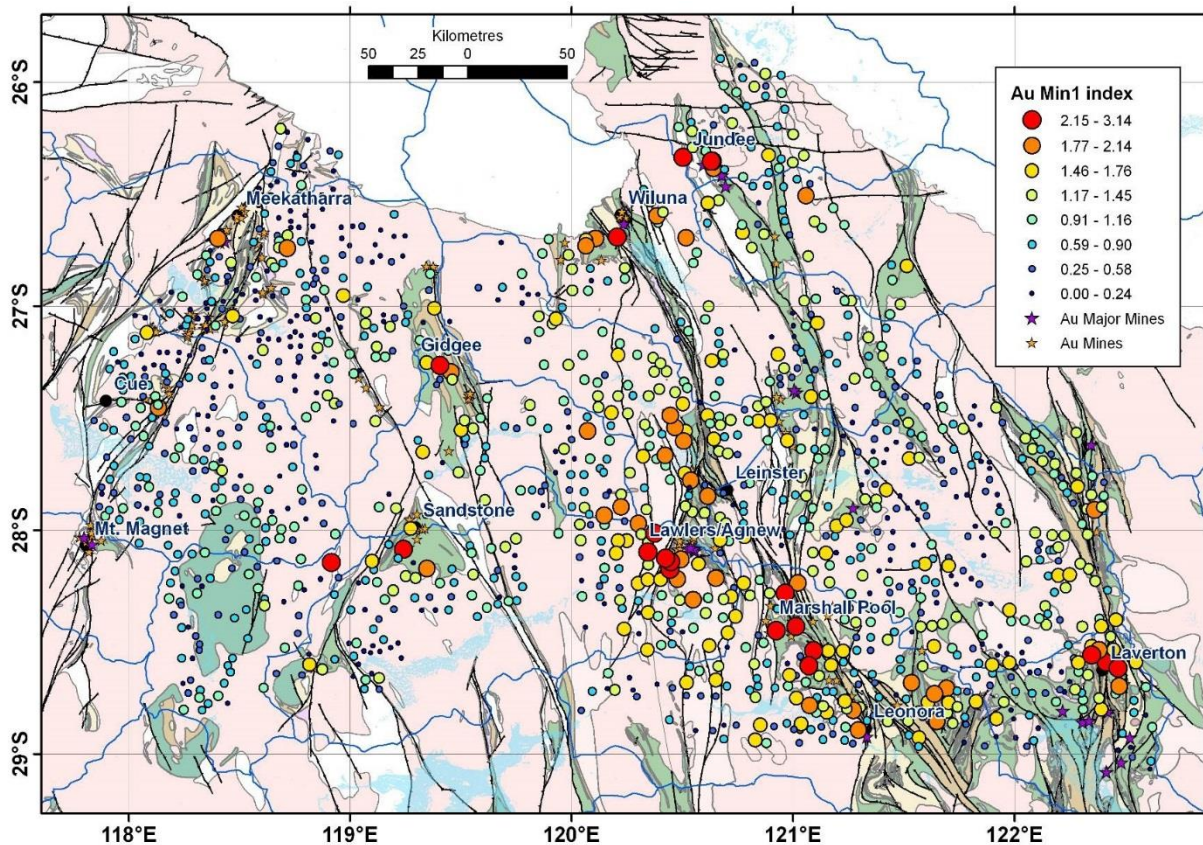


Figure 5: The construction of a geochemical index for Au was found to be superior to straight elements plots in the NE Yilgarn. The AuMin1 index was formulated after statistical treatment of the data. (Reid et al., 2010)

An important conclusion of the MERIWA M407 Project was the endorsement by industry to extend this scientific approach with studies into other areas including the NW Yilgarn. The additional biogeochemical data from the NW Yilgarn data set will generate geochemical anomalies that will warrant follow up sampling. The results from this new Project are expected to build on the NE Yilgarn findings but, importantly, with the addition of the data from a series of projects, prospects and mine sites potentially including Garden Well, DeGrussa, Kintore, Kopai, Bentley, Gnaweeda (St Annes, Turnberry, Mistletoe, Bunarra), Boddington, Myrtle, Bounty, Bibra, Havana, Tropicana, Golden Delicious, Tanami (Titania, Oberon), Rose Dam, Moolart Well, Kintyre, Leucippus, North Miitel, Barns, Challenger and Birthday. The result will be a valuable resource for further scientific research and a practical data set for use by industry. For example, the geochemical data from the site studies may be reappraised in the light of the new data from the regional survey.

Potential for further scientific research

The biogeochemical samples collected as part of the NE Yilgarn and NW Yilgarn surveys will be made available for further scientific research and present a valuable scientific resource; CSIRO is the custodian of these catalogued samples. We will have a milled reference sample and another unmilled reference sample available for this research. The geochemical results may also serve as a basis for undertaking detailed site studies and our samples may be re-submitted for this additional work. There is a potential to combine all of these studies towards a biogeochemical atlas of Australia that would attract interest from institutions such as Geoscience Australia.

One of the interesting scientific observations from MERIWA M407 concerns phyllode ("leaf") shape of the samples. Biogeochemical data generated from NW Yilgarn will test the hypothesis that climate is affecting the regional phyllode shape and element content. Specifically it was noted in the NE biogeochemical study that there was a gradient to phyllode shape with finer phyllodes recorded within the east and north parts of the study area corresponding with sporadic rainfall and generally drier conditions. Further research on Sr isotope analyses of the vegetation may provide further support to test the hypothesis that there is a climatic driver to the geochemistry; lighter Sr isotopes may be more concentrated nearer the coast. Other metal

isotope studies (e.g. Cu and Zn) may provide important information on the origins of these elements in the vegetation as is currently being done on other regolith materials elsewhere.

The regional AEM survey being undertaken between CSIRO and the Department of Water is aimed at a better understanding of the paleochannels of the Murchison. There is potential (using H and O isotopes) to compare the AEM data with additional biogeochemical analyses to test whether the roots of the Acacia are accessing the water in the paleochannels.

1.3 Scope of this study

This study will be limited to the combined data set of the NE and NW data sets. Data from other site studies (including those from recent CSIRO-AMIRA projects) will be included in the database but not discussed in the context of the regional studies except summarised in the Atlas box plot diagrams. This has been, and will be done, as part of site study reports and scientific papers.

1.4 Project Objectives

The principal scientific objective of this project was to undertake a large regional survey to determine if biogeochemical techniques can be successfully applied to the less explored NW section of the Yilgarn Craton.

The three secondary scientific objectives for this Project were as follows:

- 1) Analyse over 750 mulga (*Acacia* spp.) foliage ("leaves" and small supporting stem) samples from the NW Yilgarn; these have been collected near boreholes and wells that have been sampled for groundwater.
- 2) Statistically compare the effectiveness of biogeochemistry against other techniques from the same area. Data sets to be compared including the geology, groundwater and other geochemical data on the MINEDEX database. The analysis will add value to the outputs of the MERIWA Project M414 on groundwater samples and specifically test whether trees can be used as a substitute - or be complementary to - the groundwater samples. In addition, results will also be compared with biogeochemical data sets from outside the NW Yilgarn to test the effectiveness of the method on data already generated from site studies.
- 3) Determine whether biogeochemistry supports the mineral endowment potential of the NW Yilgarn, principally in the Narryer Gneiss Terrane. The Au and U prospectivity of this region in particular has been highlighted recently by a number of exploration companies. If successful, this biogeochemical method of exploration would be particularly useful in the extensive areas of cover in this region.

2 Study areas

2.1 Climate

The north Yilgarn Craton is semi-arid to arid and has a generally Mediterranean style climate with hot, dry summers and cool, wet winters. Mean annual rainfall is between 200-300 mm and the annual evaporation is between 2500 and 4000 mm (Meekatharra; Bureau of Meteorology, 2016). Rainfall is episodic and bimodal occurring with peaks in summer and winter. Mean average maximum temperature is ~ 38°C in January, 19°C in July and average minimum temperatures range from ~ 24°C in January to ~7°C in July.

2.2 Geology

The geology of the north Yilgarn Craton is comprised of variably distributed Archaean-aged granites and greenstones (Figure 3). The greenstones occur in a series of longitudinal belts, including the Norseman-Wiluna, Yandal, Duketon, Meekatharra, and Windimurra (Myers and Hocking, 1998; Morris and Sanders, 2001). Cassidy et al. (2006) summarise the tectonic evolution of the Yilgarn Craton. The NE Yilgarn is split by a continental divide; to the east is the Southern Cross Domain and to the west is the Murchison Domain, which are both part of the Youanmi Terrane. Both domains in this area have granitic rocks and granitic gneiss associated with extensive northeast oriented greenstone belts (Williams, 1975; Myers, 1997). The granitic rocks comprise granodiorite-monzogranite, with deformed and metamorphosed monzogranites. The greenstones comprise mafic and ultramafic volcanic rocks underlain by quartzite, BIF and minor felsic volcanics. The Narryer Terrane in the NW part of the study area contains some of the oldest rocks in the Yilgarn Craton (>3.3 billion years old; Myers, 1990). It is composed of a tectonically interleaved and deformed mixture of granite, mafic intrusions and metasedimentary rocks. The rocks have experienced multiple metamorphic events at amphibolite or granulite conditions, resulting in often complete destruction of original igneous or sedimentary (protolith) textures. The Narryer Gneiss Terrane is adjacent to the northernmost margin of the Yilgarn Craton and is abutted on the north by the Gascoyne Complex metasedimentary and metagranite orogen.

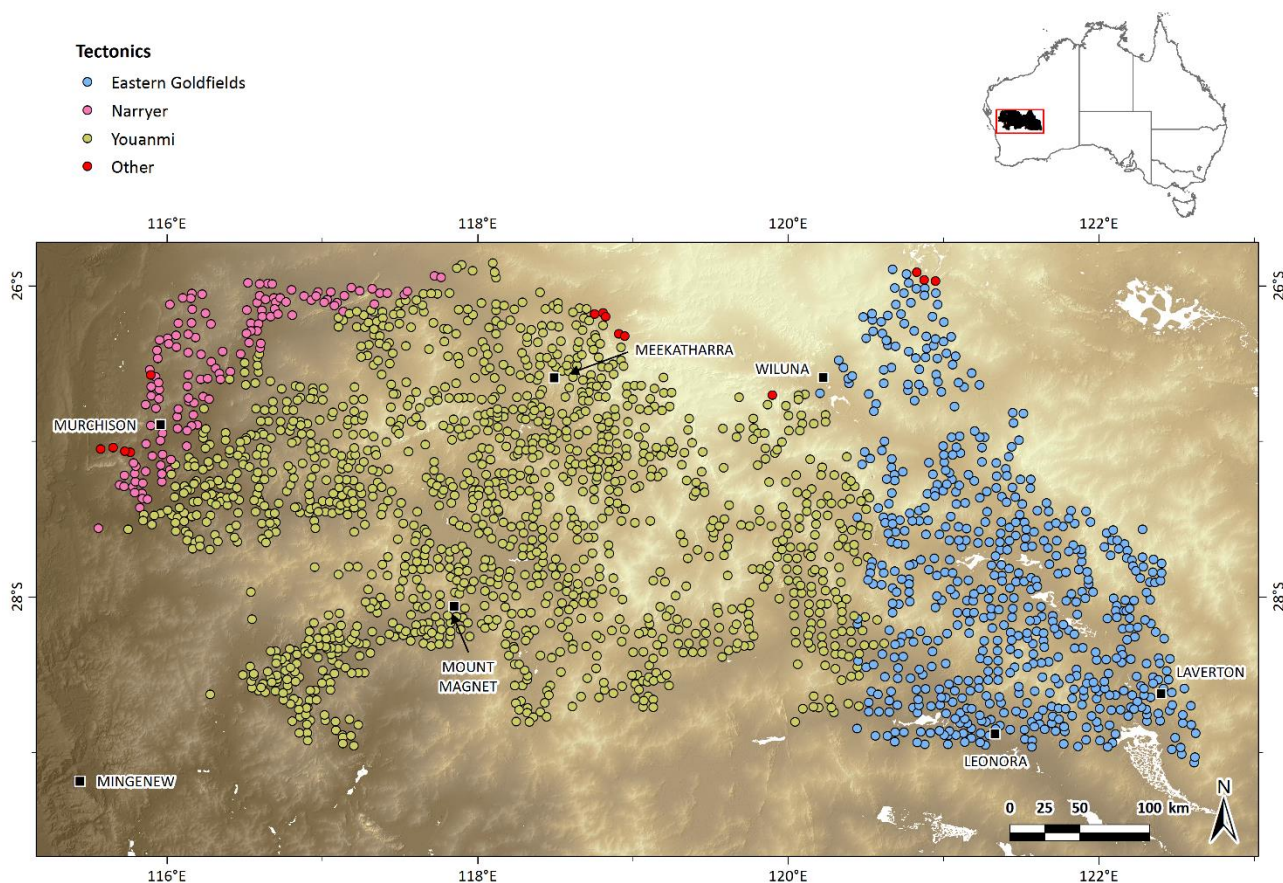


Figure 6: Location of samples over the north Yilgarn. The three major tectonic groups are shown.

2.3 Mineral deposits

There are many mineral deposits in the north Yilgarn Craton, covering various commodities, particularly in the NE. The numerous Ni deposits are hosted by greenstones associated with ultramafic volcanic rocks, particularly concentrated along the Agnew-Wiluna greenstone belt (Hagemann and Cassidy, 2001). There are Archaean orogenic Au deposits throughout the region particularly associated with greenstone structures including the large Sunrise Dam and Agnew camps as well as Meekatharra-Mount Magnet and Yandal belt districts. There are several VMS deposits including Jaguar, Bentley, Teutonic Bore and several smaller ore bodies which make up the Quinns Prospect. Secondary carnotite-style deposits (calcrete uranium) are prevalent along the drainage systems throughout the region, and include the world class Yeelirrie deposit; other U occurrences are found in the NW Yilgarn bordering and within the Murchison River catchment. There are many other deposits including several V-Ti-Fe deposits (greenstones near Windimurra, Barrambie and Youanmi stations).

2.4 Physiography

The northern and southern Yilgarn are separated by a diffuse physiographical boundary termed the Menzies Line (Figure 7; Butt et al., 1977). Numerous researchers have discussed the Menzies Line, a geobotanical divide running approximately EW at 29.5°S (Butt et al., 1977). South of this line, the dominant flora is generally *Eucalyptus* spp. (often in mallee form in more arid areas). To the north, *Acacia* (mulga/wattle) or *Triodia* (Spinifex) spp. commonly dominate (Figure 8). Northern groundwater is relatively fresh and neutral (Gray, 2001), while soils are dominantly acid, sandy with red brown hardpans (Teakle, 1936) and lack significant pedogenic calcrete horizons or they are located deeper in the regolith (Anand and Paine, 2002); groundwater calcrete is common above the palaeochannels. The southern Yilgarn has saline and acid

groundwater, and eucalypt vegetation, and the soils are dominantly alkaline.

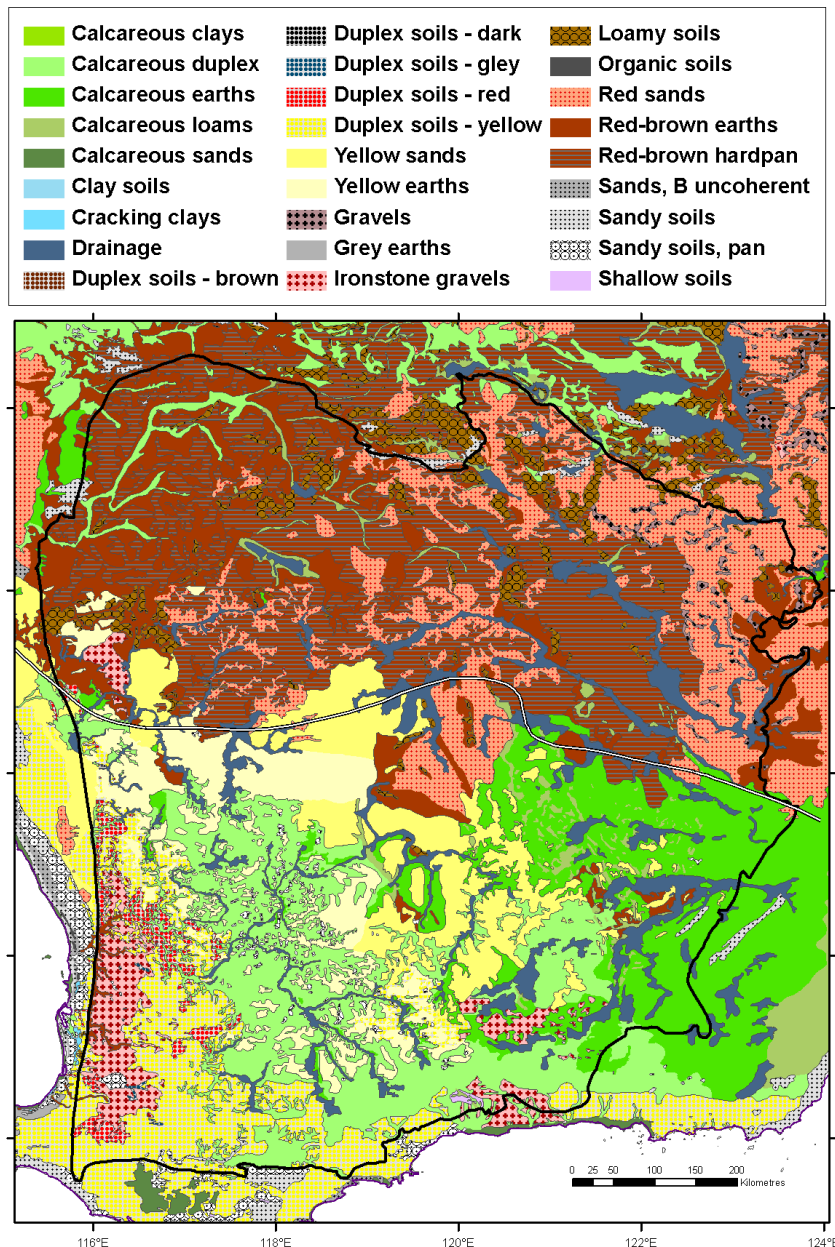


Figure 7: Main soil types (modified from Northcote, 1978) and drainages of the Yilgarn Craton, demonstrating change in major soil types across the Menzies line (E-W trending double line, Butt et al., 1977).

The dominant landforms of the north Yilgarn Craton are sandplains, plateaus, breakaways, colluvial and alluvial plains, bedrock, salt lakes, and sand dunes (Jutson, 1950). The landforms are generally gently undulating with low relief; the elevation across the sampling area ranges from 350 to 600 m ASL, gradually decreasing north to south. The relatively flat surface belies the complex underlying regolith that has been exposed to significant events of weathering, erosion, deposition and a variety of climatic conditions pre and post burial.

2.5 Vegetation

In general the vegetation profile of the north Yilgarn Craton is open woodland dominated by *Acacia aneura* (a mulga) across most landscape settings (Figure 8). *Triodia* spp. (spinifex) are common across sand plains and sand dunes. *Callitris glaucophylla* (white cypress pine) is present along breakaways throughout the region. River gums (*Eucalyptus camaldulensis*) are prominent trees that occur along watercourses

throughout the N Yilgarn.

Mulga has an irregular distribution across central and southern Australia. It is a shrub or tree, up to 10 m high with many different forms and phyllode (modified stalk that resembles a leaf) types (Miller et al., 2002). The tree has bright yellow, oblong flowers and terete to elliptic phyllodes, 2-11 cm long and up to 1 cm wide. *Acacia aneura* is a dominant mulga species of many shrublands or woodlands of inland Australia (Moore, 2005). Early site studies have been conducted with this species at Jaguar and Moolart Well (Anand et al., 2007), Big Bell, Harris Heights, Millawarrie and Blackmans (Marshall and Lintern, 1995). These studies highlighted the potential for prospect-scale sampling of mulga for mineral exploration.

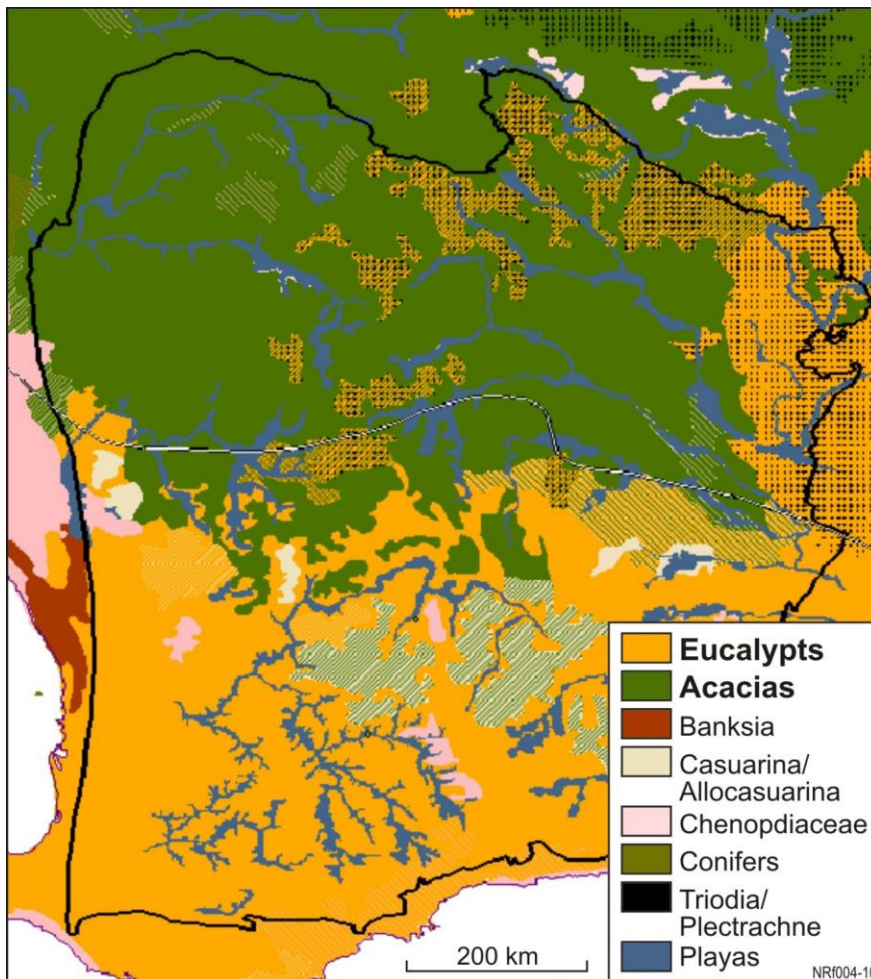


Figure 8: Main vegetation types and drainages of the Yilgarn Craton (replotted using data from Geoscience Australia, 2003; from Reid et al., 2010).

2.6 Regional studies

This new biogeochemical survey is located in the NW Yilgarn Craton and partly within the Narryer Gneiss Terrane which contains some of the oldest rocks in the Yilgarn (Figure 9). The survey area comprises over 66000 sq km. The majority of the NW Yilgarn is relatively under-explored compared with the NE and central areas, despite bordering Mt Magnet, Cue and Meekatharra, which are well known for their Au endowment and active mines. Brownfield opportunities are sought by companies operating in these areas and biogeochemistry is a technique that has been used by companies and CSIRO in similar covered regolith settings further east at Jaguar, Bentley, Duketon, Garden Well and Gossan Hill. In addition, greenfield opportunities, for example, reside with companies operating in the Murchison where there are known U prospects but trees has never been tested there for their potential there to reveal concealed mineralisation.

The NW Yilgarn has relatively few operating exploration licenses (compared with the NE) even though the geology may be favourable for mineral deposits. The existing NE biogeochemical survey lies to the east of the NW survey (Figure 9). This is a larger survey containing more samples and covering a larger area. The data from this survey will be compared with the new NW regional survey. The VS regional data set (Figure 9) was included in this report. It underwent a slightly different analytical procedure and the data are not quality controlled as with the NW and NE data sets; however it is included here as an additional resource. Several questions will be addressed by the combined NE and NW biogeochemical surveys.

Can vegetation detect buried lithology?

One of the purposes of our approach is to investigate the potential for any extensions to prospective greenstone belts that may be hidden from conventional approaches such as magnetics and gravity. In the NE survey, apparent extensions of greenstones buried by transported overburden were identified by plant geochemistry.

Is there better association between hydrogeochemistry and biogeochemistry in the NW compared with the NE Yilgarn?

The hypothesis that groundwaters and foliage are geochemically more strongly related in areas where rainfall (western part of the NW) is higher and more reliable will be tested. Groundwaters are notably fresh in the NW Yilgarn particularly for samples taken within the valleys compared to the flanks of the valleys. There is a significant active river catchment (Murchison) in the NW which is lacking in the NE where some drainages are choked with salt and/or calcrete; winter rainfall is more reliable in the NW compared with the NE which receives less rainfall related to sporadic summer depressions emanating from the north.

Comparison with other geochemical studies

One of the scientific strengths of the Project will be to directly compare the biogeochemical and groundwater data from identical sites i.e. does the chemistry of the NW Yilgarn tree samples reflect the groundwater data in which they reside? In other words, is it necessary to take groundwater samples or can we rely on the biogeochemical samples to identify the underlying chemistry of the rocks. There are several geochemical surveys that have been undertaken by GSWA and CSIRO of regolith materials in the north Yilgarn Craton. These include a Laterite Atlas and MINEDEX data base. A comparison will be made between elements from the biogeochemistry survey and with the geochemical data from these two sources.

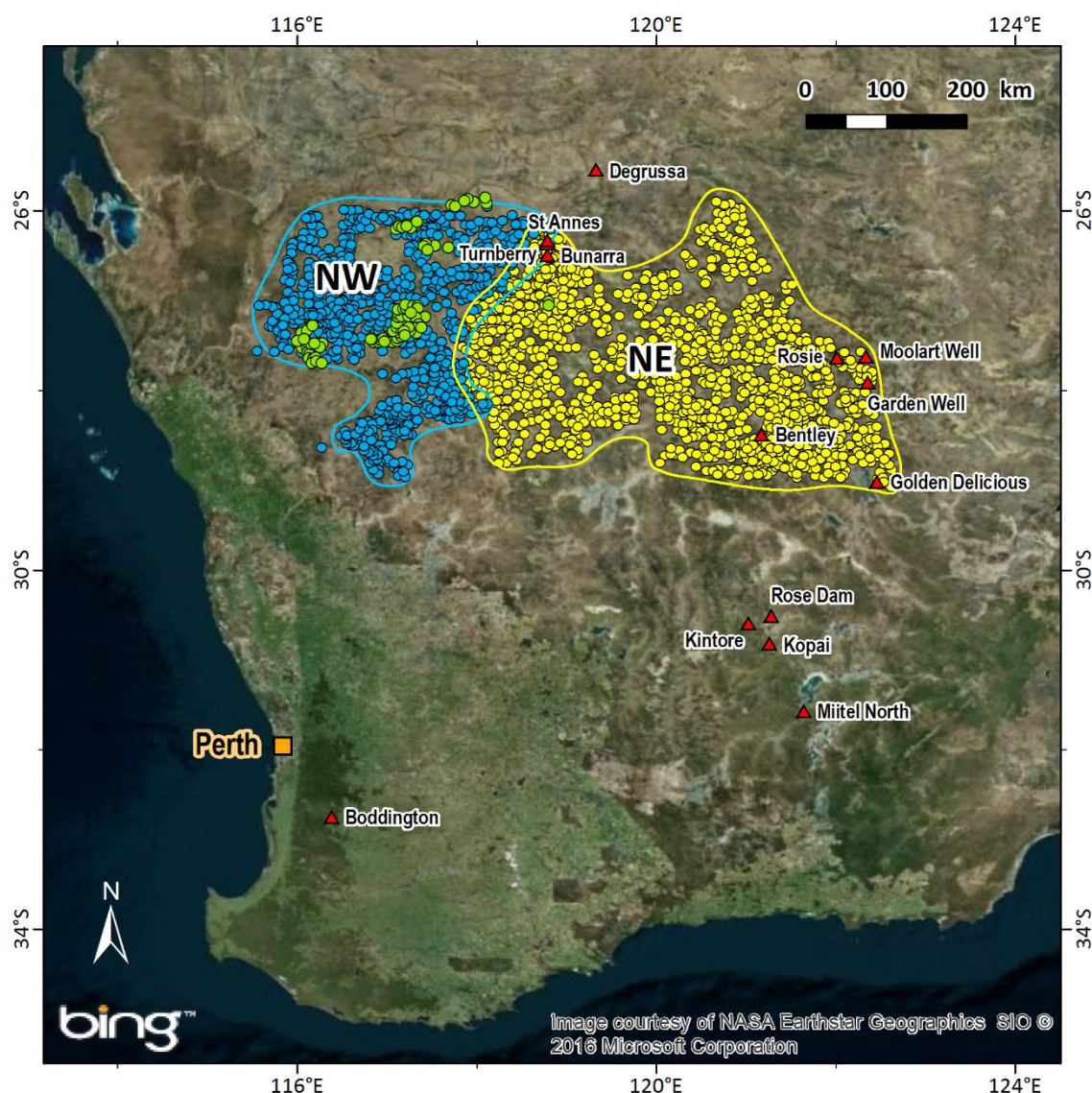


Figure 9: The NE (yellow) and NW (blue) study areas and selected mineral deposits and prospects (red circles) in Western Australia where biogeochemistry has been undertaken and data will be included. The green dots are the locations of an additional regional data set (VS). Many sites (red circles) were investigated as part of CSIRO AMIRA P778 and P778A.

2.7 Site studies

Numerous prospect-scale orientation studies have been independently completed by the exploration industry, CSIRO and universities to unequivocally demonstrate that native Australian vegetation is indeed drawing up metals such as Au, Zn and Cu from within the regolith and bringing them to the surface. CSIRO has recently completed two AMIRA projects (P778 and P778A) which detailed the geochemistry of a number of prospects (Au, Ni, VMS and U). Thousands of vegetation samples have been analysed as part of recently completed projects. Location of site studies for the biogeochemical data base are shown in Figure 9. The geochemical data for these studies is shown in the Geochemical Atlas (and compared with the regional studies) and data are discussed in site studies cited in the references.

3 Methods

3.1 Sample collection

As with the NE Yilgarn hydrogeochemical and biogeochemical sample collection, sites for the NW Yilgarn surveys were determined in the same way by using topographical maps with water well positions marked, combined with GPS/Arc GIS on a field laptop and printed maps. Sample locations are shown in Figure 6; significant gaps in the sampling density are apparent. Many sites were difficult to access, with numerous wells being abandoned or previously recorded locations sometimes being inaccurate by hundreds of metres. Trees and shrubs were chosen close to the groundwater sample to give potentially the most accurate correlation between the plant and groundwater chemistry. A calico bag was filled with terminal branches from around the tree at a consistent height (generally chest height), ensuring the sample was as free of dust as possible. Trees were selected that had no seedpods or flowers, and had been minimally grazed.

Several factors are of great importance when sampling vegetation, including the following:

- 1) The plant species must be widely distributed and have an extensive root structure (Dunn, 2007; Hulme and Hill, 2003); mulga certainly has a wide-ranging distribution and has a significantly large rooting volume.
- 2) The age of the sampled plant must be relatively consistent (tree height and width was recorded), and the organ sampled must be healthy, as insects, bacteria or fungi can alter the chemical structure of the medium
- 3) Landscape setting greatly contributes to the plant chemical characteristics, as plants growing in drainage channels often have higher elemental concentrations than those in adjacent settings (Lintern et al., 1997; Cohen et al., 1999). This may be because of the increase in water leading to increased uptake and/or the channels having higher concentrations of elements due to them being collection areas. In this case, generally the samples were collected in or near drainage systems, which, while not ideal, is consistent.
- 4) Samples should be collected at the same time because of potential seasonal variation in element concentrations. This was not practicable for large surveys of this type due to logistics. Samples were taken over several months.

Photographs were taken of the samples after they had been dried. The samples were classified according to phyllode type; the phyllode is a plant adaptation to aridity and is a modified leaf stalk (petiole) equivalent to a leaf in its form. All the foliage (phyllode and phyllode stalk) of the plants in the data set are assumed to belong to *Acacia aneura*. However, “mulga” trees, while common in the areas sampled, may not be the same species. This is because *Acacia* trees from different species may appear morphologically similar; this is exacerbated by the wide variety of phyllode shapes and sizes that belong to *A. aneura* (Figure 10 and Figure 11). Close examination of flowering parts are the common way to discern different species and so it is entirely possible that some of the samples collected do not belong to *A. aneura*. Some element concentrations from the NE Yilgarn survey related to plant structure show that finer phyllodes e.g. terete had more K, Na, Ca, Rb, Sr and Mg probably as a result of greater surface area-to-volume ratio (Reid et al., 2010). Some collected samples back in the laboratory were identified as clearly not mulga and excluded from the final data set.

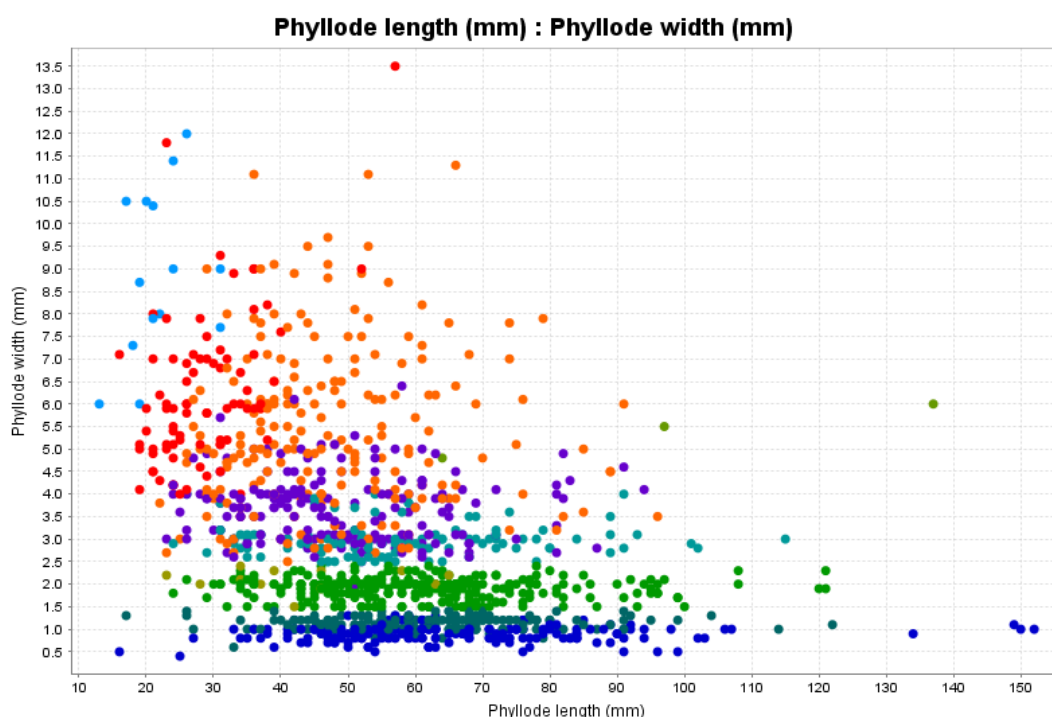


Figure 10 Population split by phyllode shape for NE Yilgarn mulga samples. Explanations of the shapes can be seen in Figure 11. Oblong shaped phyllodes are blunter than broad linear form (Reid et al., 2010).

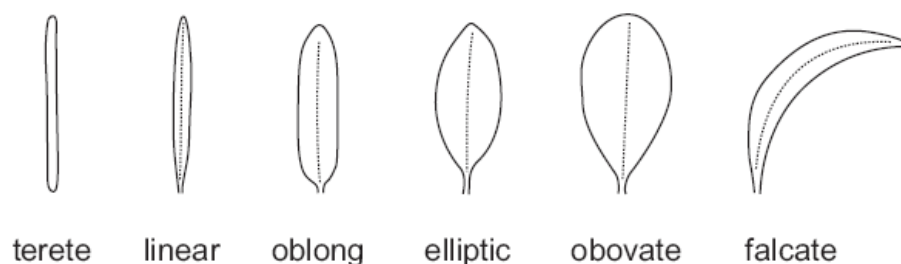


Figure 11 Common phyllode types in mulga in the NE Yilgarn (Moore, 2005)

3.2 Sample preparation

Samples dried in an oven (45°C for 48 hours) while still in calico bags. The samples were of terminal branchlets which contained phyllodes and twigs in varying proportions. In previous studies at Jaguar (Anand et al., 2007) mulga samples had a consistent proportion of phyllode to twig in each sample. In the NE survey, the phyllodes were separated from other parts of the foliage. The dried, separated samples were ground to a fine powder using a cross beater mill (Retsch GmbH, Haan, Germany) and then the milled samples were split for duplicate analyses. The mill was cleaned with ethanol and compressed air before each sample to remove all traces of the previous sample.

3.3 Laboratory analyses

The NW samples were relabelled with new sample numbers, and duplicate samples were prepared for every n^{th} sample (where n is between 15-25). The full batch was sent to Bureau Veritas Laboratories, Perth. Here, 4 g of milled sample was dissolved in 10 mL of nitric acid overnight. The following day another 10 mL of nitric

and 10 mL of hydrochloric acid was added which was then digested for 2 hours at 90°C. The solution was then sent for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Optical Emission Spectrometry (ICP-OES). The elements recorded and the detection limits and HARD (half absolute relative difference) error for each element are shown in Table 1. The HARD error is calculated from the duplicates using the following formula and is expressed as a mean of all the calculations; it provides a measure of reliability of the data.

$$\text{HARD} = ((\text{assay1} - \text{assay2}) / (\text{assay1} + \text{assay2})) \times 100 \quad (1)$$

Table 1 Detection limits and summary of errors for NW and NE data sets. HARD is the Half Relative Difference error; nd is not done where duplicate samples were commonly near or below detection limits providing irrelevant error estimates..

Element	Units	DL	HARD%		Element	Units	DL	HARD%
Ag	ppm	0.001	17.3		Nb	ppm	0.001	nd
Al	ppm	5	5.3		Nd	ppb	5	2.8
As	ppm	0.1	nd		Ni	ppm	0.1	17.2
Au	ppb	0.1	21.8		P	ppm	50	1.7
Ba	ppm	0.05	2.4		Pb	ppm	0.1	nd
Bi	ppm	0.005	13.3		Pr	ppb	2	2.6
Ca	%	0.05	1.6		Pt	ppb	1	nd
Cd	ppm	0.005	nd		Rb	ppm	0.01	1.7
Ce	ppb	5	2.6		S	ppm	50	1.8
Co	ppm	0.01	3.8		Sb	ppm	0.01	20.6
Cr	ppm	0.2	11.2		Sc	ppm	0.1	nd
Cs	ppb	1	3.5		Se	ppm	0.1	nd
Cu	ppm	0.2	2.8		Sm	ppb	5	3.3
Dy	ppb	5	nd		Sn	ppm	0.01	nd
Er	ppb	5	nd		Sr	ppm	0.1	1.8
Eu	ppb	2	5.8		Tb	ppb	2	nd
Fe	%	0.001	2.4		Te	ppm	0.02	nd
Ga	ppm	0.02	nd		Th	ppb	5	5.4
Gd	ppb	5	7.9		Ti	ppm	1	8.5
Hg	ppm	0.005	10.6		Tl	ppb	5	2.3
Ho	ppb	5	nd		Tm	ppb	5	nd
K	ppm	500	1.4		U	ppb	1	6.4
La	ppb	5	2.2		V	ppm	0.5	nd
Li	ppm	0.01	8.9		W	ppm	0.01	nd
Lu	ppb	2	nd		Y	ppb	1	2.4
Mg	ppm	1	1.7		Yb	ppb	5	nd
Mn	ppm	2	1.5		Zn	ppm	1	1.9
Mo	ppm	0.01	2.2		Zr	ppm	0.01	9.0
Na	ppm	10	3.4					

4 Results

4.1 Quality Control

Batch effects, replicates and standards were examined to determine the quality of data. Batch effects with some elemental analyses were noted with the laboratory and these sample batches were repeated (sometimes twice) either in whole or in part. The quality control of analyses was maintained by having laboratory standards, laboratory duplicates and CSIRO in-house reference standards. Summary statistics for each element can be seen in Table 2. The below detection samples were excluded from some statistical calculations but were given a value of half the detection limit when plotted spatially.

Scatter plots for the laboratory duplicate analyses (NW set) of some of the important ore related elements may be seen in Figure 12. Where element concentrations are well above detection the duplicates are consistent, but precision decreases as detection limits are approached (as seen with Au, Ni and, possibly, U). Other elements are shown in the Appendix. Separate quality control of the NE data set samples was undertaken as part of the previous project (Reid et al., 2010). The VS data set was an additional regional data set that was included here and supplemented the data from the NW Yilgarn area.

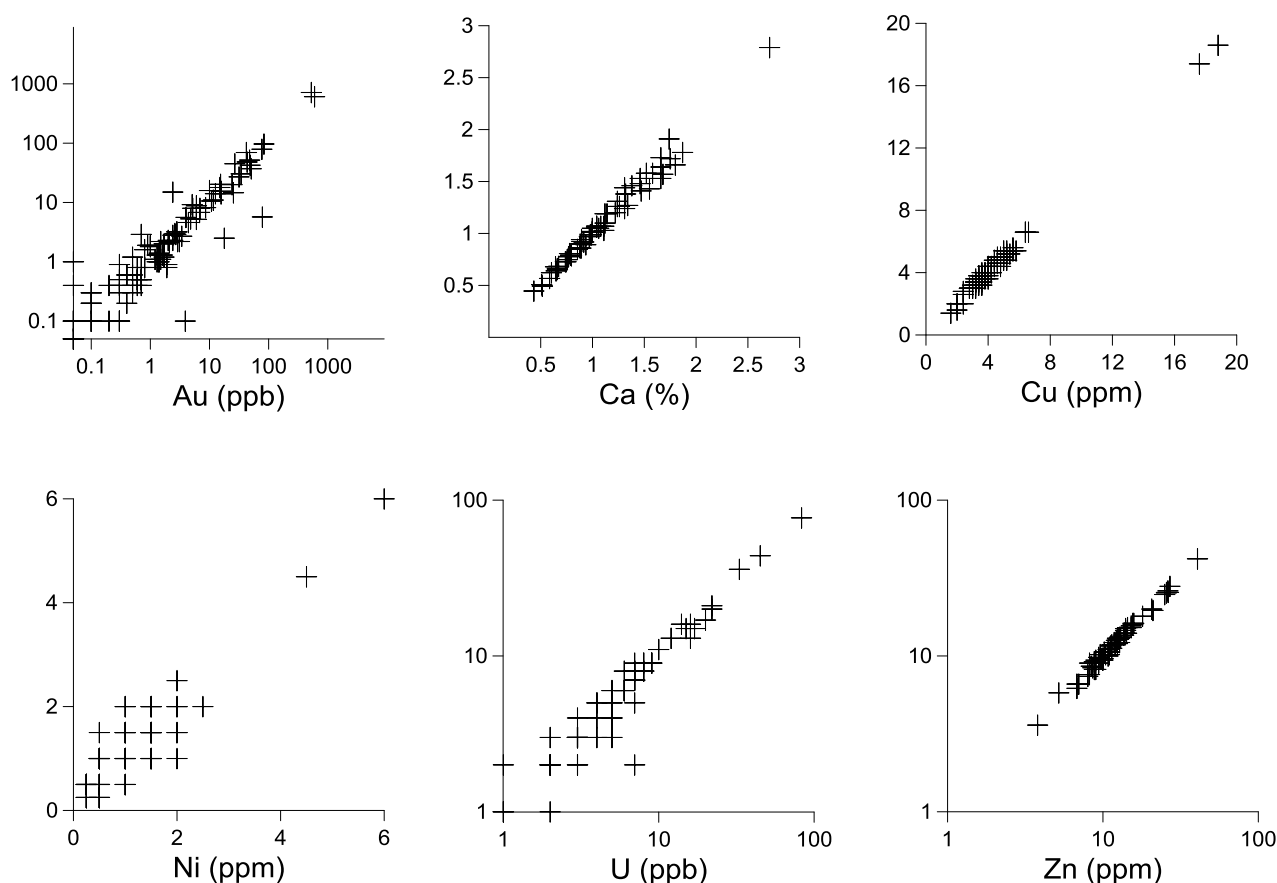


Figure 12 Duplicate analyses for selected elements for the NW Yilgarn data set.

Because a comparison was to be made between a previous data set (NE Yilgarn) and the current data, it was important that the two data sets were comparable. Some standards run on both projects were critical for this comparison to take place. There were three types of standards included with the analyses:

- 1) Bureau Veritas standards including a standard that was run in previous NE Yilgarn project for comparison

- 2) Internal CSIRO standard Mulga R1 that was used for the NE Yilgarn project for comparison
- 3) Other internal CSIRO standards that were not run for the NE Yilgarn project.

The internal CSIRO standards were run "blind" in the analytical batches and were assigned sample numbers as if they were samples unknown to the analysts. Agreement was found to be acceptable between the standards. The greatest differences arose when standards were near detection limits. Some element data is shown in Figure 13 and Figure 14 for the standards and other element data are reported in the Appendix.

The VS data set was independently quality controlled and separate standards were used and not shown here. With some elements e.g. Fe there were clear differences between the VS and the NE and NW data sets; which are discussed under individual elements.

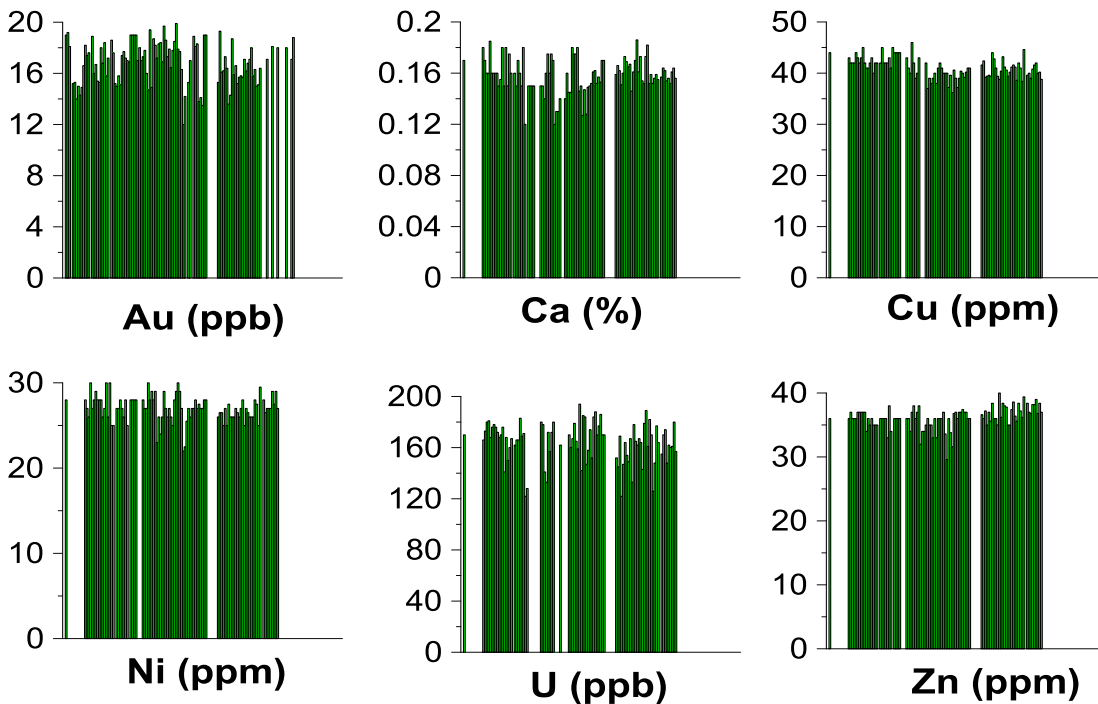


Figure 13: Replicate analyses of selected elements for standard ST257 (Bureau Veritas) run over several biogeochemical projects.

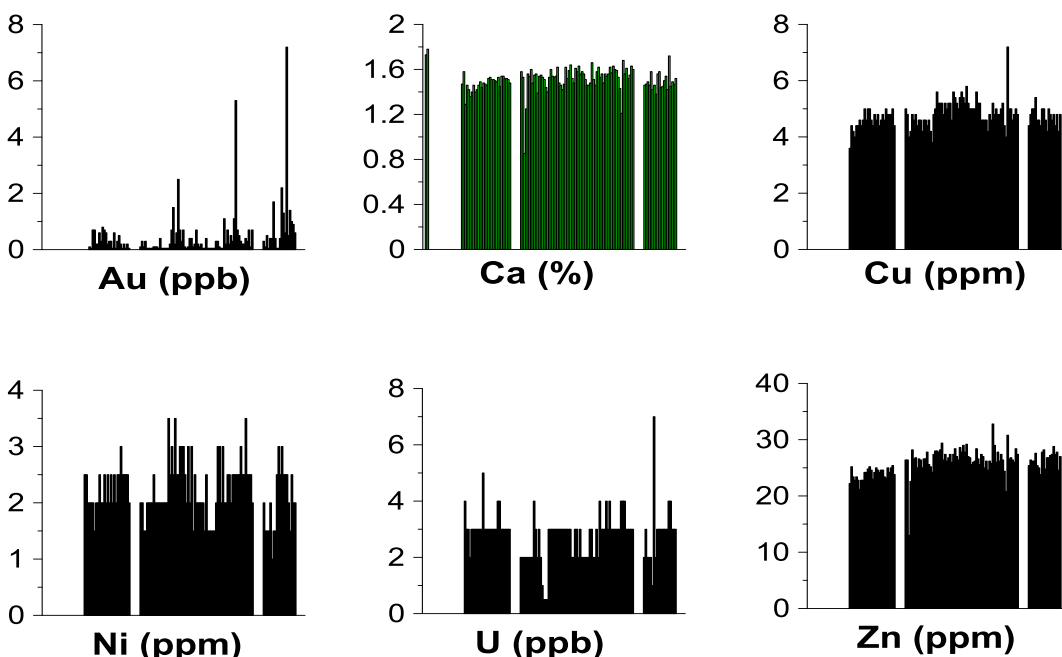


Figure 14: Replicate analyses of selected elements for standard Mulga-R1 run over several biogeochemical projects.

Table 2 Summary statistics and percentiles (1-99) for North Yilgarn mulga phyllode samples. Some elements were not analysed for some of the samples. Some of the minimum statistics were half detection limit.

	Cases	Minimum	Maximum	Mean	Median	Std Dev	1%ile	5%ile	10%ile	25%ile	75%ile	90%ile	95%ile	99%ile
Ag_ppm	2130	0.001	0.088	0.01	0.002	0.01	0.001	0.001	0.001	0.001	0.006	0.012	0.016	0.04
Al_ppm	2130	2.5	875	136	120	90	10	30	45	75	180	250	300	405
As_ppm	2130	0.05	19.7	0.16	0.1	0.52	0.05	0.05	0.05	0.05	0.2	0.3	0.4	0.9
Au_ppb	2130	0.05	28	0.51	0.4	0.86	0.05	0.05	0.05	0.1	0.7	1	1.445	3.069
B_ppm	2130	2	449	29	26	19	12	14	16	20	34	44	52	92
Ba_ppm	2130	0.025	89	2.58	1.05	5.29	0.2	0.3	0.4	0.6	2.15	5.39	10	26
Bi_ppb	2130	2.5	260	5.47	2.5	11	2.5	2.5	2.5	2.5	2.5	10	20	45
Bi_ppm	2130	0.0025	0.26	0.01	0.0025	0.01	0.0025	0.0025	0.0025	0.0025	0.0025	0.01	0.02	0.045
Ca_ppm	2130	610	48900	11411	10700	4305	4582	6200	7091	8590	13300	16800	19100	26883
Cd_ppm	2130	0.0025	0.31	0.01	0.0025	0.01	0.0025	0.0025	0.0025	0.0025	0.005	0.01	0.02	0.04
Ce_ppb	2130	2.5	4700	492	350	461	47	95	135	210	606	980	1400	2437
Co_ppm	2130	0.005	1.7	0.08	0.07	0.08	0.005	0.005	0.02	0.05	0.1	0.14	0.18	0.39
Cr_ppm	2130	0.1	12	0.83	0.6	0.86	0.1	0.1	0.2	0.4	1	1.6	3	4.2
Cs_ppb	2130	0.5	176	13	12	8.55	3	5	6	8	16	21	26	42
Cu_ppm	2130	0.4	22	4.42	4	1.97	1.4	2.2	2.4	3	5	6.8	8	11
Dy_ppb	2035	2.5	260	27	15	29	2.5	2.5	5	10	35	55	85	150
Er_ppb	2035	2.5	140	13	10	15	2.5	2.5	2.5	2.5	15	30	45	80
Eu_ppb	2035	1	90	9.27	6	9.85	1	1	1	4	12	20	28	50
Fe_ppm	2130	5	2670	202	170	140	40	65	80	120	245	345	447	680
Ga_ppm	2130	0.01	0.26	0.05	0.04	0.03	0.01	0.01	0.01	0.04	0.06	0.08	0.1	0.16
Gd_ppb	2035	2.5	385	41	30	43	2.5	2.5	10	15	50	85	125	225
Hf_ppb	2130	0.0005	35	3.61	2.5	2.93	0.003	2.5	2.5	2.5	2.5	9.5	10	15
Hg_ppm	2130	0.0025	0.315	0.02	0.02	0.01	0.005	0.01	0.01	0.015	0.025	0.0298	0.03	0.04
Ho_ppb	2035	2.5	55	5.14	2.5	6.04	2.5	2.5	2.5	2.5	5	10	15	35
K_ppm	2130	1300	20500	8577	8310	2282	3934	5346	5961	7090	9880	11500	12600	15269
La_ppb	2130	2.5	3800	371	255	371	27	60	80.5	140	446	795	1070	1935
Li_ppm	2130	0.005	5.02	0.14	0.09	0.21	0.02	0.03	0.04	0.06	0.16	0.26	0.39	0.84
Lu_ppb	2035	1	12	1.32	1	1.07	1	1	1	1	1	2	4	6
Mg_ppm	2130	0.5	5420	1254	1170	522	460	650	720	900	1490	1850	2150	3090
Mn_ppm	2130	5.5	1450	156	82	188	10	16.5	21.5	37	199	398	562	944
Mo_ppm	2130	0.01	98	1.48	0.24	4.52	0.01	0.01	0.01	0.04	1.1	3.558	6.767	22
Na_ppm	2130	10	6120	315	180	440	30	40	60	100	360	660	1000	2237
Nb_ppm	2130	0.0005	1.14	0.01	0.01	0.04	0.0005	0.003	0.004	0.006	0.016	0.024	0.032	0.07
Nd_ppb	2035	2.5	2460	270	180	281	20	45	60	105	330	580	805	1420
Ni_ppm	2130	0.2	33.5	1.52	1.5	1.31	0.25	0.25	0.5	1	2	2.5	3.5	5.845
P_ppm	2130	80	2260	649	620	176	360	450	480	540	730	850	960	1227
Pb_ppm	2130	0.05	3.9	0.26	0.2	0.28	0.05	0.05	0.05	0.05	0.3	0.6	0.8	1.1
Pr_ppb	2035	1	646	73	50	74	6	12	16	28	90	156	214	377
Pt_ppb	2130	0.5	6	0.56	0.5	0.25	0.5	0.5	0.5	0.5	0.5	1	1	1
Rb_ppm	2130	0.02	18	4.03	3.67	2.09	0.76	1.34	1.74	2.58	5.07	6.7	7.78	10.8
Re_ppb	2130	0.5	105	6.34	4	8.86	0.5	0.5	0.5	2	7	14	21	48
S_ppm	2130	145	25900	1380	1240	1446	820	960	1030	1130	1360	1490	1600	3000
Sb_ppm	2130	0.005	0.49	0.01	0.005	0.02	0.005	0.005	0.005	0.005	0.01	0.03	0.04	0.08
Sc_ppm	2130	0.05	0.6	0.09	0.05	0.06	0.05	0.05	0.05	0.05	0.1	0.2	0.2	0.3
Se_ppm	2130	0.05	7.4	0.19	0.1	0.25	0.05	0.05	0.05	0.05	0.2	0.4	0.5	0.8
Si_ppm	2035	2	280	68	66	32	8	22	30	46	88	108	124	163
Sm_ppb	2035	2.5	370	43	30	43	2.5	10	10	15	50	90	125	225
Sn_ppm	2130	0.01	0.9	0.05	0.04	0.06	0.01	0.01	0.01	0.01	0.06	0.1	0.14	0.3
Sr_ppm	2130	0.21	497	62	54.2	41	9.6	17.6	24	37	78	103	124	223
Ta_ppb	2130	2.5	135	3.06	2.5	4.00	2.5	2.5	2.5	2.5	2.5	2.5	5	20
Tb_ppb	2035	1	44	4.84	4	5.48	1	1	1	1	6	12	16	28
Te_ppm	2130	0.01	0.06	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Th_ppb	2130	2.5	450	46	40	35	2.5	10	15	25	55	85	110	180
Ti_ppm	2130	0.5	14	2.22	2	1.55	0.5	0.5	0.5	1	3	4	5	8
Tl_ppb	2130	2.5	265	13	10	18	2.5	2.5	2.5	2.5	15	25	40	98
Tm_ppb	2035	2.5	15	2.72	2.5	1.20	2.5	2.5	2.5	2.5	2.5	2.5	2.5	10
U_ppb	2130	0.5	210	8.49	6	10	1	2	3	4	9	16	21	59
V_ppm	2130	0.25	4.5	0.57	0.5	0.41	0.25	0.25	0.25	0.25	1	1	1	2
W_ppm	2130	0.005	0.78	0.02	0.01	0.04	0.005	0.005	0.005	0.005	0.02	0.04	0.05	0.13
Y_ppb	2130	0.5	2370	219	130	267	13	27	40	68	258	492	709	1324
Yb_ppb	2130	0	75	7.83	5	8.92	0	2.5	2.5	2.5	10	15	25	48
Zn_ppm	2130	2	77	14	12.8	5.24	5.6	7.4	8.4	10.2	15.8	19.6	22.6	31
Zr_ppm	2130	0.005	0.8	0.12	0.11	0.08	0.0131	0.03	0.04	0.07	0.1525	0.22	0.27	0.4

The categories for the data are data source, geology, regolith, tectonic and phyllode shape. Classes for each category were determined from their location, data source membership or phyllode shape e.g. regolith category has the classes colluvium, in situ, LAC (lacustrine-alluvium and calcrete) and sandplain. The number of class cases for each category varies considerably and, presumably, has had a bearing on the interpretations drawn about relationships between elements for each class (Figure 17); for example data for granite (n=1397) would be more robust than for dolerite (n=32).

Probability plots of the data sets may flag potential bias in the element analyses between analytical batches.

However, in this study, the data categories broadly correspond with tectonic categories. For example, NW Yilgarn data set encompasses the Youanmi Terrane while the NE Yilgarn data set includes the Eastern Goldfields Terrane. Therefore, elemental differences between data categories may be due to geological differences rather than any analytical bias. This is borne out by comparing probability plots of the same elements of the data source category (Figure 15) and the tectonic category (Figure 16); the probability plots are quite different suggesting that any concerns about analytical bias are unjustified. Furthermore, analytical standards confirm that the NE and NW data sets are comparable.

Comparing means and variances between different variables provides a method where statistical significance may be calculated. However, performing multiple Student's t tests on classes may increase the family-wise (Type 1) error rate which is the probability of making one or more false interpretations among all the hypotheses when performing multiple hypotheses tests. There are several ways to minimise this happening with one of the more conservative methods being the Bonferroni correction method. Here, the significant results of Student's t results are reported but the lesser number satisfying the Bonferroni correction (in addition) are additionally documented i.e. means of pairs showing the strongest differences between each other.

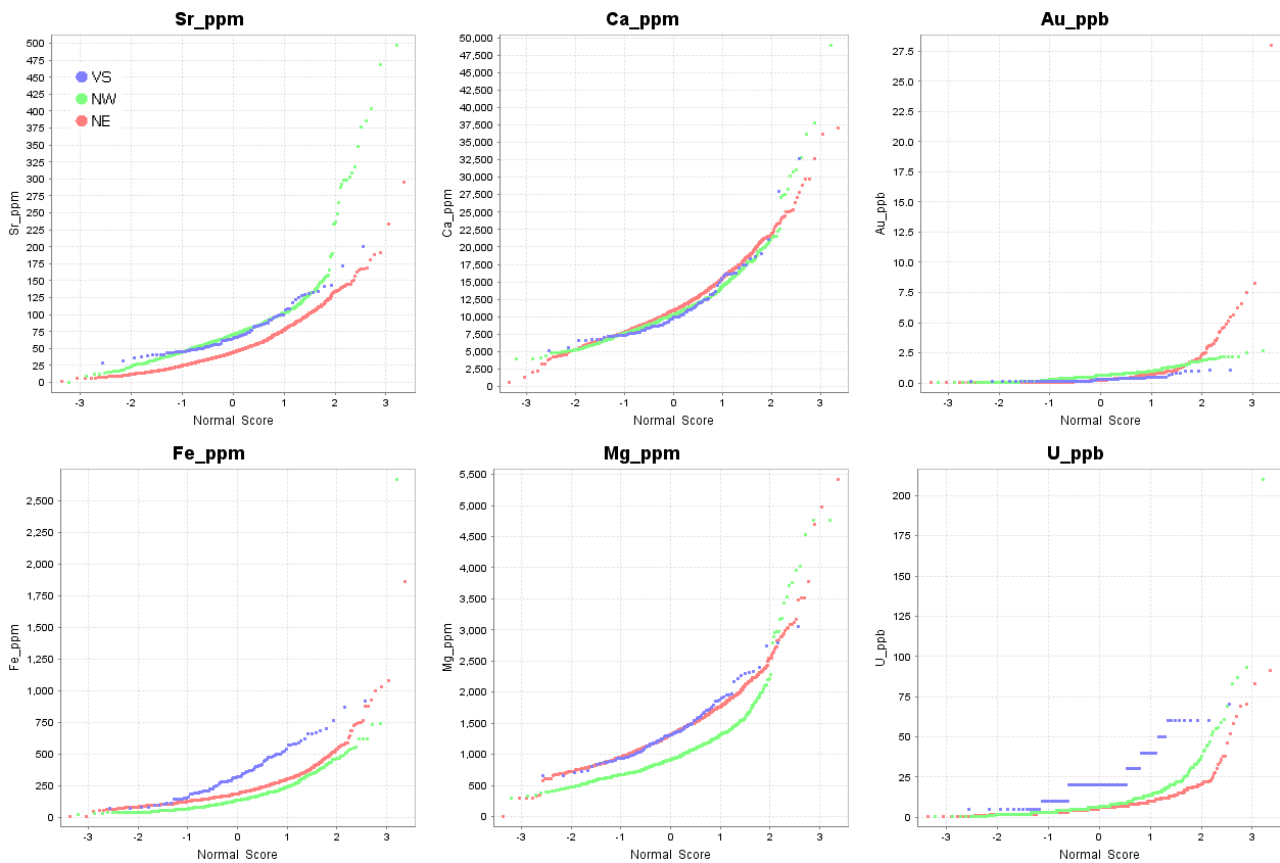


Figure 15: Probability plots of the data source category. Note the divergence of some elements for some data sources e.g. NE Yilgarn has lower Sr values.

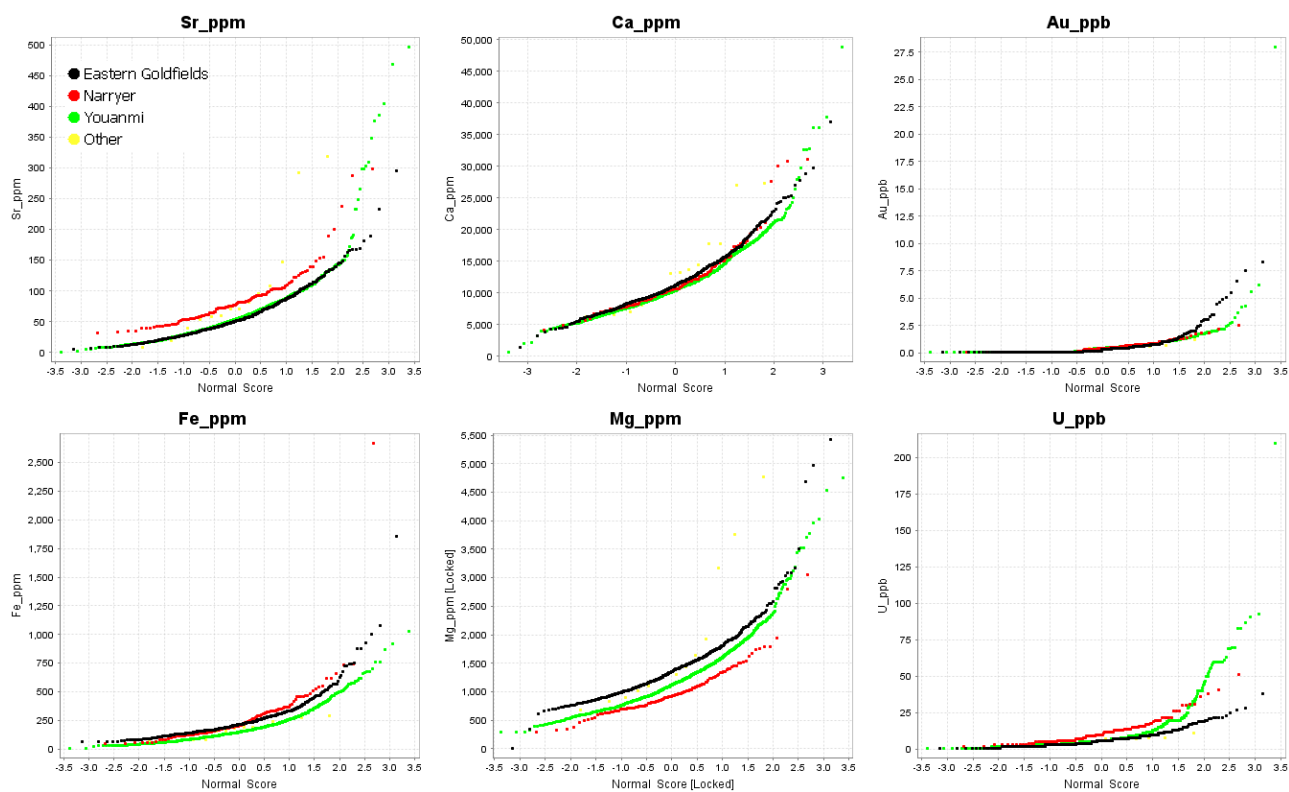


Figure 16: Probability plots of the tectonic category. Note the divergence of some elements for some data e.g. Eastern Goldfields has higher Mg values.

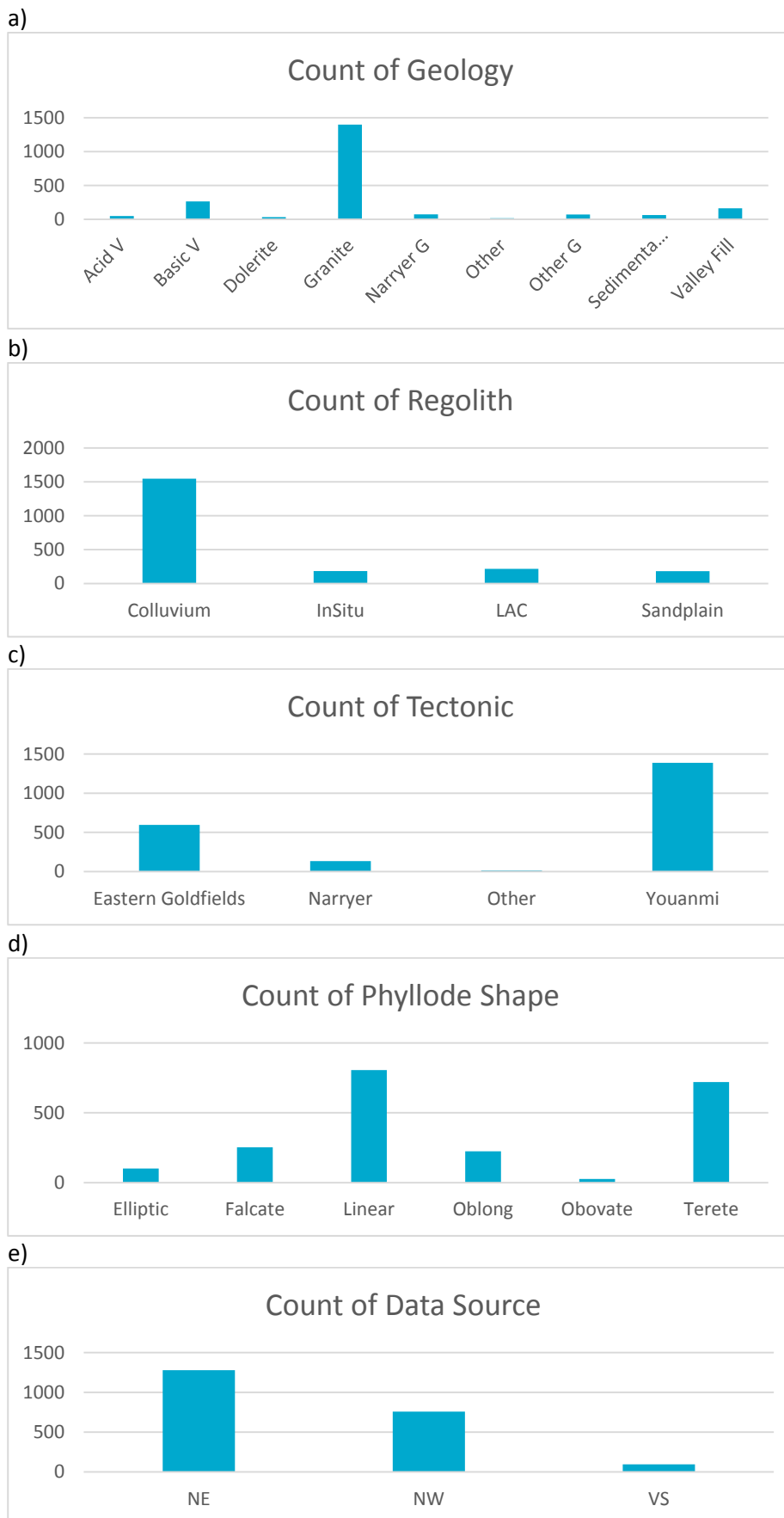


Figure 17: Comparison of case numbers (samples) occurring in each group for each of the categories analysed in the regional study a) geology category, b) regolith category, c) tectonic category d) phyllode shape category and e) data source.

4.2 Distribution of phyllode class

One of the features of the NE Yilgarn data set was mapping the distribution of phyllode classes. Combining NE with the NW (and VS) data sets, there is a significant difference in the distribution of phyllode classes that was sampled over the north Yilgarn. This probably reflects a real difference in the availability of the phyllode class to sample and therefore a real difference in the distribution of phyllode class occurrence. Samplers, while charged with the task to sample the nearest tree to the groundwater sampling site, may introduce bias and may, inadvertently, sample trees with a phyllode class previously sampled. It is clear from Figure 18 that the terete phyllode class is most common in the northern NW Yilgarn compared with the NE where linear are sampled more frequently. Interestingly of the terete phyllodes sampled in the NE most are in the northern part. Thus, an EW trend is clear for the north Yilgarn considered as a whole (blue circles) with linear replacing terete with increasing distance from the west (red circles). Therefore, differences in elemental concentration between linear and terete phyllodes may be due to locality rather than shape.

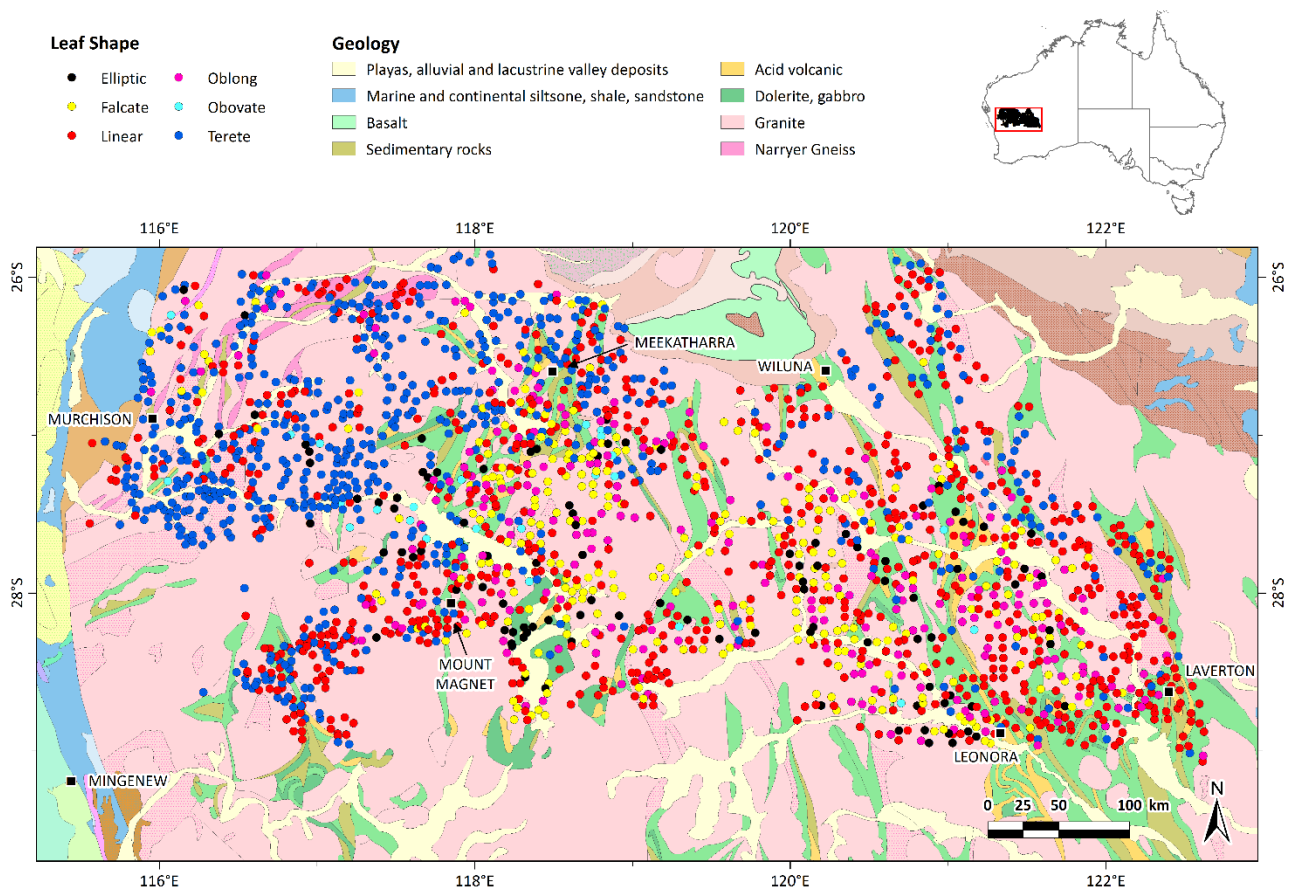


Figure 18 Distribution of phyllode class across the north Yilgarn

The probability plots for the elements showed that there were some differences in the data for elements which needs to be considered with other category differences such as data source, regolith geology, etc. For example, if terete class are inherently more Na-rich then these phyllodes will be different regardless of other factors. Some elements in the NE Yilgarn survey (e.g. K, Na, Mg, Ca and Sr) showed some probability divergence indicating inherent differences in the elemental content of certain phyllode types. These were thought to be attributable to surface area to volume ratio of the different phyllode class shapes. For the NY data set selected elements are shown in Figure 19. Elements not showing this divergence are shown below this in Figure 20.

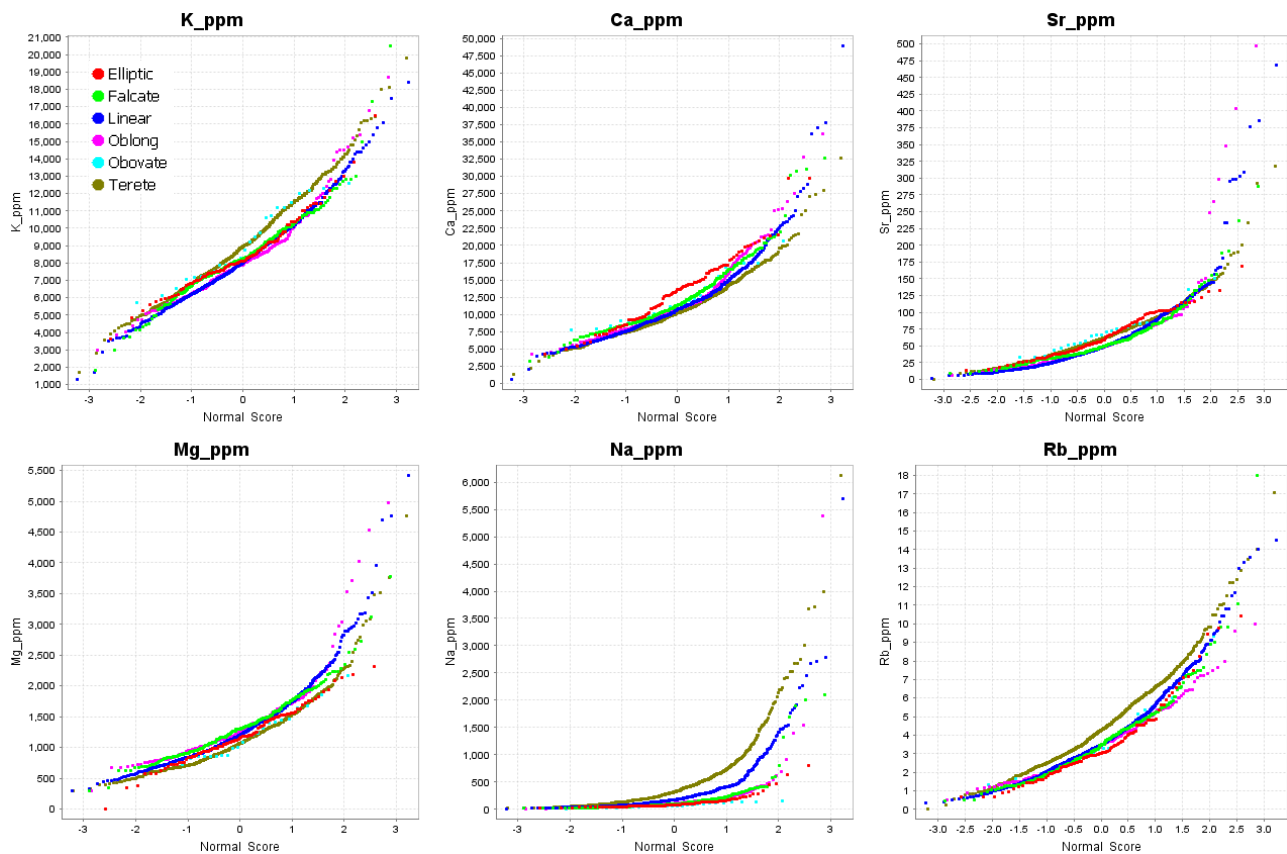


Figure 19: Examples of elements that showed some probability divergence in the NE Yilgarn data set. Now that NW Yilgarn has been added to the data, Sr and Mg do not show divergence as with the NE Yilgarn alone.

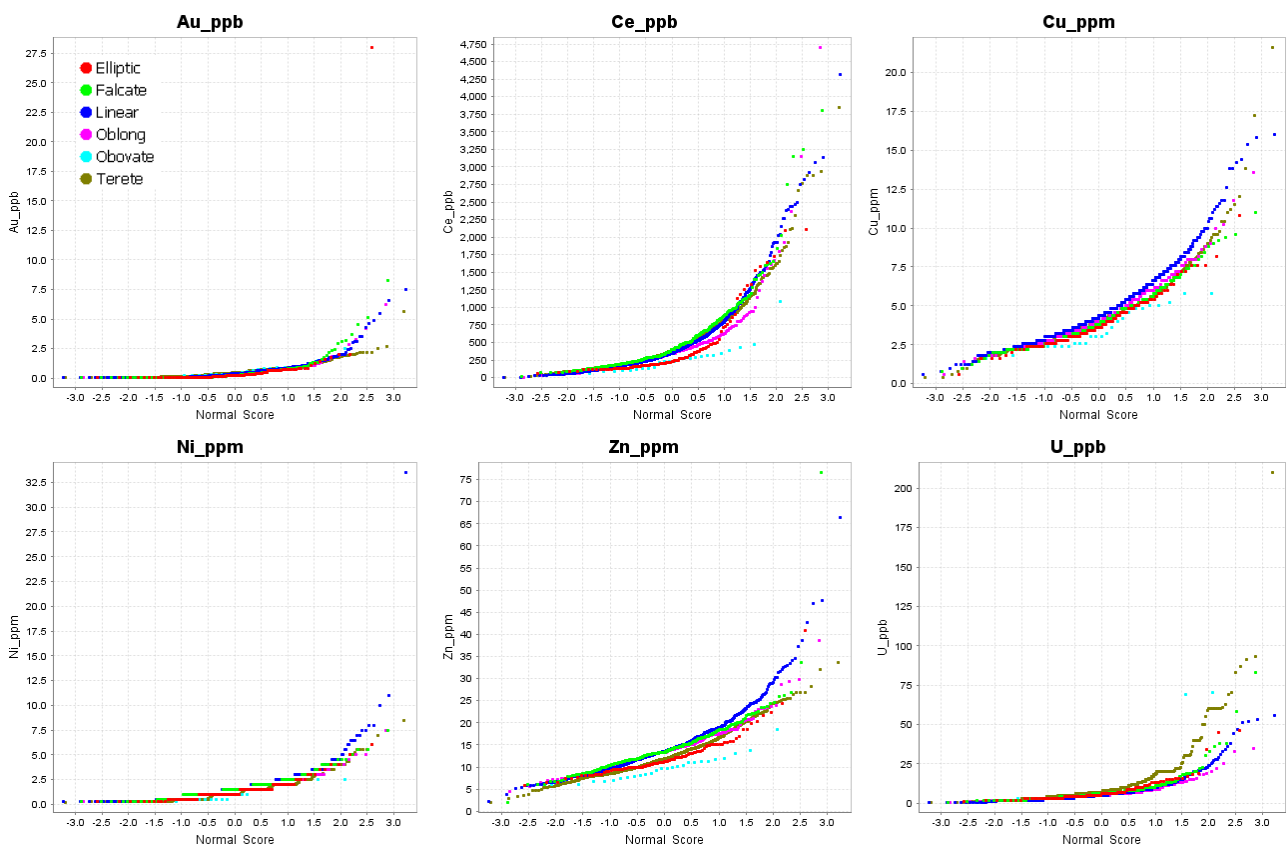


Figure 20: Examples of elements mostly showing little probability divergence.

4.3 Alkaline Earth Metals

Calcium and Mg are essential plant elements whereas Sr is not, but commonly substitutes for Ca in carbonates and other minerals and probably oxalate in plants. The alkaline earth metals (Ca, Mg, and Sr) for the N Yilgarn do not appear to show any broad trend in concentration gradients.

The distribution maps of the Ca (Figure 21), Mg (Figure 23) and Sr (Figure 24) show some interesting trends. While Ca shows a fairly heterogeneous distribution across the north Yilgarn, Mg is more concentrated in the east and Sr in the west; there are some elevated single values for Mg in the west. The reasons for these trends are unclear but higher Mg may be related to more greenstones in the east. The scatter plot Ca vs. Sr suggests that the higher Sr in the Narryer Gneiss may be the cause of these elevated Sr values in the upper north Yilgarn.

Mean and standard deviation for Ca, Mg and Sr are 1.14%, 0.125%, 62 ppm and 0.43%, 0.52%, 40.1 ppm, respectively (Table 2). All data are above the detection limits. There are significant differences (Student's t, $p=0.05$) between:

- 1) Terete-shaped phyllodes and all other phyllode types, with terete having the lowest mean Ca concentrations. For Mg, the differences between phyllode types are less marked and only significantly so between elliptic-oblong, falcate-terete, falcate-linear and falcate-oblong. For Sr, the significant differences occur between elliptic-falcate, elliptic-linear, falcate-terete and linear-terete. This finding contradicts the findings from the NE Yilgarn which show the terete class had the highest Ca concentrations.
- 2) NW and NE data sets with Ca means of 1.11% and 1.16% respectively. Data set category classes are more significantly different for Mg with means of 0.1% and 0.14% between NW and NE. The Sr mean for the NE data set (51 ppm) is significantly lower than NW (78 ppm) and VS (74 ppm). It is unclear why there is a divergence in association between these alkaline earth metals (which are normally strongly associated) for the data sets.
- 3) Several of the geological classes for Ca, the greatest of which are between dolerite-granite, other gneiss-valley fill and dolerite-other gneiss but these are not significant once the Bonferroni correction test is applied.
- 4) Tectonic class Eastern Goldfields and Youanmi for Ca.
- 5) Each of the tectonic classes for Mg. The Mg means (%) for Eastern Goldfields, Narryer and Youanmi are 0.14, 0.10 and 0.12, respectively.
- 6) Several of the geological classes for Mg. The highly significant differences (which pass the Bonferroni correction test) are between basic volcanic-granite, basic volcanic-Narryer Gneiss, basic volcanic-valley fill and Narryer Gneiss-sedimentary rocks. The basic volcanic mean is 0.14 % and the granite is 0.12 % Mg.
- 7) Several of the geological classes for Sr. The most significant of these differences are between Narryer Gneiss and nearly every other class. The mean concentration of Sr is 88 ppm (20-30 ppm greater than most other classes) which may partly explain why the NW data set (containing the Narryer Gneiss) has the highest Sr mean; we can speculate that the Narryer Gneiss may have higher Sr in regolith.
- 8) Narryer-Eastern Goldfields and Narryer-Youanmi for Sr.
- 9) All the regolith unit pairs for Sr compared except for colluvium-sandplain.

Summary: Within the alkaline earth data there are enough significant differences between classes within several categories so that mulga may be used, with further statistical treatment, to discriminate for classification purposes.

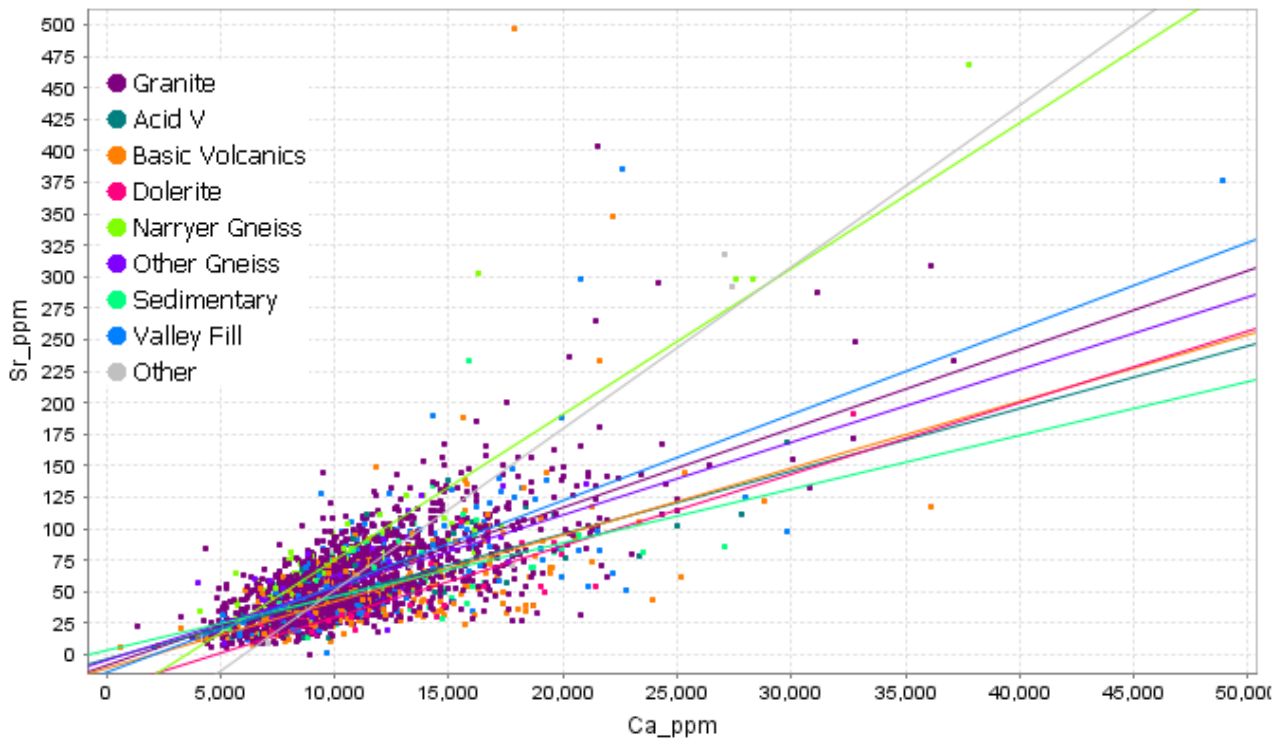


Figure 21: Scatter plot of Ca (ppm) vs. Sr (ppm) colour coded by geology. Regression lines are shown for Ca on Sr.

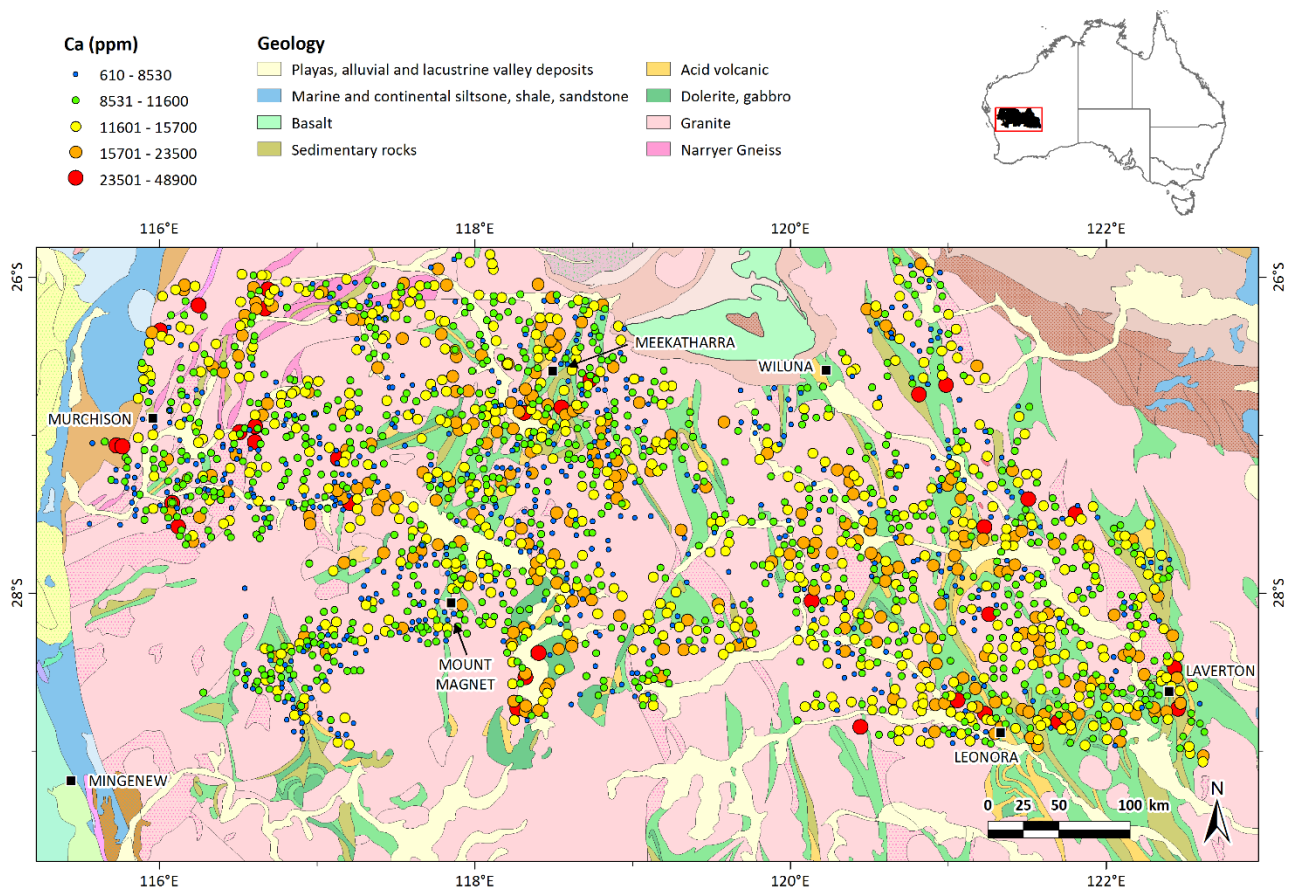


Figure 22: Distribution of Ca in the north Yilgarn mulga phyllode samples.

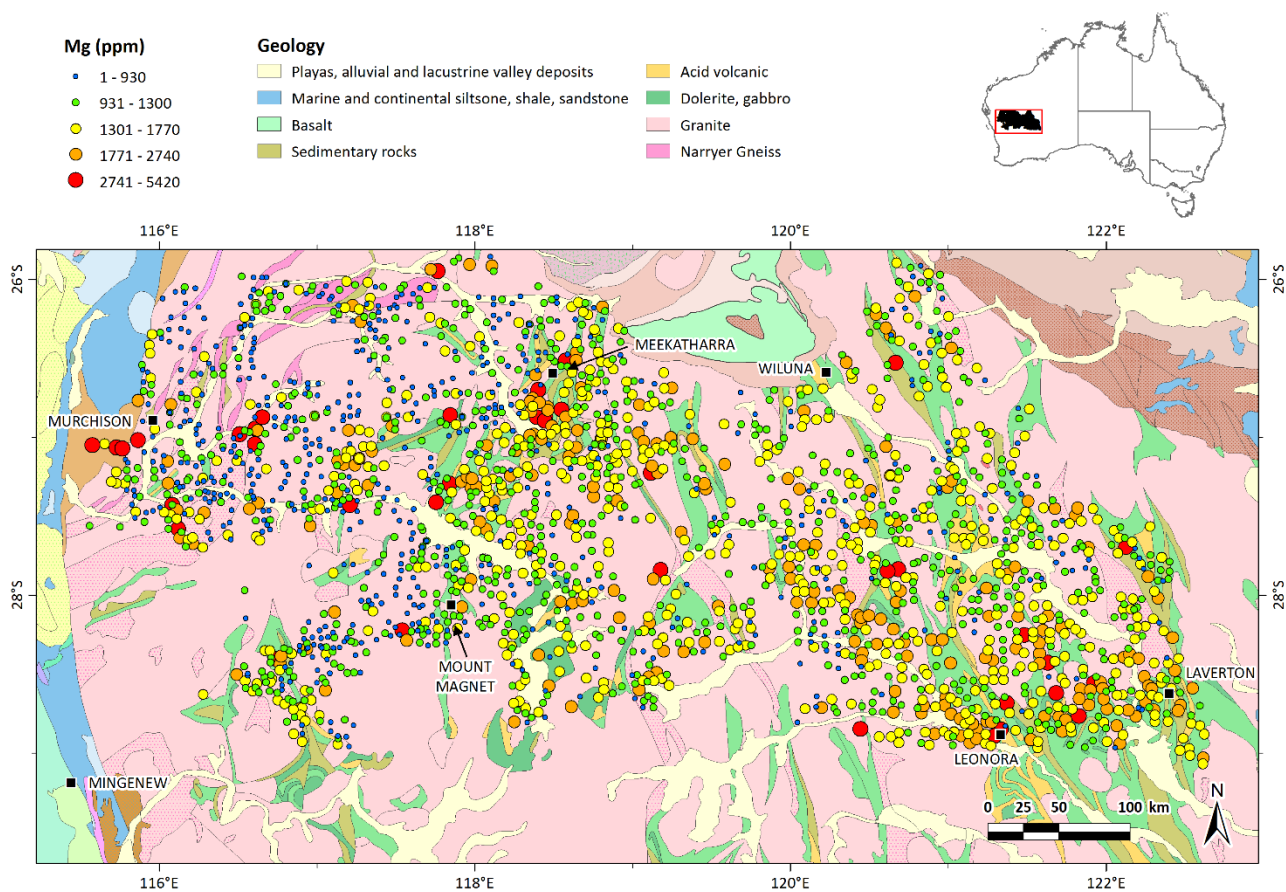


Figure 23: Distribution of Mg in the north Yilgarn mulga phyllode samples.

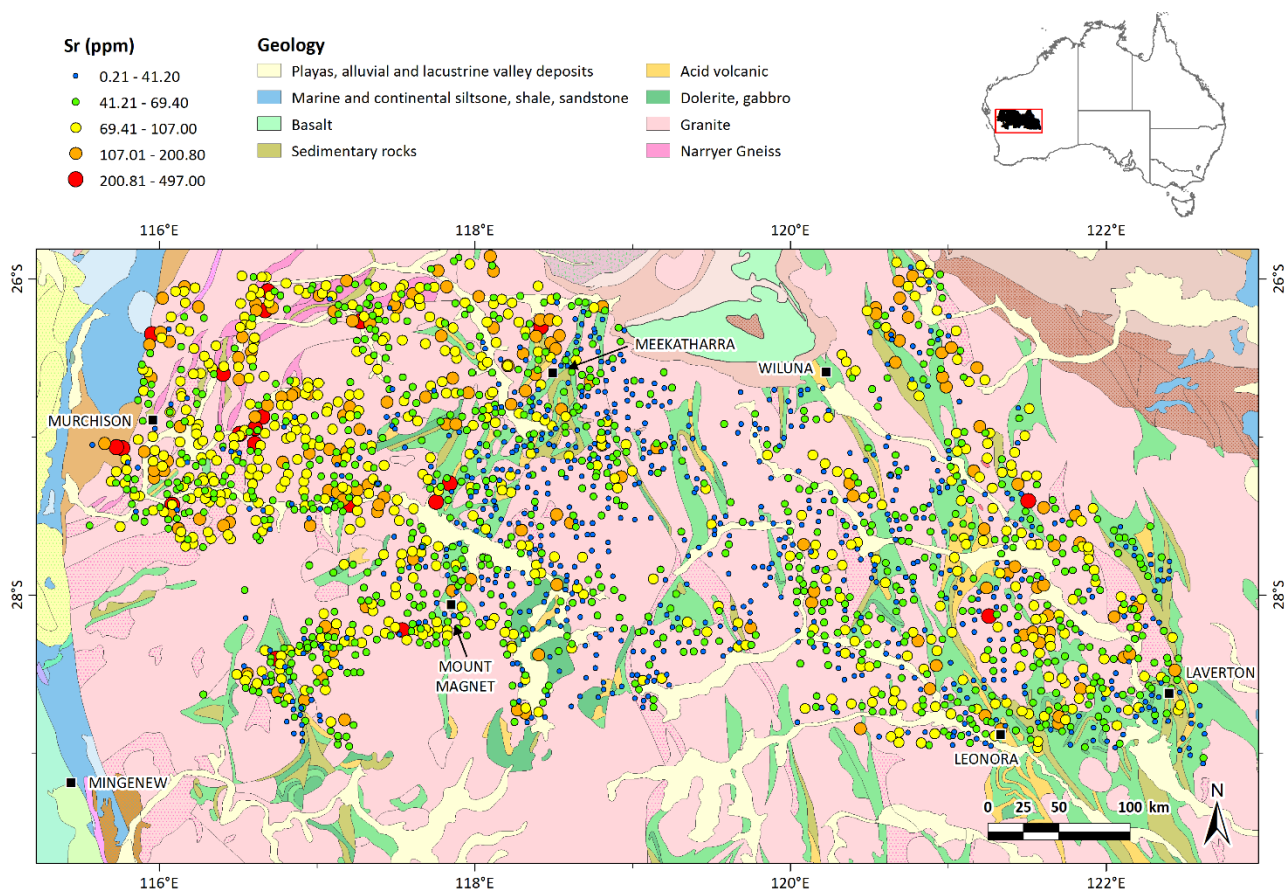


Figure 24: Distribution of Sr in the north Yilgarn mulga phyllode samples.

4.4 Iron and related elements

It has previously been suggested (Reid et al., 2010) that Fe, Al, Th and Zr are associated with dust on plants particularly those that may be growing along roads and which may lead to higher than expected concentrations of these elements to be reported. The Th was included to account for clays (Nathan Reid, pers. comm.) although Al is found in many clays. Thorium distribution is shown in Figure 26. Clearly there is a gradient of higher concentrations in the east particularly east of Murchison; there is also a broad zone of low concentrations between Meekatharra southwards to Mt Magnet and further west. With Fe, Al and Zr the same trends are apparent but are weaker. In addition, clusters of high concentrations of Fe and Al are apparent in the E part of the distribution map. Spatially large associations over several tens of km² are unlikely to be attributable to areas that are more (or less) susceptible to dust contamination than other areas; more likely is that random samples near roads or animal troughs that are likely to adsorb more dust. It is possible that these clusters are due to an analytical artefact but this hypothesis is not supported by detailed scrutiny of the standards, replicates and analytical batch sequence.

Of Fe, Al, Th and Zr, only Fe is recognised as an essential plant nutrient although Al has been suggested to be included as another (Dunn, 2007). Notwithstanding the status of Fe as an essential plant nutrient, high concentrations of Fe should be treated suspiciously. Red colouration of leaves and phyllodes is commonly seen next to unsealed roads and occasionally around water bores suggesting windblown dust is a major contributor. Even if vegetation is washed, there is no guarantee that the dust has been entirely removed since it can penetrate the stomata of plants. Aluminium is strongly correlated with Fe for phyllode category (0.82) but is not easily visually recognised on vegetation as with Fe (red). Aluminium is found in clays (as well as within Fe oxides (oxyhydroxides)) and because of this, Al is even more likely to occur as dust particles than Fe itself. With these elements, and the minerals they are associated with, a host of siderophiles such as Ni, Co, and Mn and chalcophiles such as V, Cr, Cu, Zn and As may be correlated with Fe and/or Al and data interpretation treated with caution.

The distribution maps for Fe, Al, Th and Zr show concomitant clusters of high concentrations and of low concentrations for these elements. High concentrations include large areas to the NW, 100 km east of Murchison and in the SE as well as smaller clusters elsewhere e.g. near Wiluna. Low concentrations include a large area in the SW. It is unclear whether elevated levels are due to dust, natural elevations of these elements or an analytical issue, but for whatever reason these data should be treated with caution.

Mean concentrations (ppm) of Fe, Al, Th and Zr are 200, 136, 0.046 and 0.12, respectively (Table 2). Iron and Al are considered here to represent the group of elements (of the four) that may be associated with dust. It was observed:

- 1) All phyllode classes are significantly different in Fe concentration from one another except for linear-falcate, elliptic-oblong and falcate-oblong pairs.
- 2) For Fe, the phyllode classes that most significantly differ are obovate-terete, elliptic-terete and linear-obovate pairs. For Al, elliptic class (mean of 116 ppm) is dissimilar to all other phyllode classes except for oblong class; obovate (77 ppm) is dissimilar to all other types.
- 3) Data sources are all significantly different from one another for Fe and Al. For example, VS class has a mean of 350 ppm Fe compared with NE (216 ppm) and NW (160 ppm). This suggests that the Fe data may be due to an analytical effect.
- 4) For Al and Fe, the Youanmi terrane is significantly different from Eastern Goldfields and Narryer terranes;
- 5) Sandplain class (mean of 177 ppm Fe) is significantly different from all other regolith units; all regolith units for Al have similar means (between 133-137 ppm).

Summary: These group of elements have been used to determine if plants may be used to detect dust contamination. The data suggest a strong E to W "more dust" trending pattern. The VS data show abnormal behaviour suggesting that these are problematic and should be used cautiously.

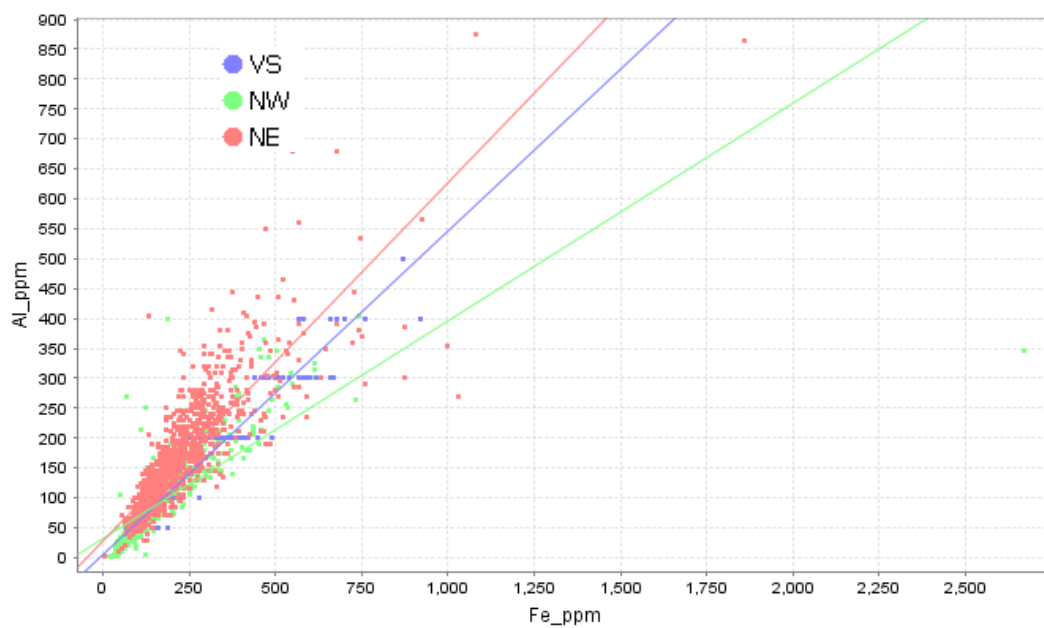


Figure 25: Scatter plot for Fe (ppm) vs. Al (ppm) for mulga in the north Yilgarn. Colour-coded by data source.

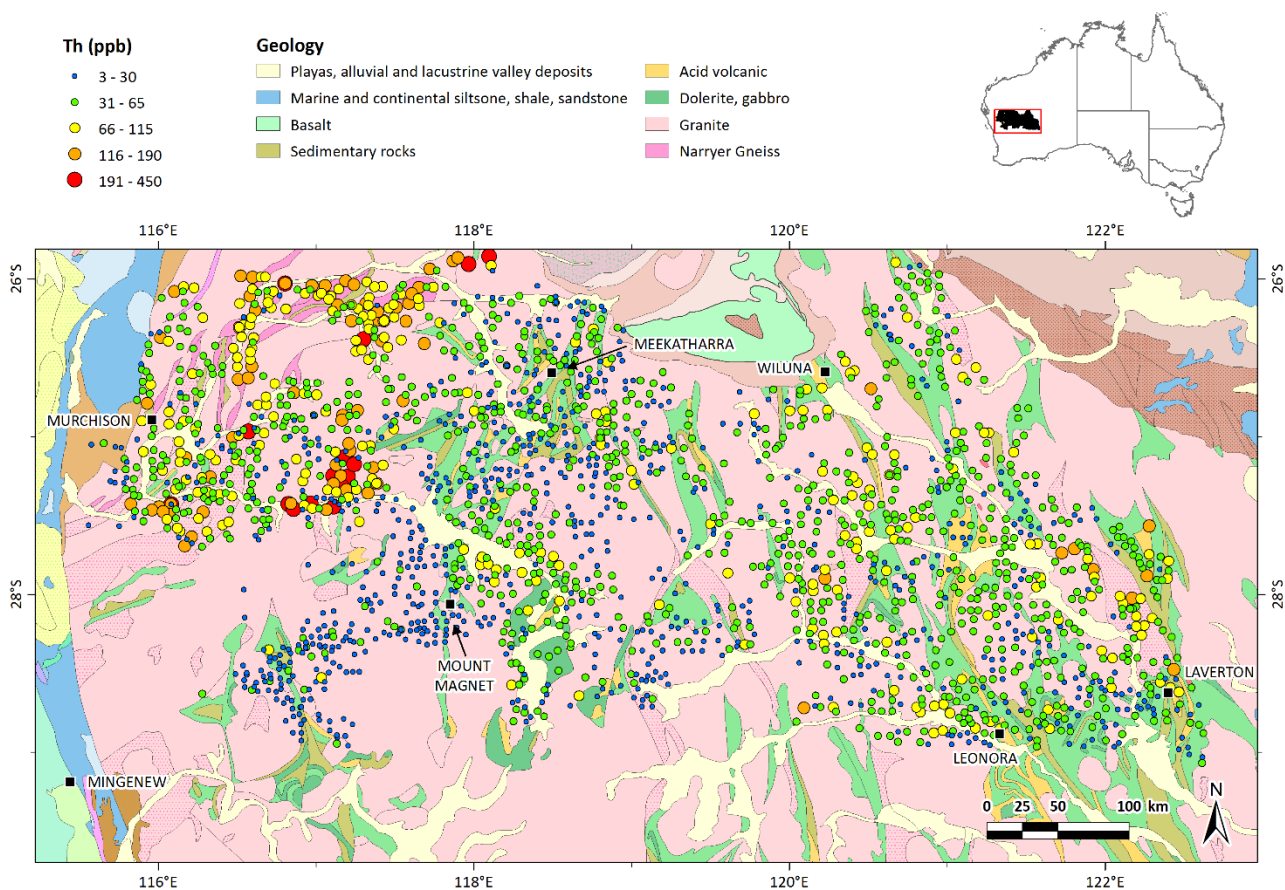
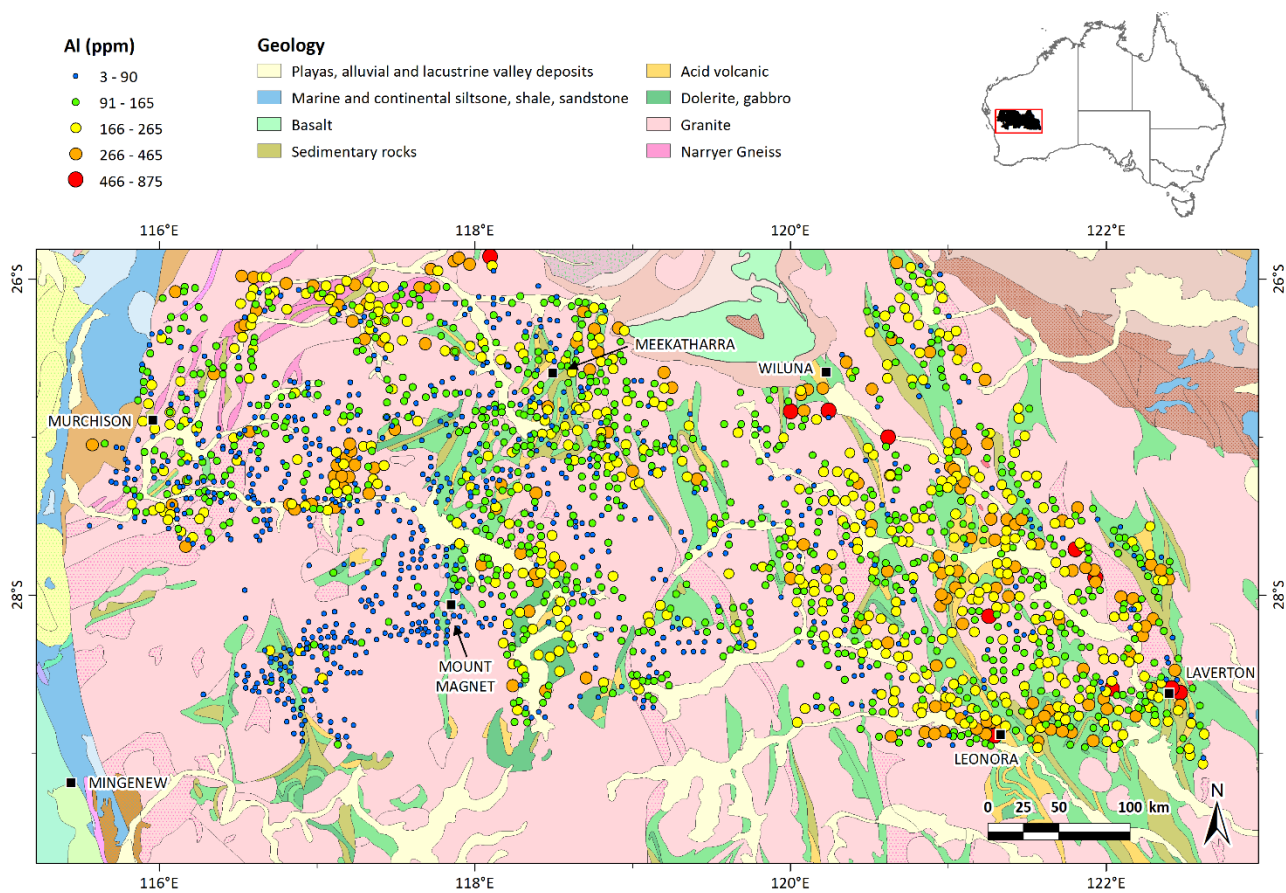
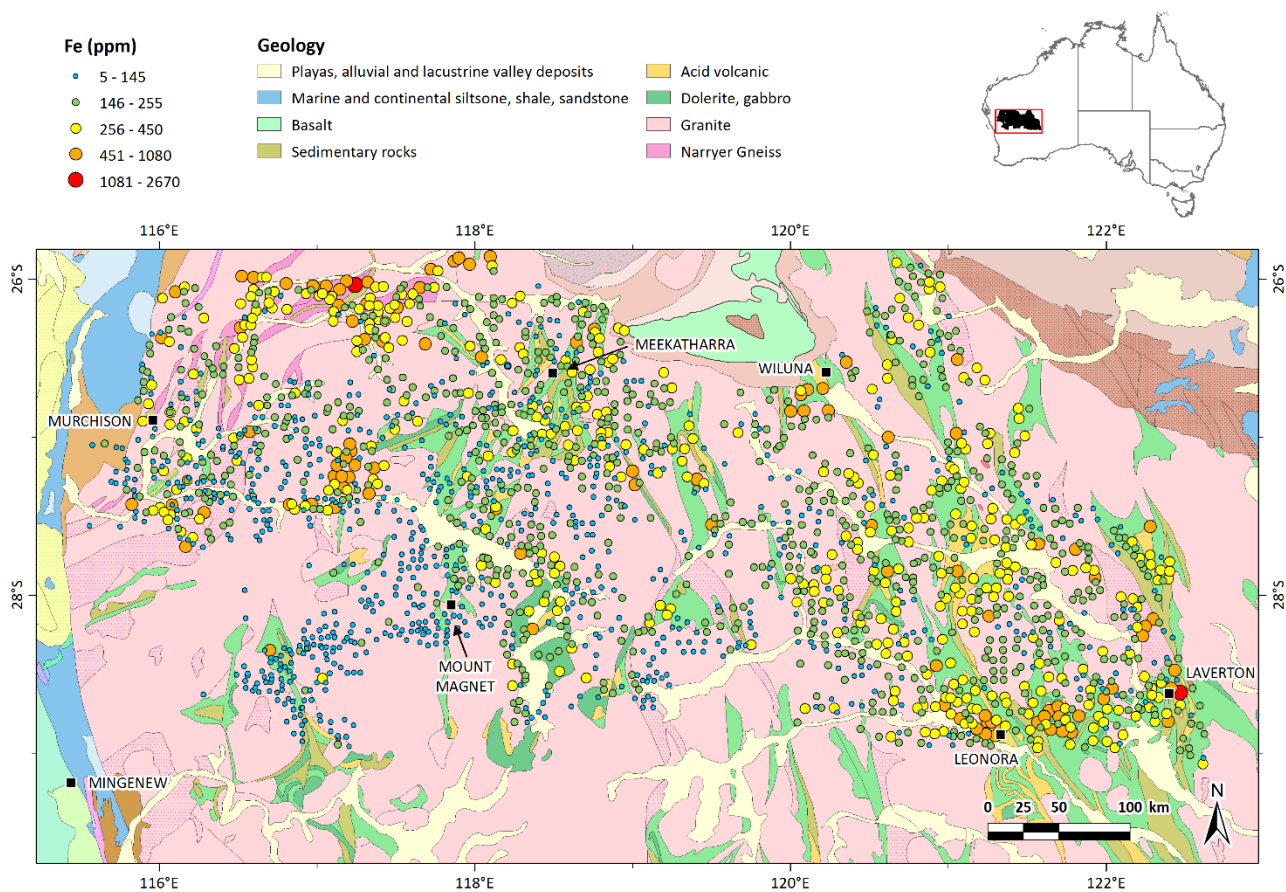


Figure 26: Distribution of Th in mulga phyllodes in north Yilgarn.



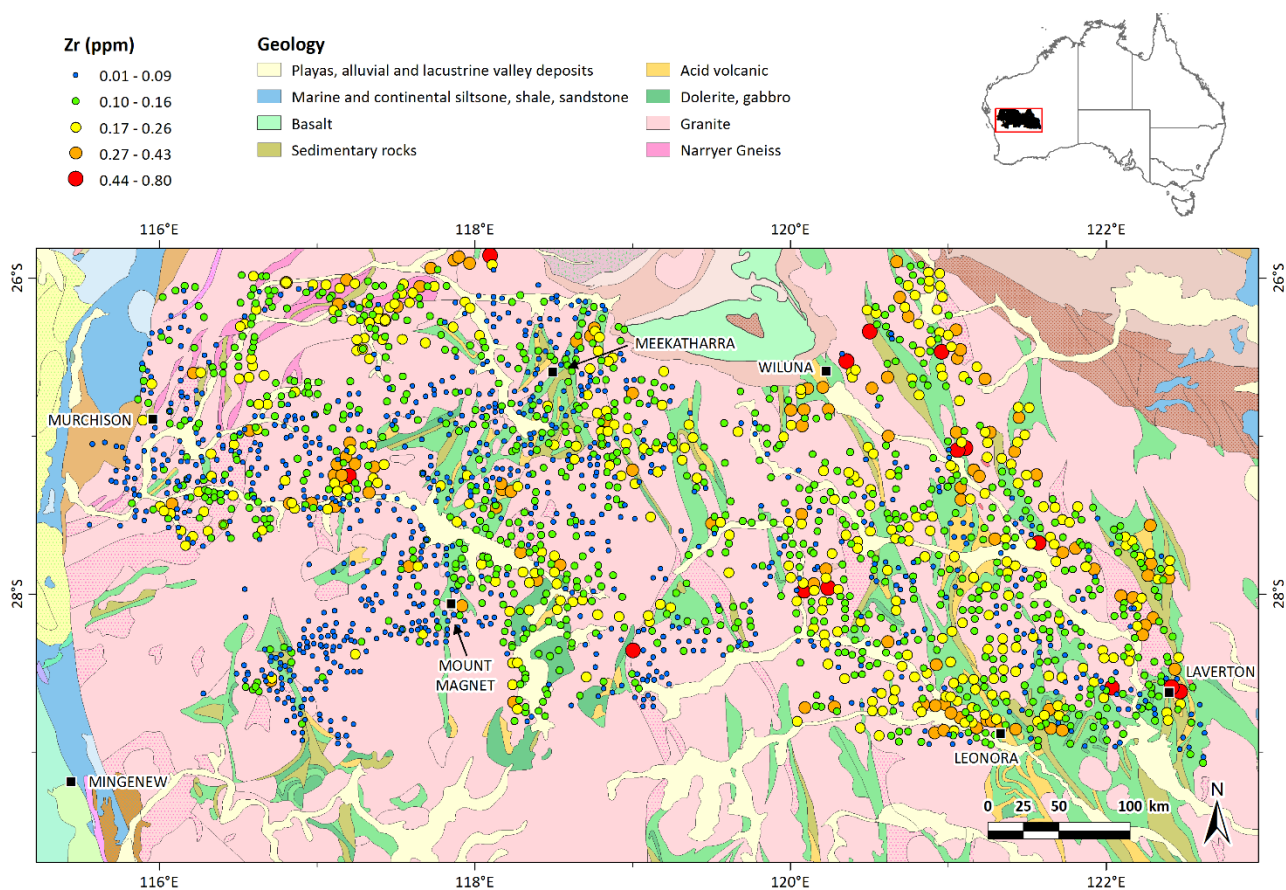


Figure 29: Distribution of Zr in north Yilgarn mulga phylloides

4.5 Gold

Gold is not an essential trace element in plants and its distribution is shown in Figure 30. Mean and standard deviation (ppb) for Au is 0.51 and 0.86, respectively. More than 68% of the Au data are above or at detection limit (0.1 ppb; Table 2). There are significant difference (Student's t, $p=0.05$) between:

- 1) Oblong-shaped leaves and terete shaped leaves with the latter having a greater mean concentration but no other leaf combinations differ statistically.
- 2) NW, NE and VS data sets with means of 0.65, 0.45 and 0.3 ppb, respectively. However, nearly all of the highest values of Au > 3.7 ppb (>99th percentile) occur in the NE Yilgarn with many associated with areas containing known Au deposits that have been previously discussed (Reid et al, 2010).
- 3) The geological class granite (mean of 0.48) with basic volcanic (0.64), Narryer Gneiss (0.62) and sedimentary rocks (0.68); and for valley fill sediments (0.42) with Narryer Gneiss (0.62) and sedimentary rocks (0.68) class.
- 4) The regolith class in situ (0.61) with lacustrine-alluvium-calcrete (0.43) and sandplain; and for colluvium (0.51) with lacustrine-alluvium-calcrete (0.43) regolith class.

There are no significant differences for Au values between tectonic classes i.e. Eastern Goldfields, Narryer Terrane and Youanmi. Clusters of above mean Au concentrations are found about 50 km north of Mt Magnet and about 125 km east of Murchison; the significance of these is not known.

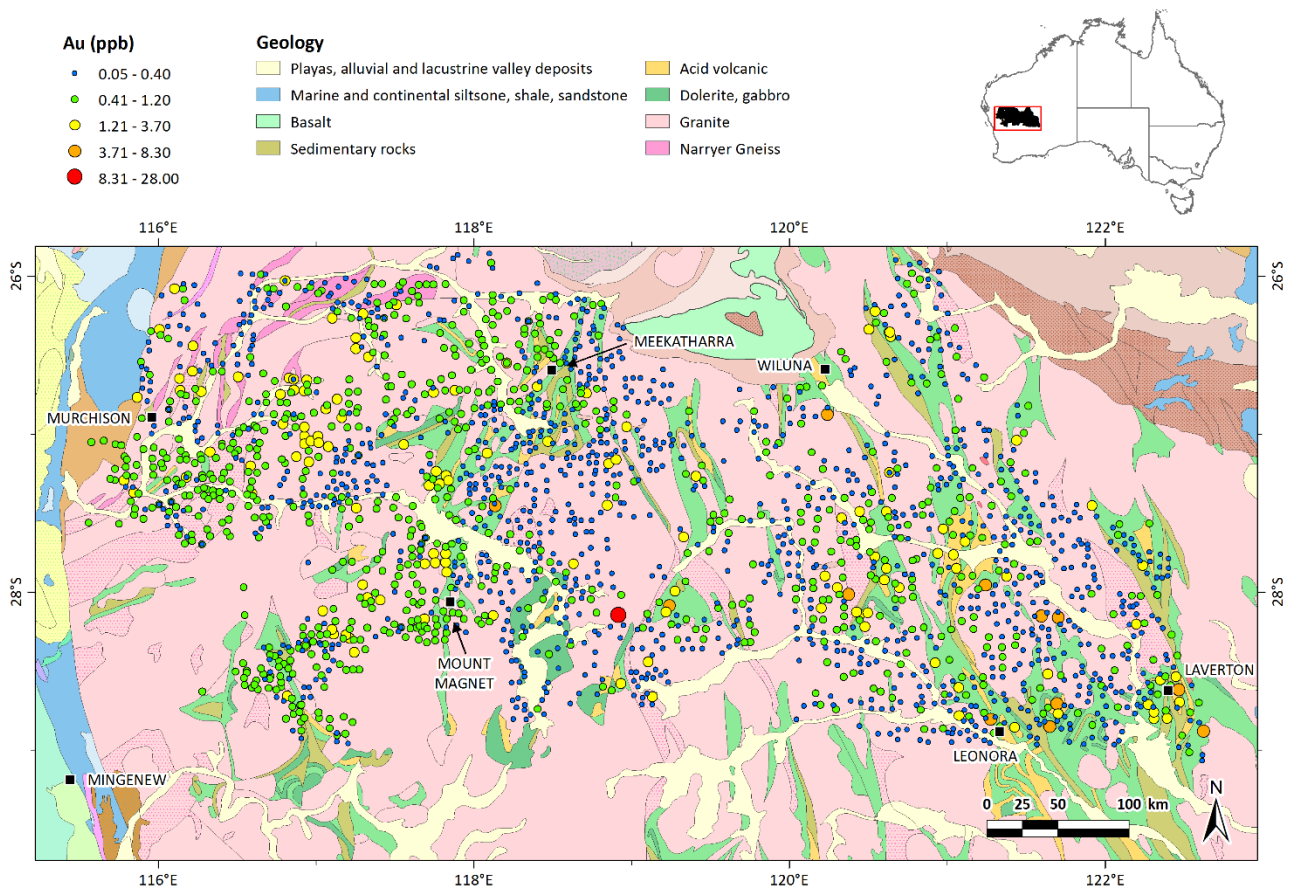


Figure 30: Gold distribution in mulga for the north Yilgarn.

Summary: It is not the intention of the data set to highlight regions of "anomalous Au". Random spot samples of Au, however, are worth following up outside the known mining areas. The potential Au endowment of the Narryer Gneiss is not reflected in these mulga data.

4.6 Copper and Zinc

Copper and Zn are essential plant nutrients involved in several physiological processes (including carbohydrate and protein metabolism) and disease resistance (Dunn, 2007). Copper concentrations have no particular E-W or N-S distribution trend from the geochemical maps while for Zn there are clearly higher concentrations in the east (particularly NE) compared with the west part of the maps (Figure 31 and Figure 32); this is confirmed with Student's t test of the data that show significant differences between each data class. The mean Cu and Zn concentrations for all samples are 4.4 ppm and 13 ppm, respectively (Table 2).

There are significant differences (Student's t, $p=0.05$) between:

- 1) Phyllode class including linear-falcate, linear-elliptic, linear-obovate, linear-terete and oblong-obovate pairs. Linear shape contains more Cu (mean of 4.7 ppm) than other phyllodes.
- 2) Some of the geology classes. Valley fill Cu is significantly lower (3.8 ppm) than basic volcanic, granite, other gneiss and sedimentary classes. Basic volcanics Cu and granite Cu concentrations are also significantly different.
- 3) Eastern Goldfields Cu (4.8 ppm) and Narryer (4.0 ppm) and Eastern Goldfields and Youanmi (4.3 ppm) tectonic classes.
- 4) Sandplain Cu regolith class and all other regolith classes.
- 5) Elliptic and terete phyllode classes and all other phyllode classes except between each other and also between obovate Zn and all other classes; obovate contains the lowest mean Zn (9.7 ppm).
- 6) Geological classes for Zn including basic volcanics-dolerite, -granite, -Narryer gneiss, -valley fill and granite-Narryer gneiss, granite-valley fill, Narryer gneiss-other gneiss, Narryer gneiss-sedimentary rocks, other gneiss-valley fill and sedimentary rocks-valley fill pairs.
- 7) All tectonic classes for Zn.
- 8) All regolith classes for Zn except between in situ and (LAC) lacustrine-alluvium-calcrete class.

Summary: These elements are well regulated by plants as they are essential nutrients. Nevertheless, significant differences occur between classes within categories suggesting that there may be other external factors e.g. soils or regolith of basic-volcanics that may assert additional control of these elements within plants.

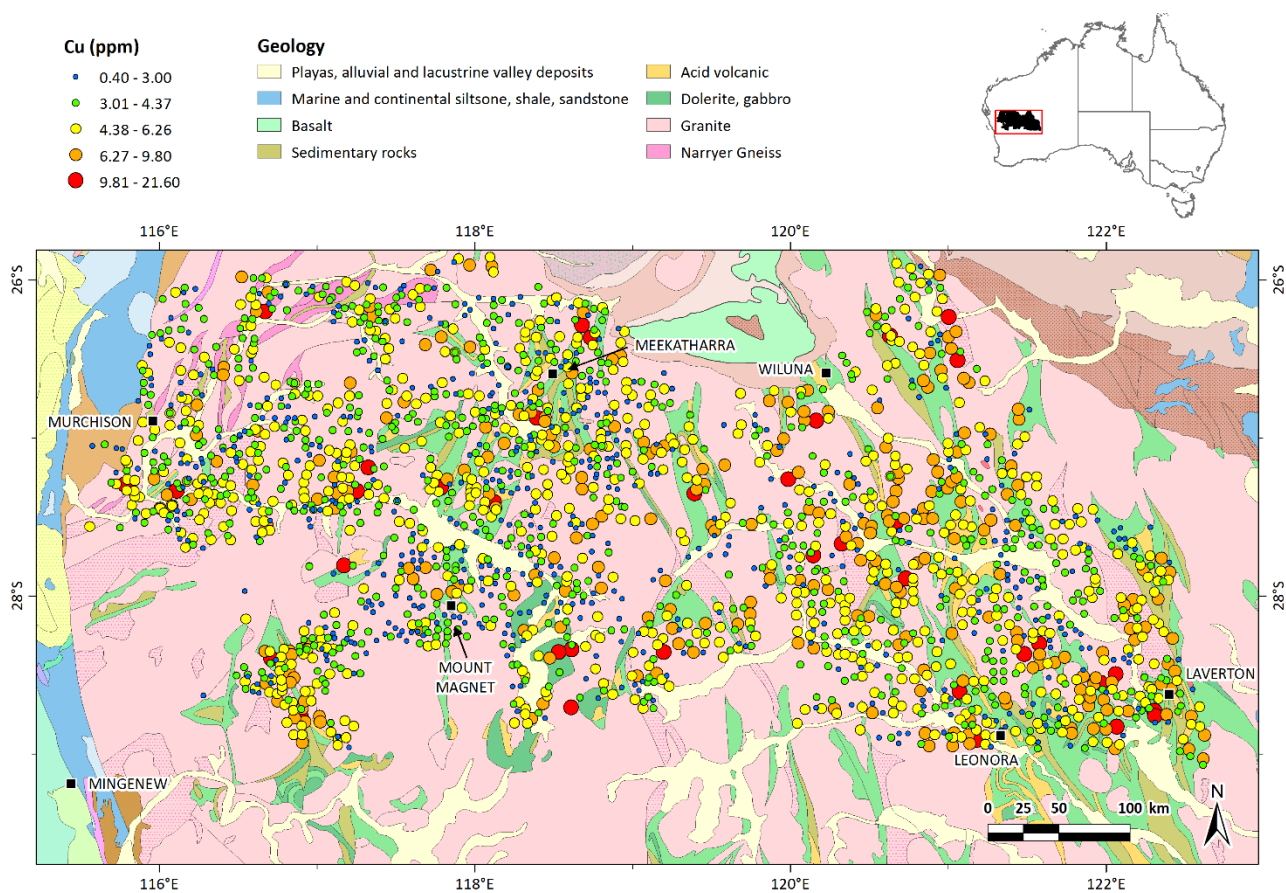


Figure 31: Copper distribution in north Yilgarn mulga phylloides

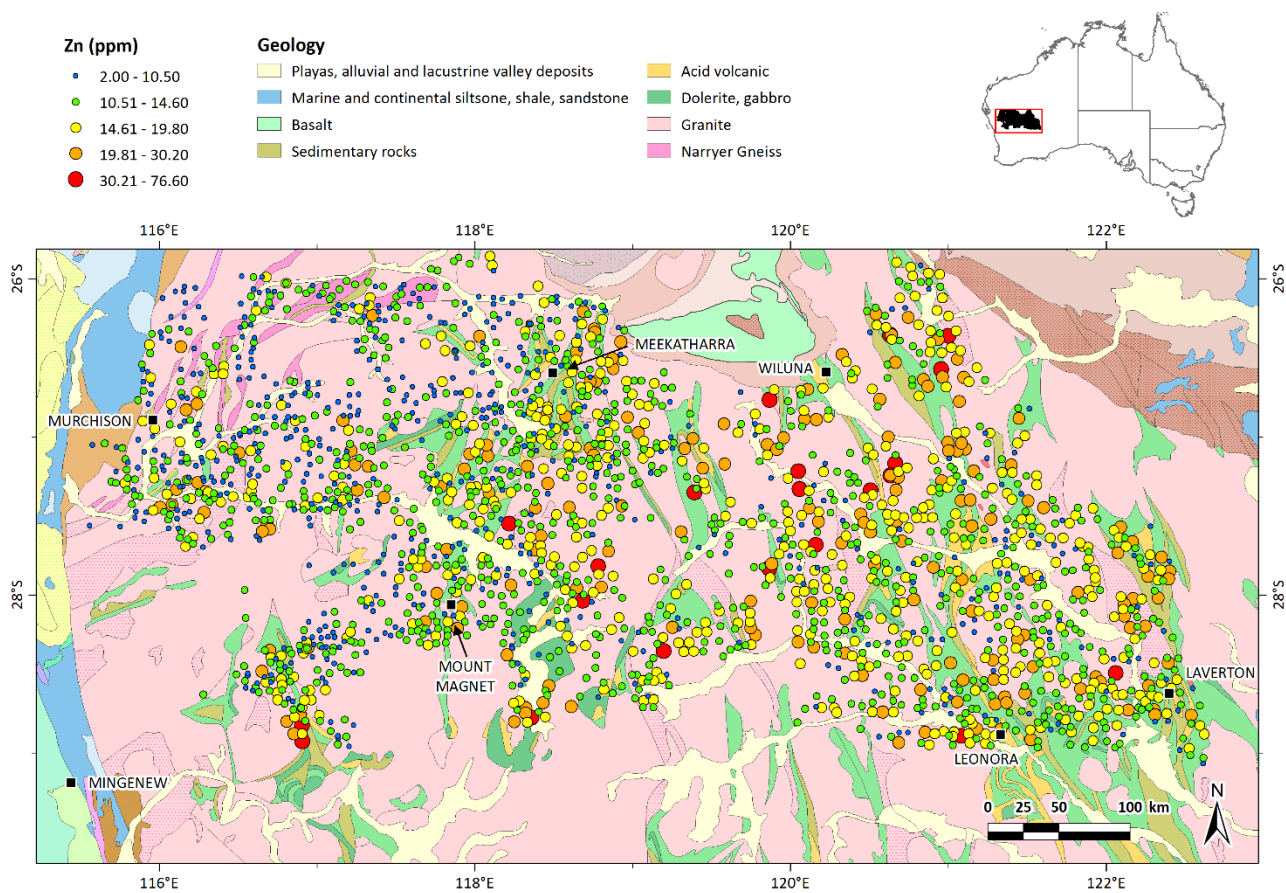


Figure 32: Zinc distribution in north Yilgarn mulga phylloides.

4.7 Nickel

Nickel is an essential trace element present in the enzyme urease and possibly in the translocation of N (Dunn, 2007). It can occur in extraordinary concentrations in plant sap as Ni citrate within so-called hyper-accumulator plants e.g. some plants growing over serpentine rocks endemic to New Caledonia (Dunn, 2007). A study of Ni in plants growing over the North Miitel Ni deposit (Western Australia) concluded that much of the Ni present in plant tissue was due to haul road dust, and neither did it locate the presence of mineralisation (Lintern et al., 2013c). Nickel (and Co) concentrations in phyllodes for the NE study showed an association with Ni deposits and were stronger than any indices that were devised (Reid et al., 2010). The mean concentration of Ni is 1.5 ppm and is close to the detection limit of 0.5 ppm (Table 2). With these factors in mind, interpretation of Ni data should be treated with caution.

There is a strong E-W trend in the distribution of Ni with consistently higher concentrations occurring in the east (especially with nickeliferous areas) and the lowest in the western portion of the map. Examining the results in more detail the following observations are made:

- 1) Terete phyllode class (mean of 1.3 ppm Ni) is strongly significantly different from linear (1.7 ppm); obovate class is statistically different from falcate, linear and oblong; falcate-terete pair are also different.
- 2) Data category produced highly significant differences between NW (1.0 ppm mean Ni) and NE (1.8 ppm) classes and weaker but still significant differences between VS and the other two data classes.
- 3) There are numerous differences between the geology classes but the most significant are between basic volcanics and Narryer gneiss, granite, valley fill, between Narryer gneiss and other gneiss, sedimentary rocks, and between sedimentary rocks and valley fill.
- 4) Tectonic category classes are significantly different from each other.
- 5) Regolith category classes are all significantly different from each other except for in situ-sandplain and in situ-colluvium classes (failed Bonferroni correction).

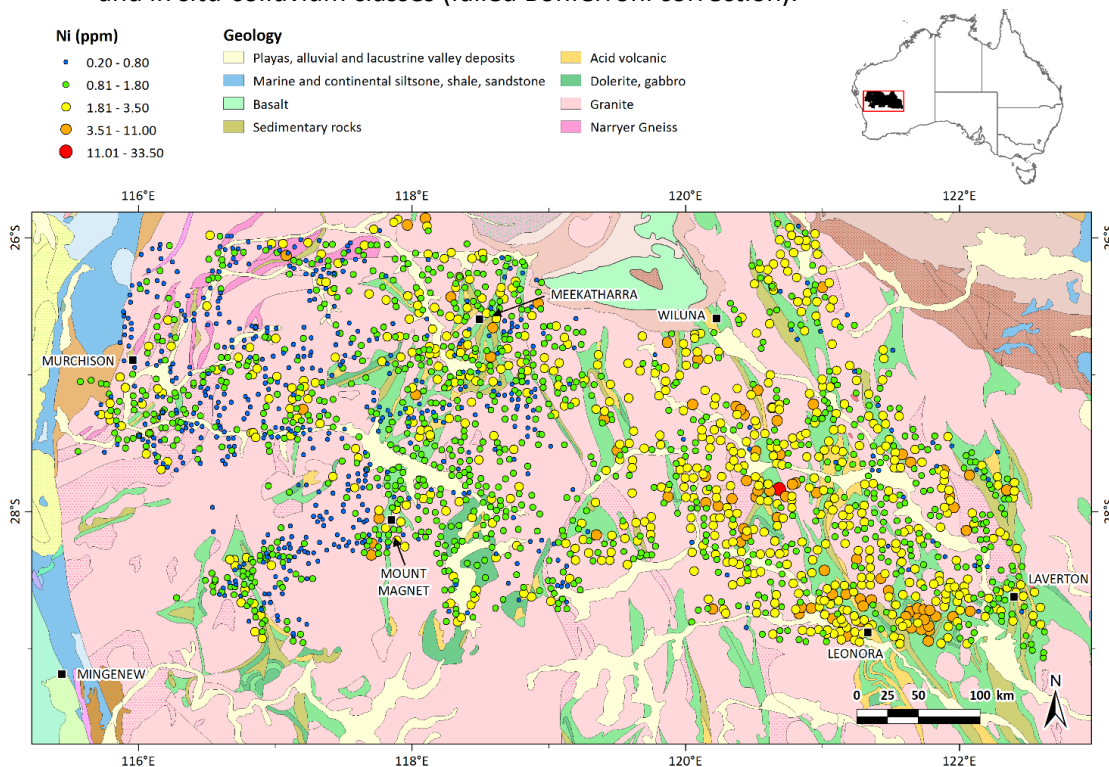


Figure 33: Nickel distribution in north Yilgarn mulga phyllodes

Summary: The general nickeliferous endowment of the eastern N Yilgarn is reflected in higher Ni concentrations in mulga for this area and particular so near known Ni mineralisation. Nickel is an essential trace element but clearly the controls on its uptake are tempered by concentrations within the environment on which mulga grow.

4.8 Uranium

Uranium is not a trace element required by plants. It is easily analysed in vegetation, even at the low ppb concentrations that are found, to give good reproducibility. In the NE Yilgarn biogeochemical data set it was shown that there was a relationship between U in phyllodes and some occurrences of U mineralisation e.g. near Wiluna. For the NW Yilgarn it appears from the distribution map that there are higher concentrations 200 km E of Murchison and to the upper NW of the distribution map forming an association with the Sanford and Murchison drainages (Figure 34); these areas correspond with some of the higher concentrations for Fe and related elements discussed earlier.

The mean U concentration for all samples was 8 ppb; the detection limit is 1 ppb (Table 2). The following detailed observations are noted:

- 1) Terete phyllode class is highly significantly more concentrated in U (mean of 11.4 ppb) than all other phyllode classes except for obovate (10.6 ppb).
- 2) Data category classes are all highly significantly different for their U concentrations. The VS class average is 24 ppb U while the NE is 7 ppb; this may be due to an external issue with the data e.g. analytical.
- 3) Narryer Gneiss class has a significantly higher U concentration (mean of 15 ppb) than all other geology classes; the next highest mean U concentration is 11.7 ppb for valley fill class which is also significantly different from other classes.
- 4) Tectonic classes are all markedly significant from other with respect to U concentration.
- 5) Uranium concentration for regolith units are similar except for LAC (lacustrine-alluvium-calcrete) which is markedly higher (mean of 11.4 ppb).
- 6) Uranium is correlated with Th for the entire data set.

Summary: Unlike Au, the U endowment of the Narryer Gneiss is reflected in higher U concentrations in mulga for this class over other geological classes. There is a potential problem with the VS U data which should be treated with caution during interpretation.

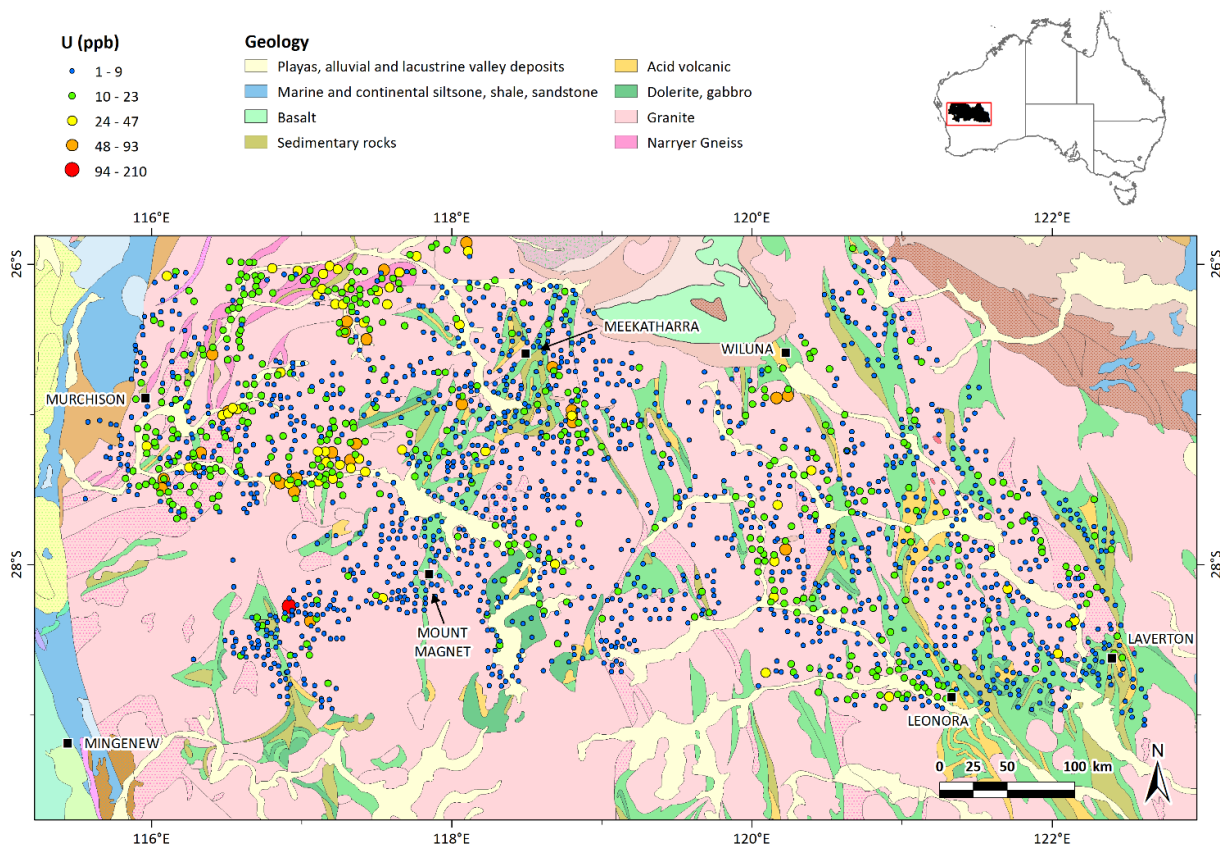


Figure 34: Uranium distribution in north Yilgarn phyllode mulga.

5 Further Analysis

5.1 Correlation between elements for vegetation

With large data sets there are a multiplicity of significant correlations which is an statistical artefact related to the size of the population; in fact if the population is large enough it can be shown that all elements are significantly correlated (positively or negatively) with one another. Prairie (1996) attempted to address the problem of low p values (when N is large) by adding a correction factor. The general conclusion is that for such large datasets, regressions that produce r^2 values <0.650 have limited predictive power, even if the associated p value is well within the area of (high) significance. The rationale considers "fully reliable" only those correlations/regressions for which r^2 is greater than 0.650, for which full mathematical reasoning and proofing is described in Prairie (1996).

The correlation matrix for elements contained within the phylloides is shown in Table 3. The correlation matrix is coloured according to the degree of correlation with stronger hues (red and green) signifying the strongest correlations. The REE elements show the strongest correlations with $r^2 > 0.9$ common. For other elements the following pairs are most correlated ($r^2 > 0.650$):

- 1) Al: Fe, Ga, Ti, Zr
- 2) Ca: Sr
- 3) Cr: Ti
- 4) Fe: Ga, Th, Ti

The Al set above (association 1) is related to dust (clay, Fe oxides, rutile and zircons). If Si (quartz) was analysed by a total digest, this would be expected to be correlated with these elements too. Calcium and Sr (association 2) are correlated (as previously discussed) and related to substitution of Sr in the lattice of Ca minerals such as calcite. Chromium and Ti (association 3) are probably related because of their association with Fe in chromite and ilmenite, respectively; Fe has a correlation coefficient with Cr of 0.64. Iron (association 4) is associated with Al and other elements found in clays (dust) such as Ga and Th.

Table 3 Correlation matrix of elements for the North Yilgarn biogeochemical data

[illegible]

5.2 Biogeochemistry vs hydrogeochemistry

Deep-rooted plants such as mulga are adapted to adsorb groundwater located many metres underground to sustain them in an arid to semi-arid environment. Whilst mulga have deep roots, they also have an extensive root system nearer the surface. These can be observed in road cuttings, open pits, other excavations as well as natural wind or creek eroded exposures. Deep-rooted mulga will be unlikely to draw water from deep sources if there is availability nearer the surface since the plant will expend more energy drawing from a deeper source. However, when water is in short supply near the surface, water will be taken up by mulga from these deeper sources and in so doing will also take up dissolved elements contained within that water. Some of these elements are beneficial for plant growth while some are toxic and may be excluded; others may be in low concentrations and toxic but are assimilated by the plant. For example, Au is known to be a toxic element to plants (Lintern et al., 2013a) in high concentrations but is taken up by the plant nevertheless. If Au occurs in groundwater, then this would be a viable pathway for it to be taken up by mulga into the plant and an explanation as to why element concentrations in groundwater are related to those in mulga. This factor was explored with the data sets.

Groundwater samples and mulga phyllode samples were taken from the same approximate location enabling a direct comparison to be made between elements from the two data sets. There were 2107 samples compared between the two data sets. Thirty-five elements were examined using scatter plots as a first pass to examine any relationships between the data. No association was observed between any of the elements and further data analysis was abandoned. An example of three scatter plots is shown in Figure 35. Selected scatter plots for the other elements are shown in the Appendix.

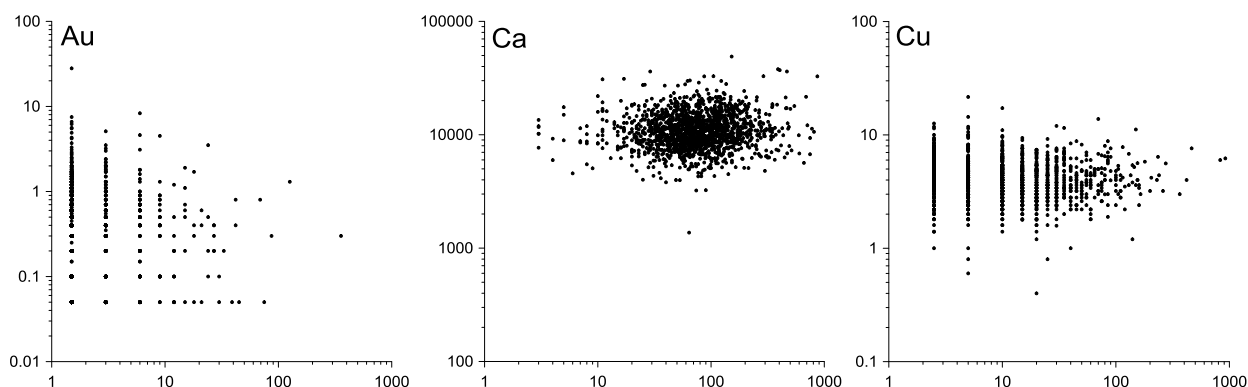


Figure 35: Element scatter plots of NY mulga phyllode vs. hydrogeochemistry data. X axis is hydrogeochemical data. Y axis is biogeochemical data. The units are nominal.

5.3 Biogeochemistry vs GSWA database

The comparison of the GSWA data with the biogeochemistry data investigates whether the near surface root system of mulga are extracting water that interacts with (and dissolves) material and elements from near the surface. These samples contain a variety of different sample types as described earlier. The nearest sample to the biogeochemistry samples was chosen and used in the comparison between the two datasets. This resulted in 912 samples with some sharing more than one neighbour; in these cases an average analysis was taken. An example of three scatter plots (mulga phyllode vs. GSWA sample for elements Au, Ca and Cu) are shown in Figure 36. Selected scatter plots for the other 48 elements are shown in the Appendix.

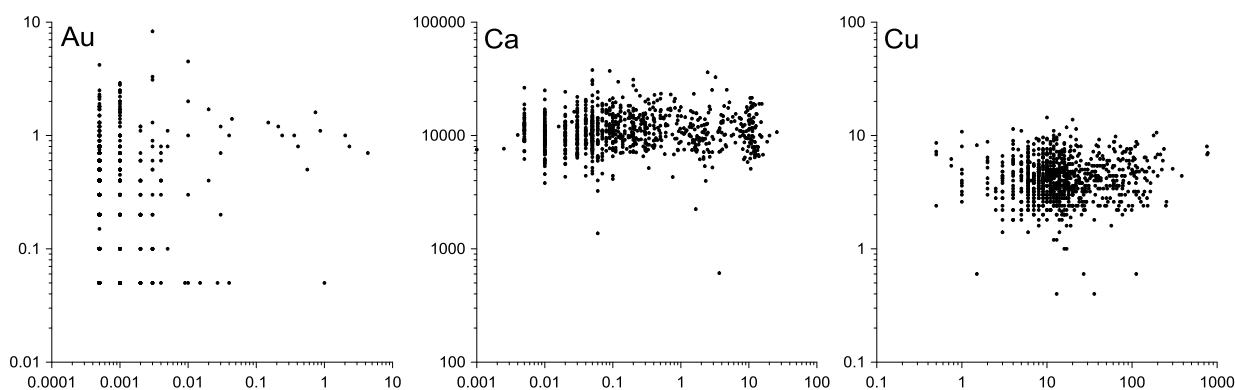


Figure 36: Element scatter plots of NY mulga phyllode vs. GSWA data. X axis is GSWA data. Y axis is biogeochemical data. The units are nominal.

5.4 Biogeochemistry vs Yilgarn Atlas

The biogeochemical data was compared with the laterite samples collected for the Yilgarn Atlas (Cornelius et al., 2008). Only 373 samples were compared because of the limited overlap of the two studies and the paucity of data. No associations between the two data sets was recorded for any of the elements. Three elements (Au, Ca and Cu) are compared in Figure 37; selected scatter plots for some of the other 45 elements are shown in the Appendix.

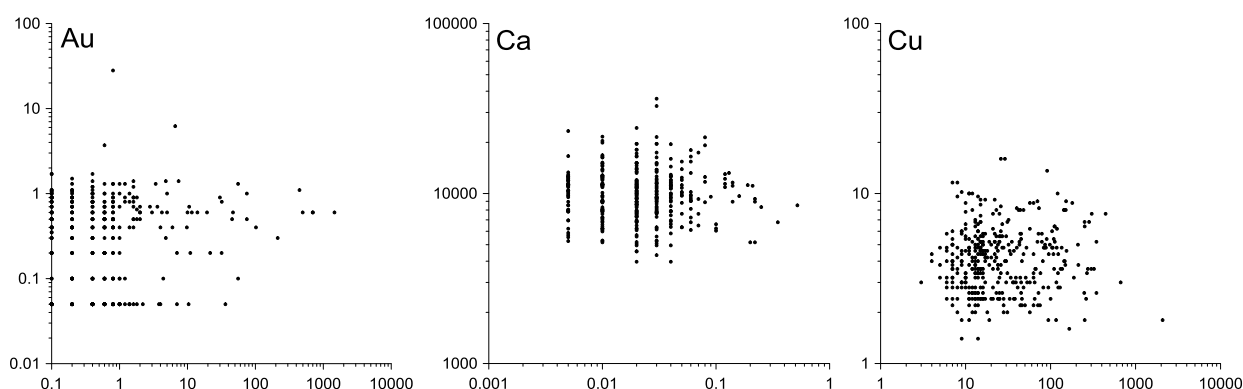


Figure 37: Element scatter plots of NY mulga phyllode vs. Laterite Atlas data. X axis is Laterite Atlas. Y axis is biogeochemical data. The units are nominal.

5.5 Indices

Indices were created to spatially examine combinations of elements for the geochemical data. These were performed for the NE Yilgarn study but were found to have limited value. However, some of the same indices were applied for this combined study (NE and NW) to investigate whether a larger data set would be of better value. The three indices created were Au Min1 (Au+Ag+As), Ni Min (Ni+Co) and FATZ (Fe+Al+Th+Zr). The rationale behind the indices is that the combinations of elements potentially provide greater predictive power to locate areas of importance as they do not rely on a single element to create an "area of interest" but, instead, several elements commonly occurring with the source mineralisation or, in the case of FATZ, a dust source. As Au concentrations in foliage are highly variable (within plant, Lintern et al, 2013a), the use of an index is potentially beneficial as it would moderate some of this variability. However, while As and Ag are commonly associated with mineral deposits, the chemistry of their uptake by mulga is poorly known and so the utility of them employed as a robust plant index requires further work. The raw geochemical data were log transformed then normalised before the indices were created. This did not include samples at

detection limit that were assigned a normalised value of zero for this exercise.

The indices show the following:

- 1) Au Min1 (Figure 38): The region with the highest values for this index occur in the western part of the north Yilgarn. The distribution pattern shown by the index is due to comparatively high concentrations of Ag that occur in this zone and Au concentrations between 0.4-1.2 ppb. Lower Ag concentrations in the NE data set resulted in the index more influenced by Au but with the larger data set it is clear that the index does not necessarily describe the best regions for Au but more likely those for Ag instead. Arsenic concentrations are generally close to detection limit and relatively uniformly distributed across the N Yilgarn and do therefore do not have much influence on the index map. The Narryer Gneiss is not particularly anomalous as a region using this index (nor Au itself; Figure 30).
- 2) Ni Min (Figure 39): This index was used in the NE Yilgarn survey to highlight areas that may be prospective for Ni mineralisation. It confirmed that areas in the Eastern Goldfields to be prospective for Ni, including active mining areas as did Ni by itself. For this study, the Eastern Goldfields area remain as the most prospective for Ni although a few additional areas in the Younami and Narryer Terranes are highlighted by the index e.g. around Mt Magnet and ~200 km NW of here.
- 3) FATZ (Figure 40): The FATZ index highlights samples that putatively have higher concentrations of dust-related elements. Dust is likely to affect individual samples, rather than areas, although the index shows some clusters of data (but with samples containing lower FATZ values); these areas includes parts of the Narryer Terrane and the south west Eastern Goldfield Terrane. The central and south west areas of the north Yilgarn set generally contain lower FATZ values. The reasons for this are unclear.

The use of the indices has been of limited value in these studies. For the Au Min1, Au, As and Ag are used in the study. Whilst a reasonable amount of information has been accumulated about the behaviour of Au in tree uptake in the Yilgarn, Ag and As have not been particularly well studied as elements are commonly close to or below detection limit. For the Ni Min1, Ni and Co were used to create the index. The only biogeochemical study of a Ni deposit to compare undertaken was that at North Miitel using *Eucalyptus* trees the Ni and/or Co contents of which were not found to be indicative of mineralisation.

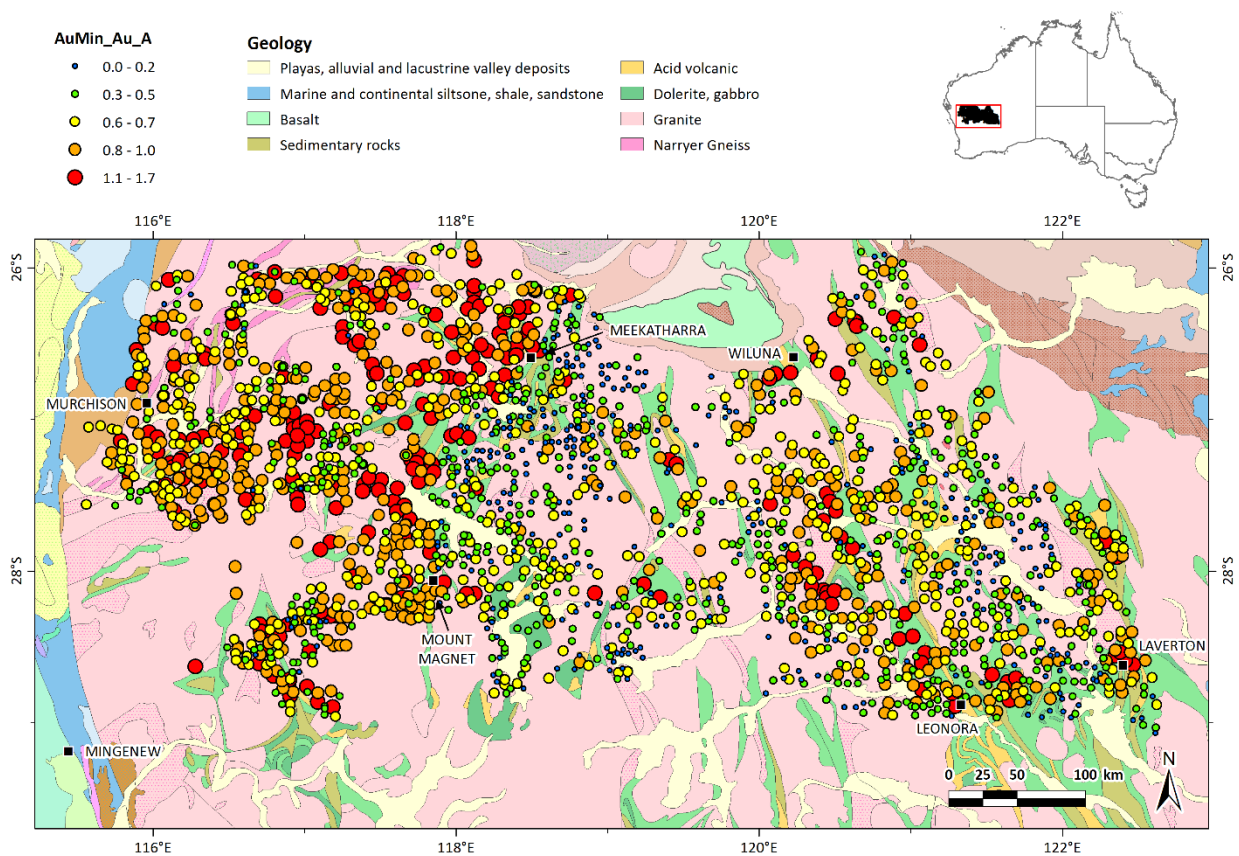


Figure 38: The Au Min1 index (Au+Ag+As), used in the NE Yilgarn study, is applied here across the north Yilgarn.

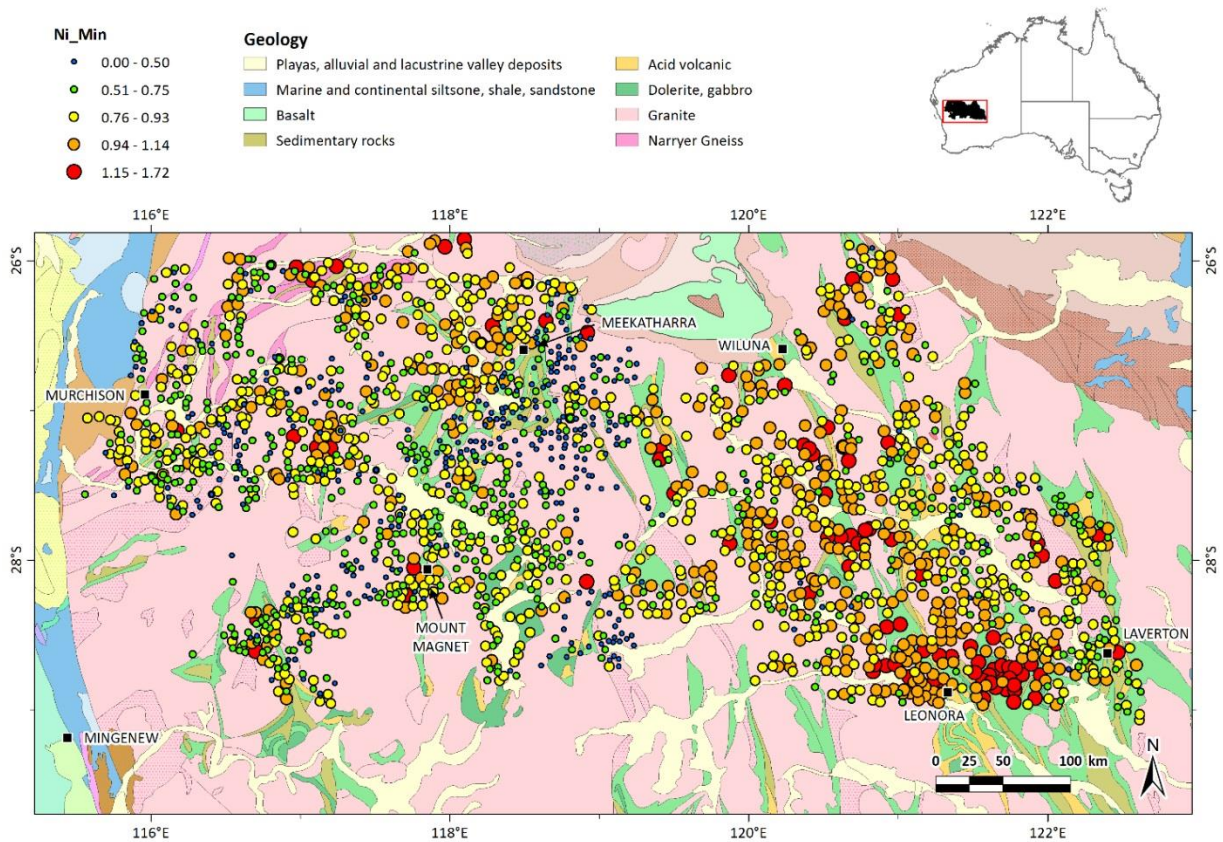


Figure 39: The Ni Min index (Ni+Co), used in the NE Yilgarn study, is applied here across the north Yilgarn.

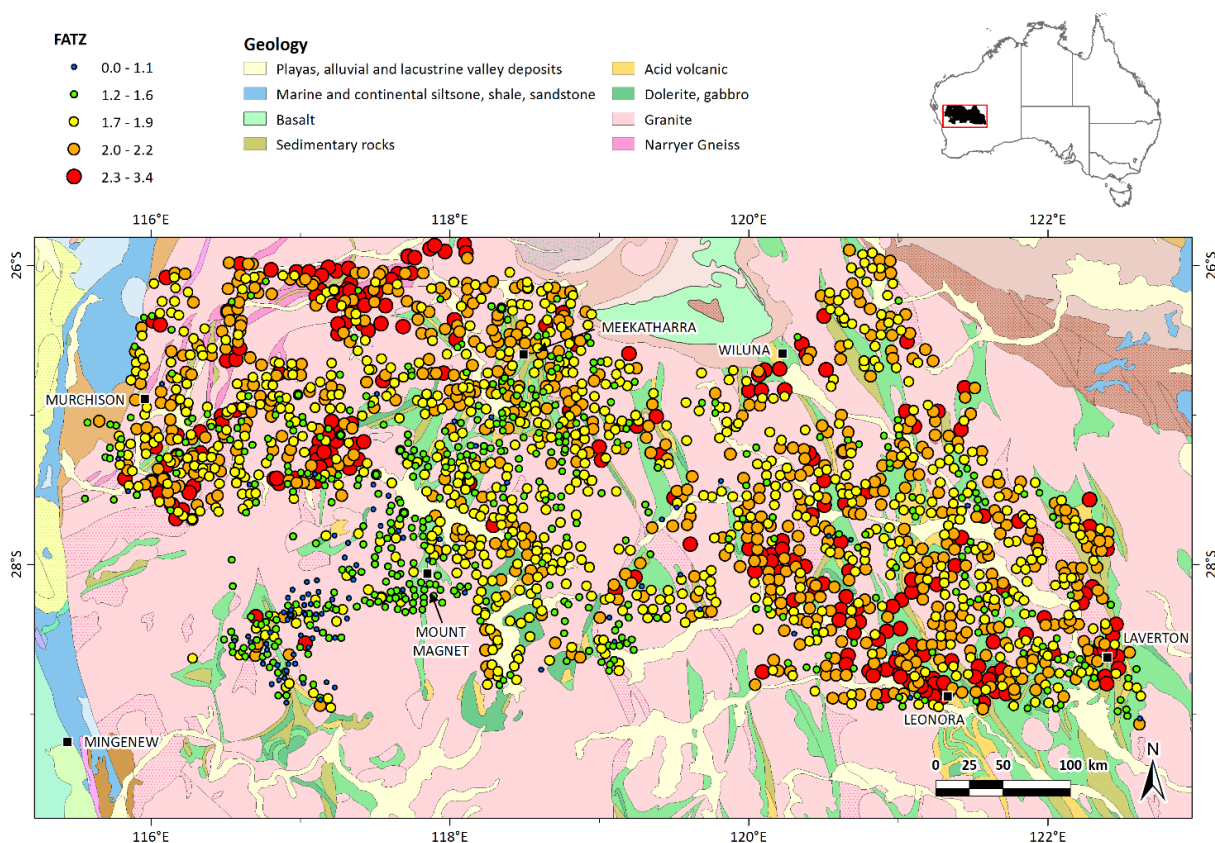


Figure 40: The FATZ index (Fe+Al+Th+Zr), used in the NE Yilgarn study, is applied here across the north Yilgarn.

5.6 Robust principal component analysis (PCA)

In order to recognise patterns in the data robust PCA was undertaken using a Box-Cox transformation (with no trim; ioGAS). Raw data for the PCA is in the Appendix. Certain elements were removed before the analysis could be undertaken (Ag, Bi, Cd, Ho, Lu, Pt, Sb, Sc, Ta and Tm). About 60% of the data (eigenvalues) were described by five principal components with most variation being described by PC1 (29%) and PC2 (13%). Examination of the eigenvectors indicates that the following element groups control the five principal components: PC1 (REE), PC2 (Al, Cr, Fe, Th, Ti, U and Zr), PC3 (Mo, P and Rb), PC4 (B, Ba, Ca, Mg, Sr) and PC5 (K, P, S, Rb and Zn). The PC1 is dominated by REE since this group of elements is most strongly correlated together (Figure 41). The PC2 appears to be related to the FATZ dust component index together with some additional elements that may be related to dust (Fe oxides and clays) including Cr and Ti; the inclusion of U may be related to clay minerals but further work is required here. The PC3 is not particularly dominated by any elements but Mo, P and Rb are the most important, with Au to a lesser extent (Figure 42). The PC4 is dominated by alkaline earth metals probably related to provenance and/or a structural factor related to phyllode shape. The PC5 appears to be a plant nutrient group possibly related to phyllode shape.

The distribution map of the scores for each sample for each PC provides another means of examining the data and identifying patterns or anomalous areas in the data. The distribution of the first 12 PCA are shown in the Appendix with the first three discussed here (Figure 43-Figure 45). The PC1 distribution map shows the samples weighted by the REE grouping. Some clustering of higher values are visible (200 km NW of Mt Magnet); the Mt Weld carbonatite south of Laverton does not show up as it is just outside the map boundary.

The RPC2 plot shows a homogenous distribution with small clusters of higher values ~50 km east of Murchison and in the Narryer Terrane to the north; it is unclear why these occur. The RPC2 and RPC3 plots are similar but RPC3 does not include the two clusters of RPC2.

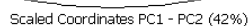


Figure 41: Spatial representation showing elemental relationships for PC1 vs. PC2

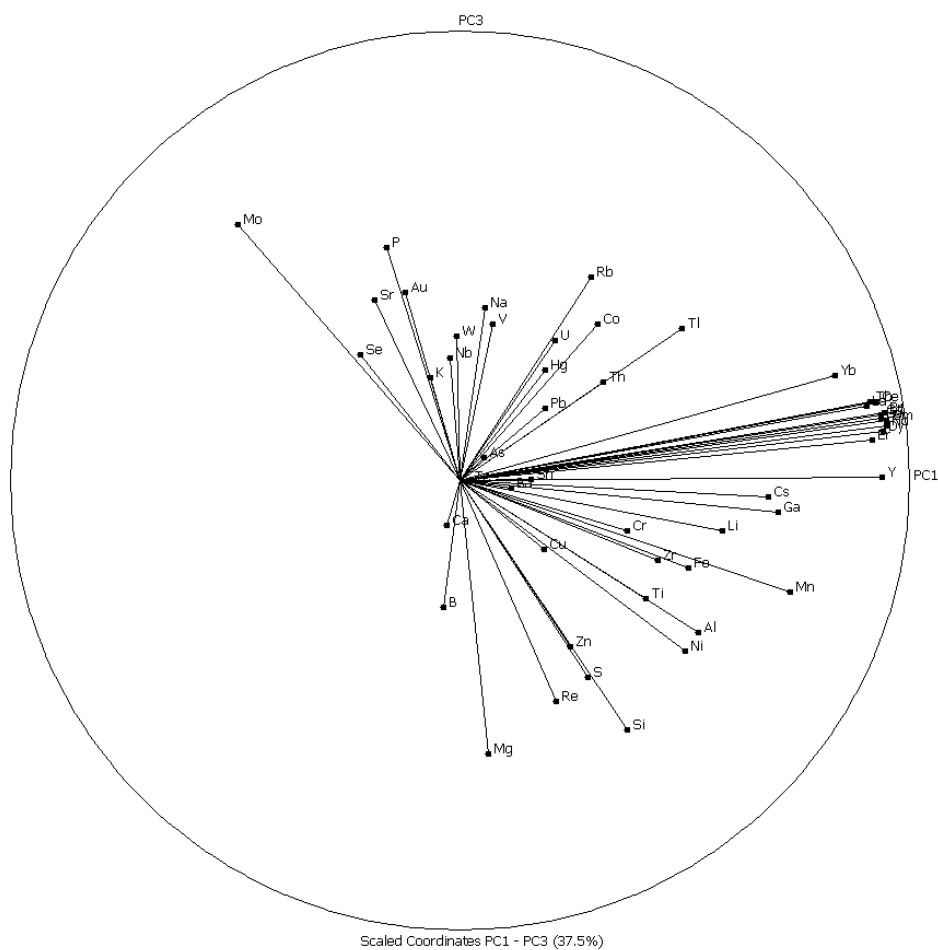


Figure 42: Spatial representation showing elemental relationships for PC1 vs. PC3.

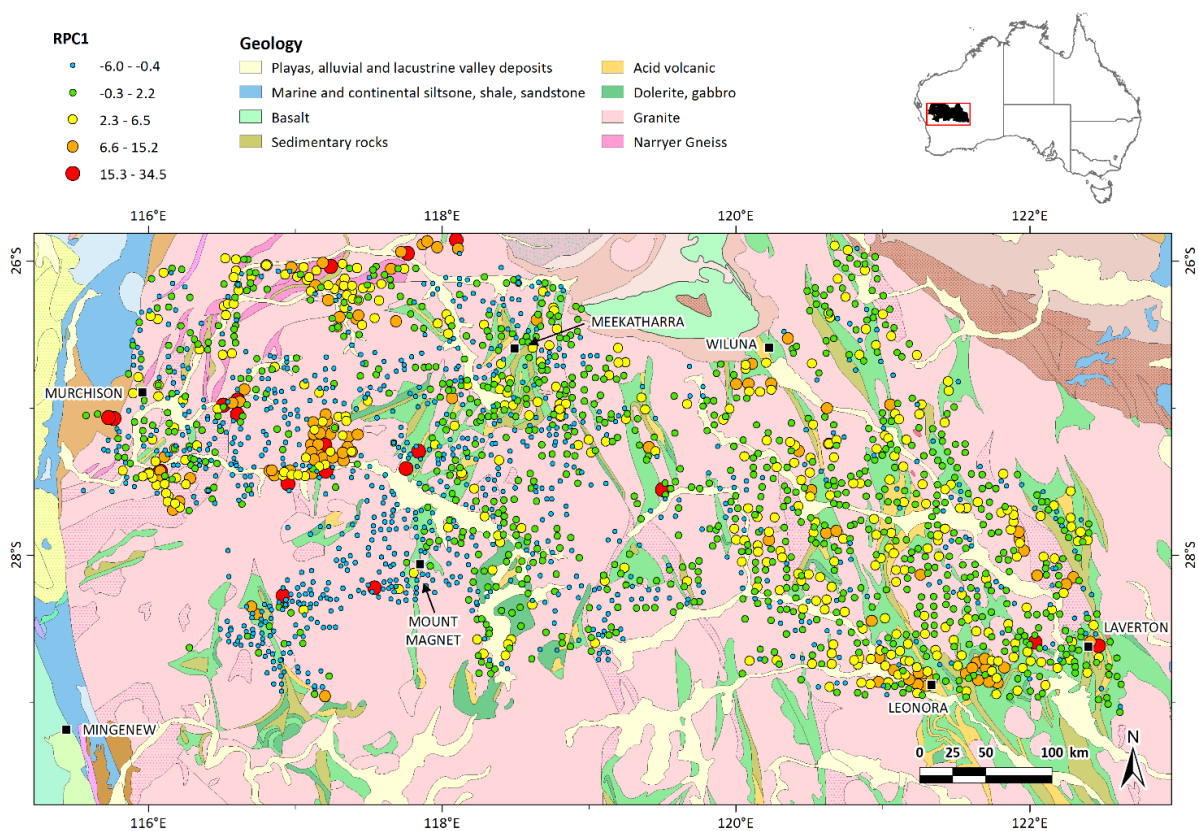


Figure 43: Robust principal component analysis for PC1.

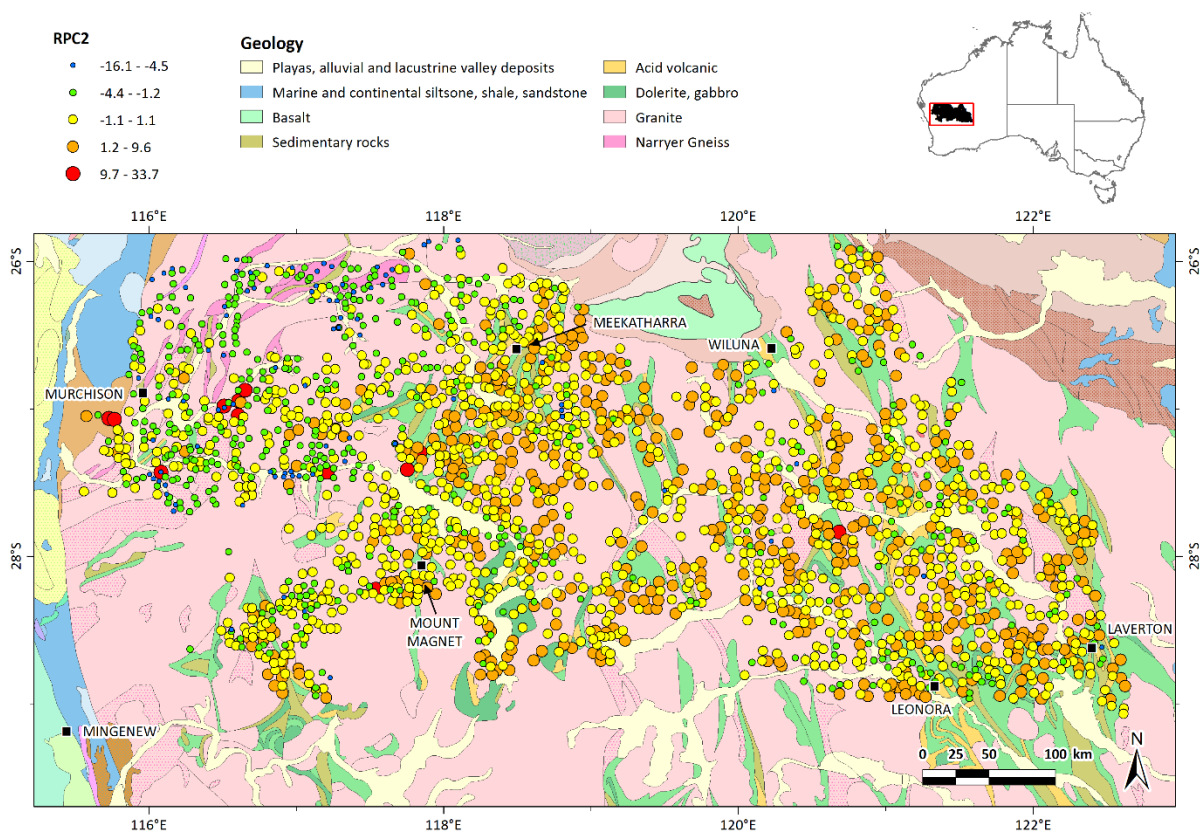


Figure 44: Robust principal component analysis for PC2.

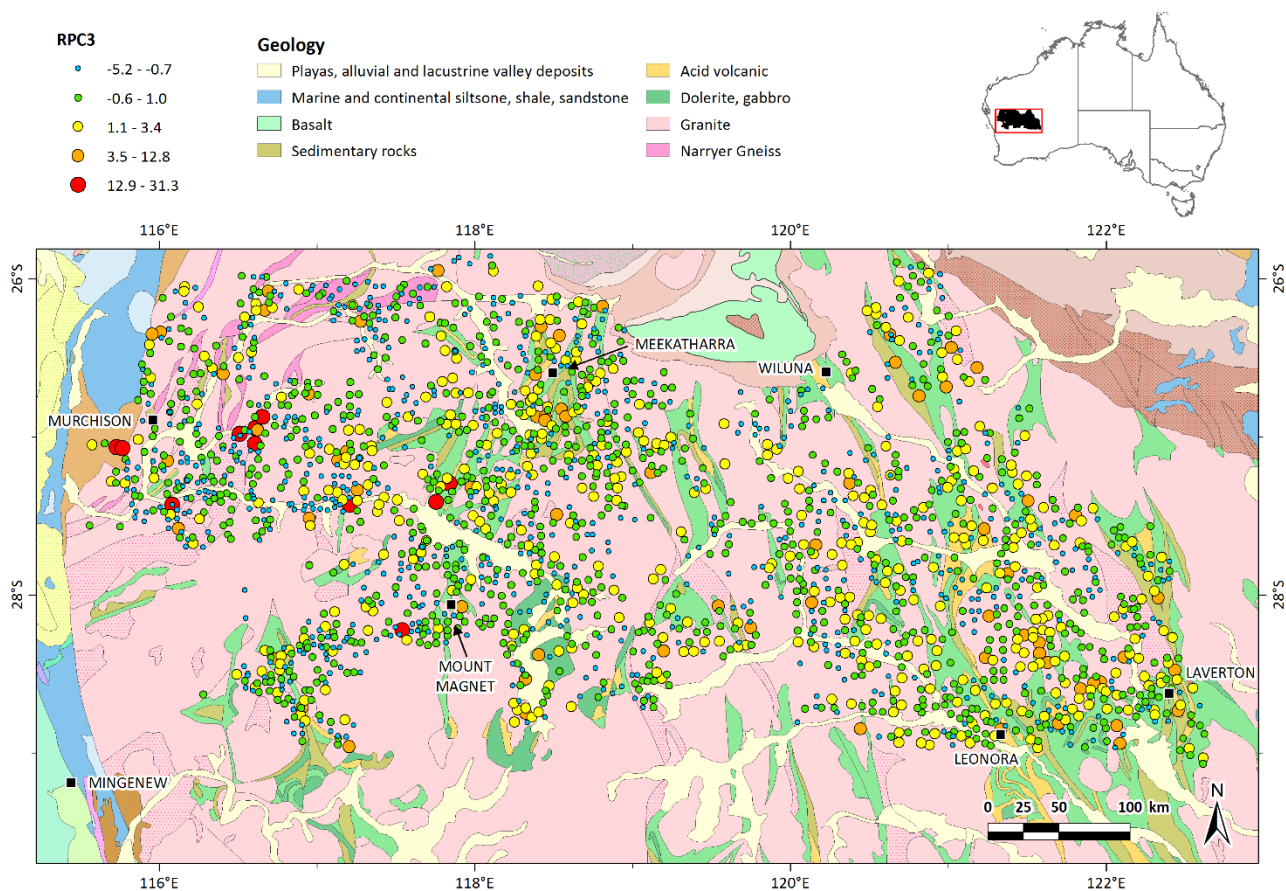


Figure 45: Robust principal component analysis for PC3.

5.7 Comparison with site studies – the Atlas

The site studies provide data from known mineral deposits and prospects. The purpose of these data is to provide mineral explorers with spread of elemental data typically found with which their own data may be compared. These data have been previously circulated to sponsors of this project and is included in this Final Report. The data is displayed as histograms for each element (as well as the source data) in the Atlas. The site data histograms include the regional data sets which facilitates comparison and sets the site data in geochemical context. An example of the histogram of the data is shown in Figure 46. The histograms form part of the "Biogeochemical Atlas of the north Yilgarn Mulga" which is included as an Appendix. The Atlas pages provide "at a glance" visual summaries of the findings for each element analysed at over twenty sites studied as well as the regional data sets. The histograms will not be discussed further as these data have been, and will be, incorporated in site study interpretations within scientific papers; for example, the North Miitel (Lintern et al., 2013b), Rose Dam (Lintern et al., 2013a), Moolart Well, (Anand et al., 2007; 2016), Kintyre (Noble et al., 2017 in press) and DeGrussa (Noble et al., 2016 in press).

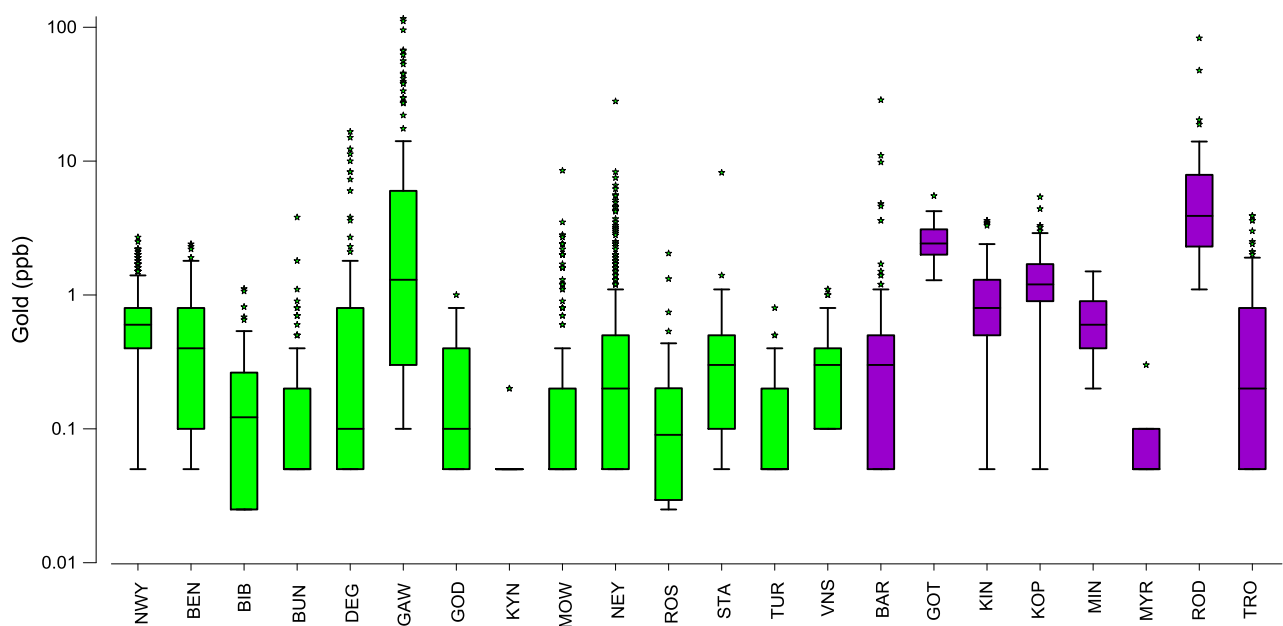


Figure 46: The histograms of the site data for Au (ppb) compared with the regional data. This histogram forms part of the Atlas pages for each element. The green and purple shading denotes mulga and *Eucalyptus* foliage sampled, respectively. The site codes are as follows: NWY (NW Yilgarn); BEN (Bentley, VMS); BIB (Bibra, Au); BUN (Bunarra, Au); DEG (DeGrussa, Cu-Au); GAW (Garden Well, Au); GOD (Golden Delicious, Au); KYN (Kintyre, U), MOW (Moolart Well, Au); NEY (North East Yilgarn); ROS (Rosie, Ni); STA (St Annes, Au); TUR (Turnberry, Au); VNS(VS) (Regional study); BAR (Barns, South Australia, Au); GOT (Golden Triangle, Au); KIN (Kintore, Au); KOP (Kopai, Au); MIN (Miitel North, Ni); MYR (Myrtle, Northern Territory, VMS); ROD (Rose Dam, Au); TRO (Tropicana, Au).

The green bars show the mulga and the purple bars the *Eucalyptus* which are part of a data set that have been compiled over several years at CSIRO. Some cautionary points on the use of these data are relevant here:

- 1) The individual elements of the Atlas may not directly pertain to the principal commodity of the deposit; for example, U at Kintore may not be a relevant comparison since it is a Au prospect and not expected to contain much U.
- 2) Some of the typical pathfinder elements for Au e.g. As, Sb, Bi may be elevated for a particular prospect but knowledge about the specific pathfinders associated with mineralisation should be examined so that these data are assessed in context.

6 Summary

The results of the NW regional data set when combined with the NE and VS data sets form a large biogeochemical data set for mulga foliage in the north Yilgarn Craton comprising over 2000 samples and covering an area of ~ 130000 sq km. The objectives of this study were to:

- 1) Analyse 750 samples from the NW Yilgarn (to add to the existing data set and extend the survey).
- 2) Compare the biogeochemical data with other geological and geochemical data including groundwater, geology and MINEDEX samples over the same area.
- 3) Compare the regional data with site data.
- 4) Assess the prospectivity of the NW Yilgarn using biogeochemical data.

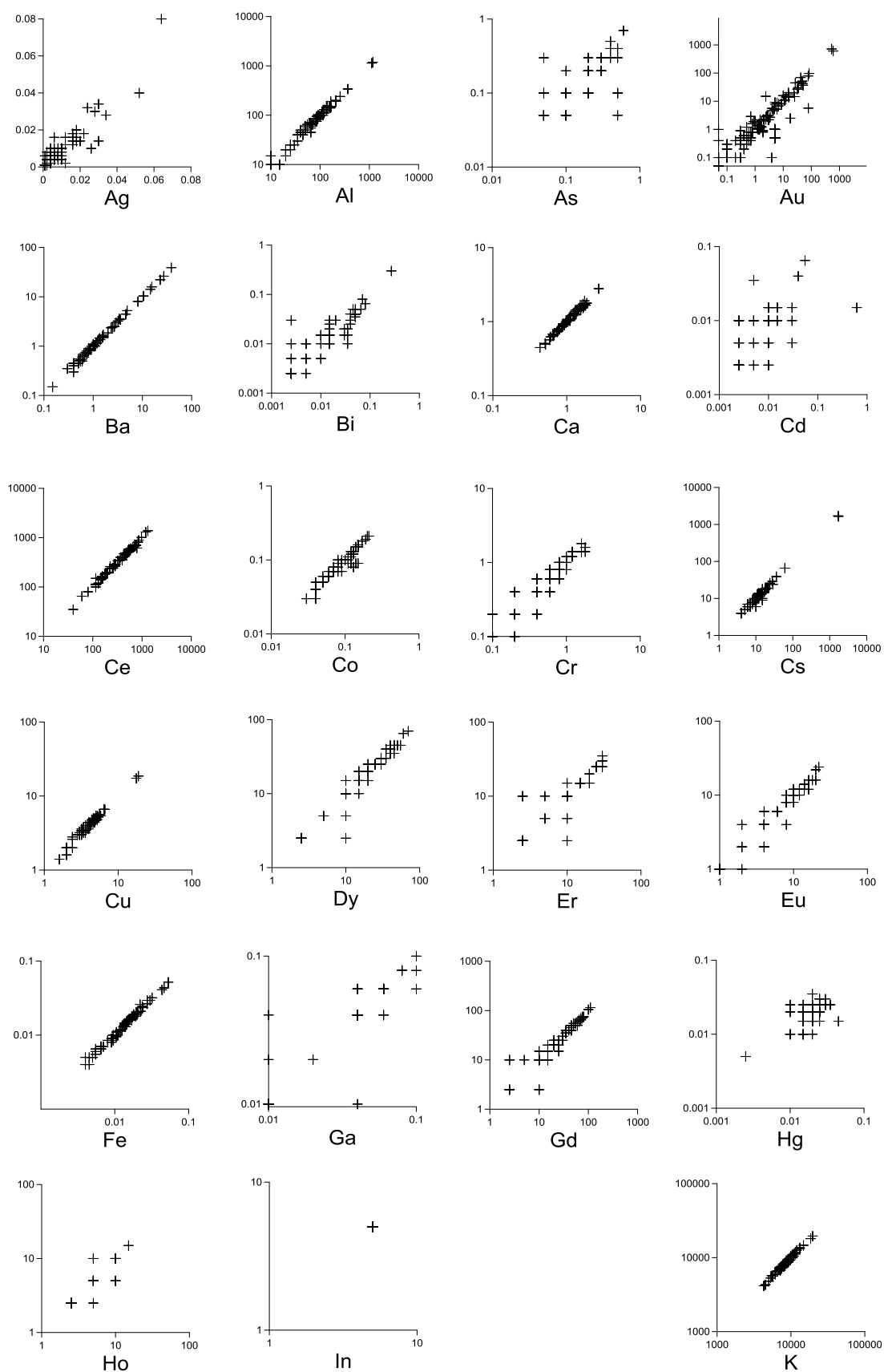
These objectives have been achieved and, in summary, some interpretations of note include the following:

- 1) Summary statistics and percentiles were produced for each element in a table to provide immediate information that can be compared with data collected by other future (site) surveys. For example, the 90th percentile for Au is 1.0 ppb and 1% of the data is over 3.1 ppb Au based on 2130 cases.
- 2) For the Yilgarn data set, there is little correlation between the hydrogeochemistry, laterite, MINEDEX and the biogeochemistry data sets suggesting that one data set cannot act as a surrogate for the others, however, each may be useful in identifying areas of interest.
- 3) Standards and duplicates were satisfactory in making the data set robust for statistical analysis.
- 4) The data were classified according to categories and classes. The significance of the t-test statistic was used as a tool to compare classes for different elements; numerous significant differences were recorded between classes for different elements suggesting, for example, that some elements (or combination of them) could be used to discriminate between different regolith and geological units e.g. Narryer Gneiss mulga phyllodes have much higher mean U concentrations than other geological classes.
- 5) The Atlas provides a preliminary interpretation of the geochemical data, how the different classes in the categories relates, and how data between sites and regional data sets compare. Element distribution plots showed the spatial distribution of elements across the north Yilgarn. Some of the regional geochemical features previously identified by the NE Yilgarn data set were not substantiated when the NW data was added to it. For example, the higher Sr values in the eastern part of the NE Yilgarn data set, which were speculated as being related to distance from coast, have a lower mean concentration than those for the NW data set. Consequently, the larger data set vindicates our expanding the geochemical data set to include a broader area as it changes our interpretation of the data.
- 6) The prospectivity of the Narryer Terrane was investigated. The Narryer Gneiss in the far NW are of the dataset has significantly higher U than the other geological classes e.g. granite, greenstones, sediments investigated but Au, Ni, Cu and Zn concentrations are similar to other geological classes. Uranium in mulga correctly identified known deposits in the NE data set.
- 7) Three indices (or multiple element combinations) were used to see if they could be used to identify regions within the element distribution maps that may be worthy of follow-up. The indices were Au-, Ni- and dust-based. Some areas were identified by the Au index and Ni index but generally there does not seem to be any great advantage in the use of the indices over the use of the individual elements themselves.
- 8) A correlation matrix table showed which elements in the phyllodes were associated to one another. The results were not unexpected e.g. the REE, Ca-Sr and Fe-Ga-Th-Ti were correlated.
- 9) The robust principal component analysis does not add significantly to the interpretation of the element distributions. Principal component (PC) 1 was influenced by REE, PC2 by dust, PC3 by Mo, P and Rb and PC4 by alkaline earth elements as evidenced by positive loadings.

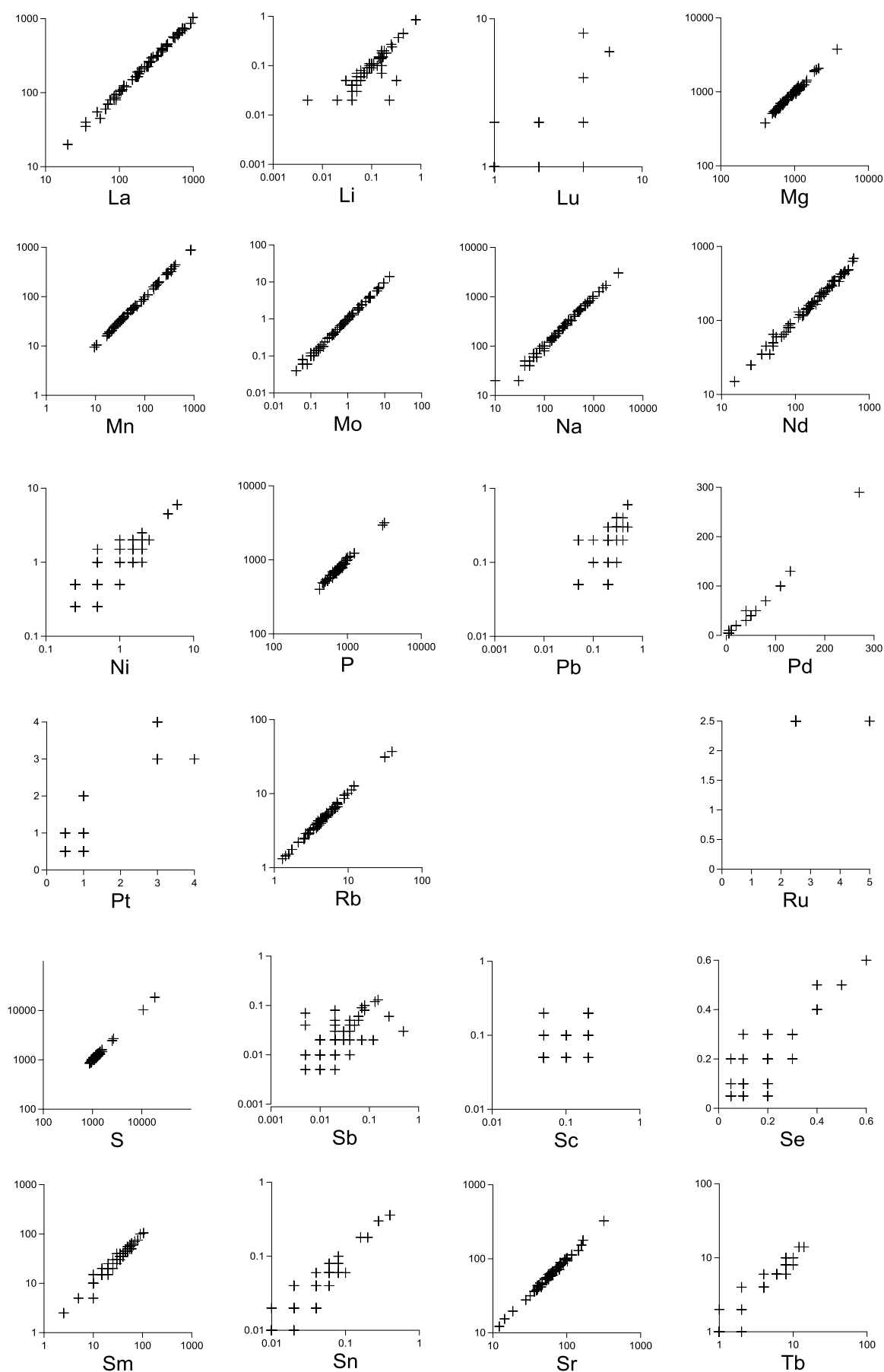
The data set generated for the North Yilgarn and compilation of the site studies into other data sets will be a powerful tool for explorers that use biogeochemistry when searching for mineral deposits. Exploration companies will be able to compare data generated within their own projects to these data and investigate whether their leases are worthy of further investigation. A regional survey has not been done before with one plant genus in Australia on this scale. Correct interpretation of biogeochemical data from prospects has been difficult before since this data has not been available. This project is part of a long-term strategy to investigate the use of biogeochemistry to mineral exploration at different scales including prospect, district, regional and national scales.

This project has advanced the discipline of biogeochemistry within Australia by establishing a large, well-controlled, high quality data set covering the northern part of the Yilgarn Craton. The classification of the data into categories and classes was not undertaken by the previous study (M411) and has added to the benefit of understanding the data here. By dividing the data into classes, elements can be assessed based on these factors before applying a statistical approach to identify if particular samples are anomalous or typical for this subset. The expected beneficiaries of this project, apart from those undertaking mineral exploration and minesite remediation include the general public. Baseline environmental studies may use the data set to ensure development projects are responsible for any changes to vegetation element contents, plant health and ecological communities. In addition, geomedical applications of biogeochemistry may, in the future, be able to alert governmental authorities as to whether toxic elements in vegetation may act as an important bio-indicators for north Yilgarn communities and station owners.

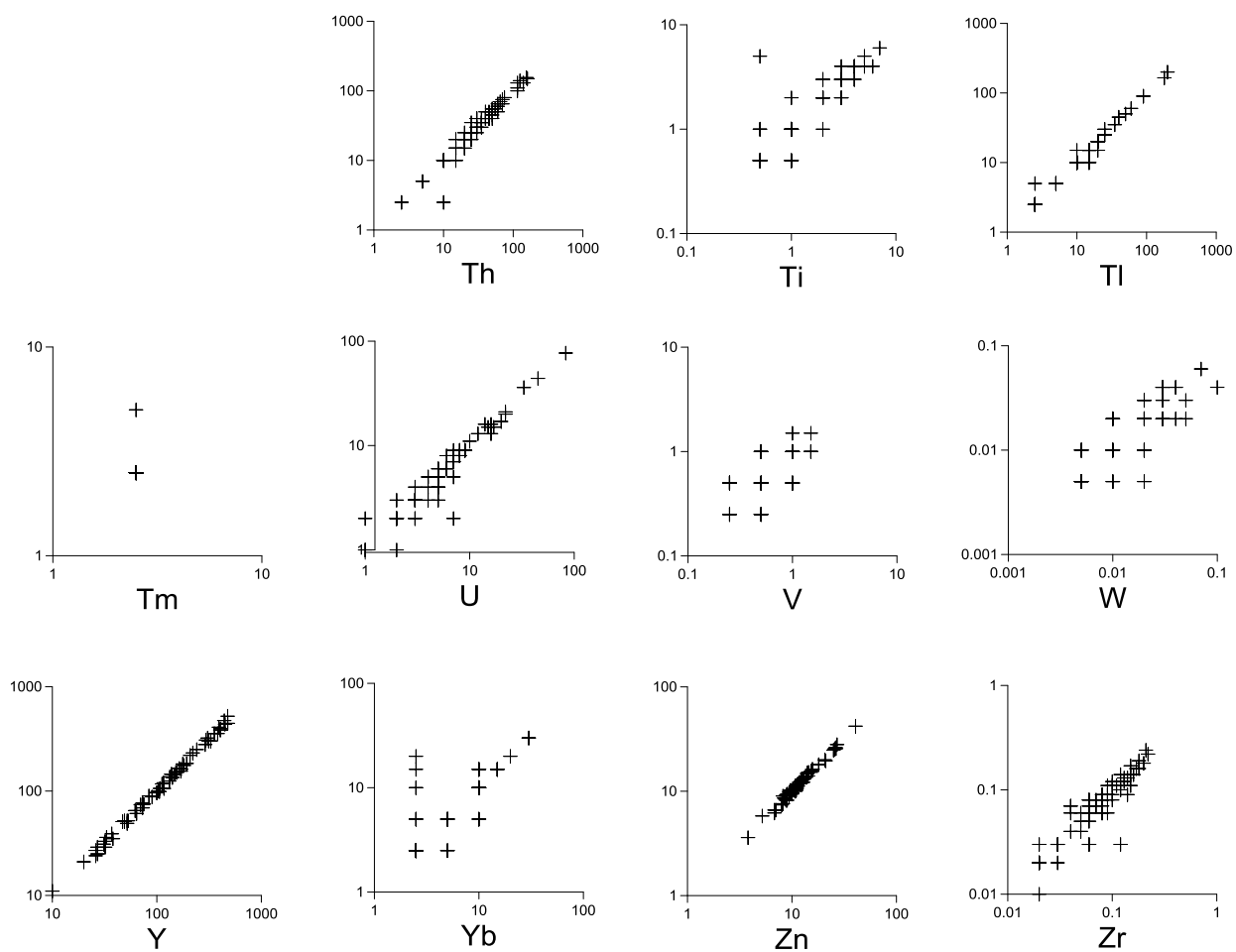
APPENDICES



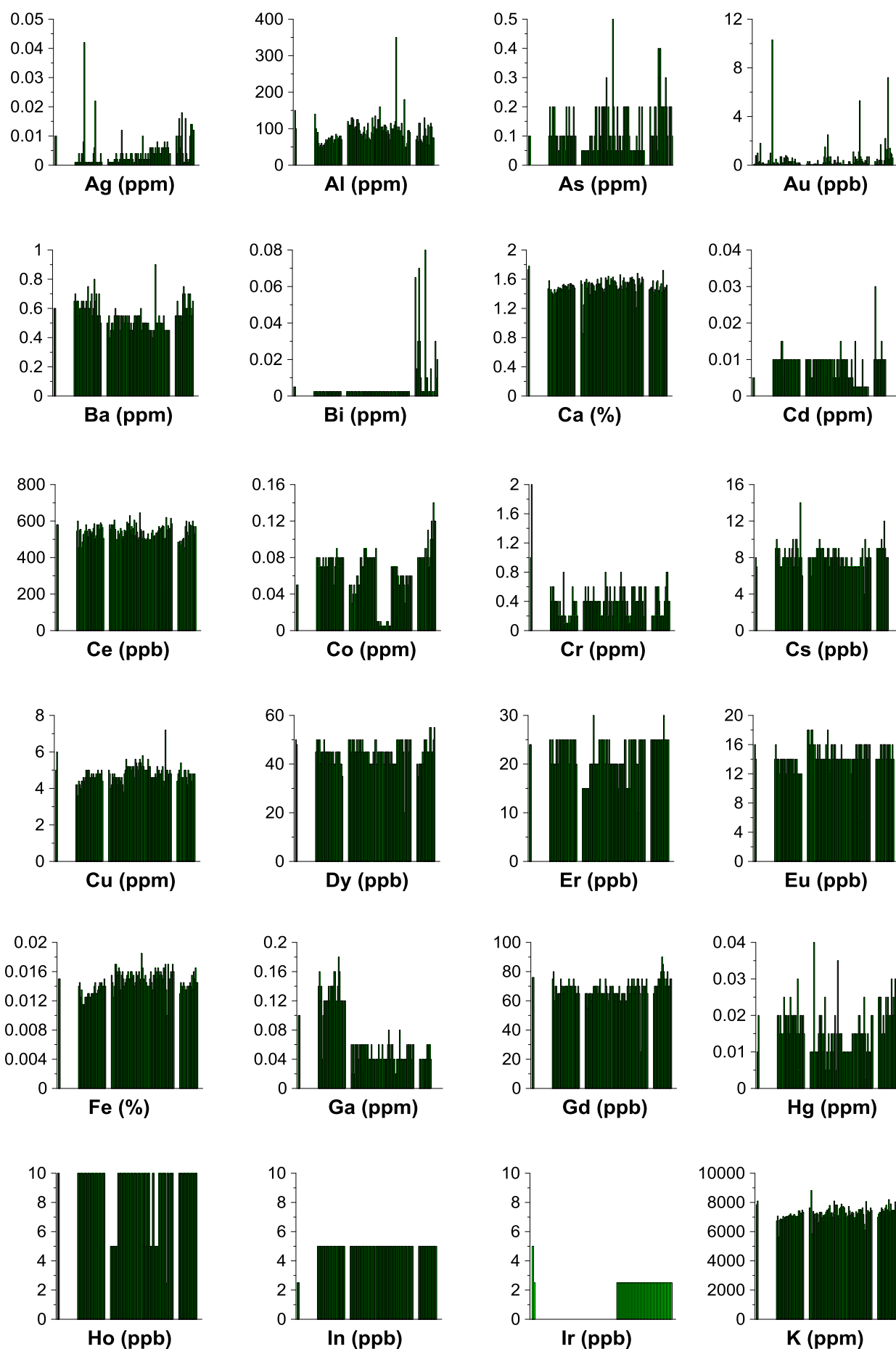
Appendix Figure 1: Results for duplicate analyses



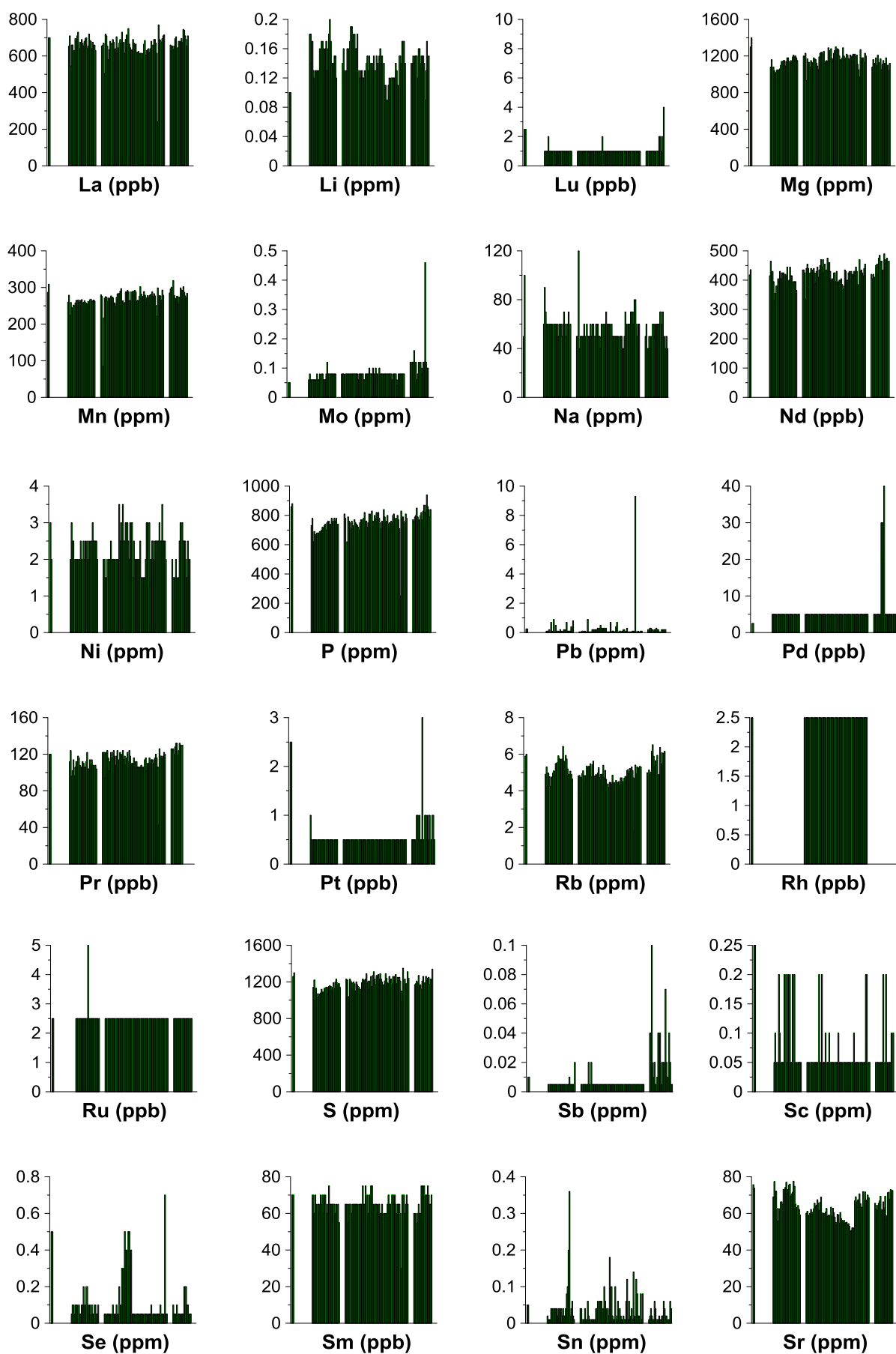
Appendix Figure 1: Results for duplicate analyses (continued)



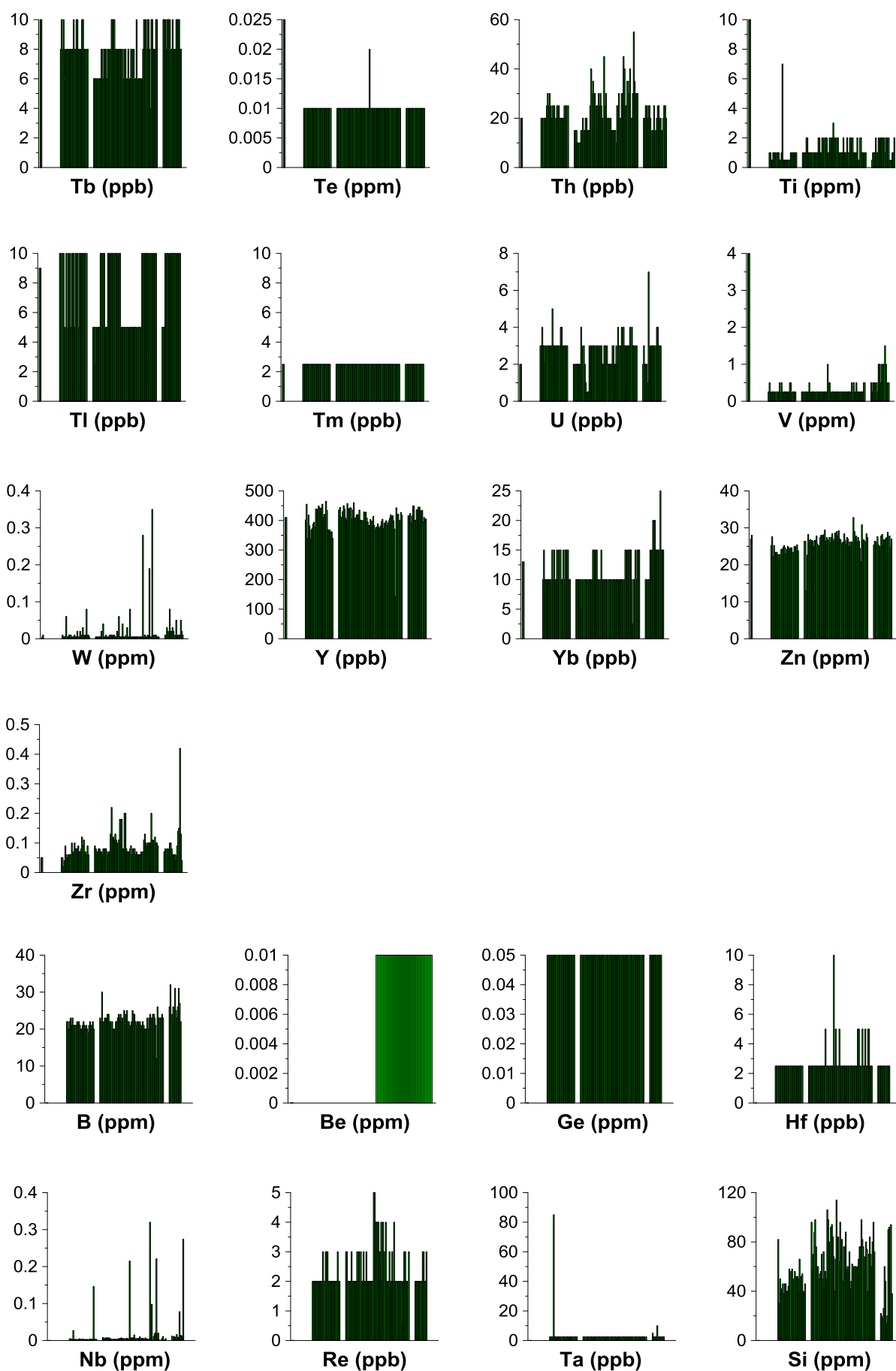
Appendix Figure 1: Results for duplicate analyses (continued)



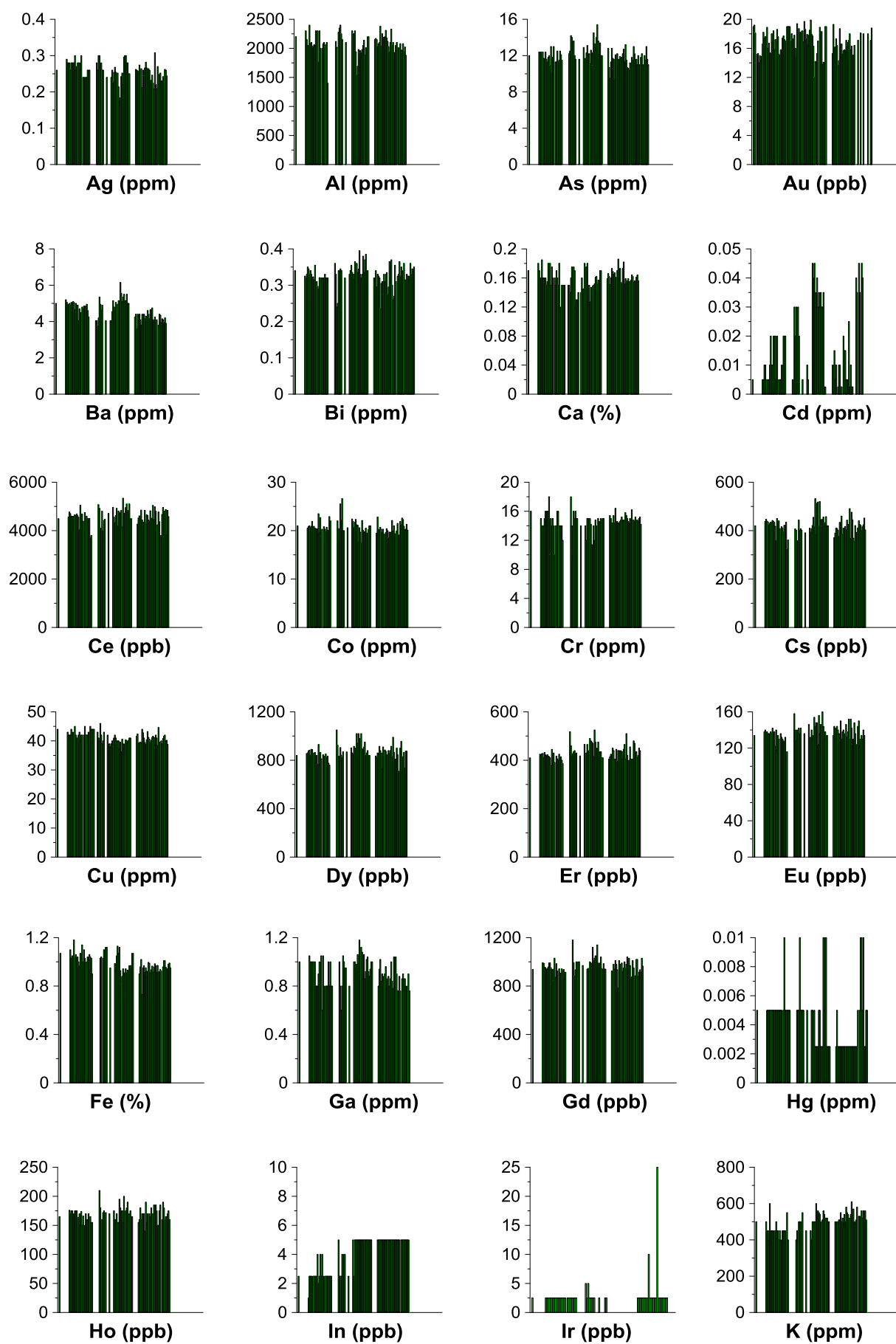
Appendix Figure 2: Internal CSIRO Mulga R1 standard replicates. Displayed are standard samples run for several biogeochemical projects including NE Yilgarn and NW Yilgarn data sets.



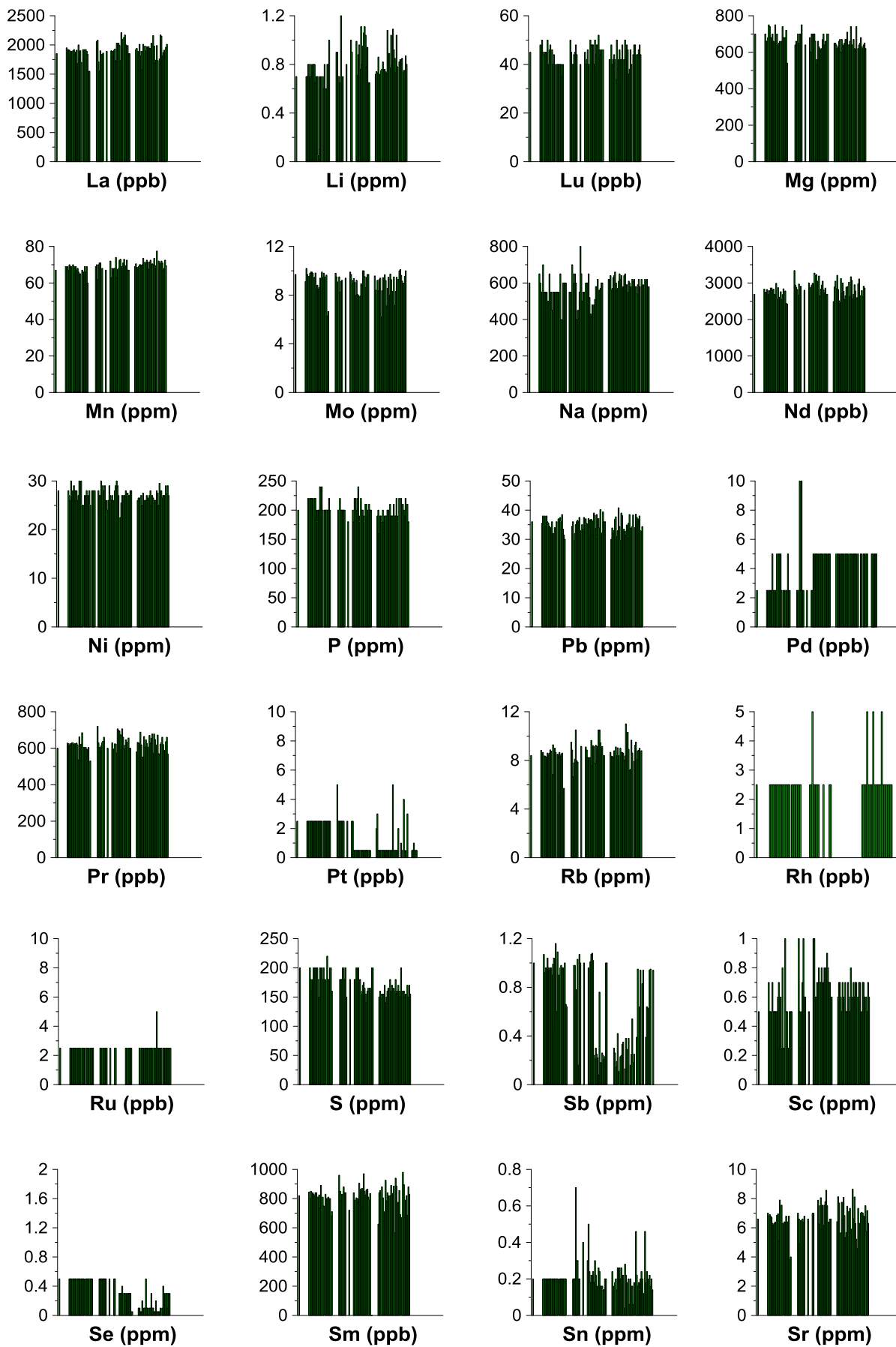
Appendix Figure 2: Internal CSIRO Mulga R1 standard replicates. Displayed are standard samples run for several biogeochemical projects including NE Yilgarn and NW Yilgarn data sets (continued).



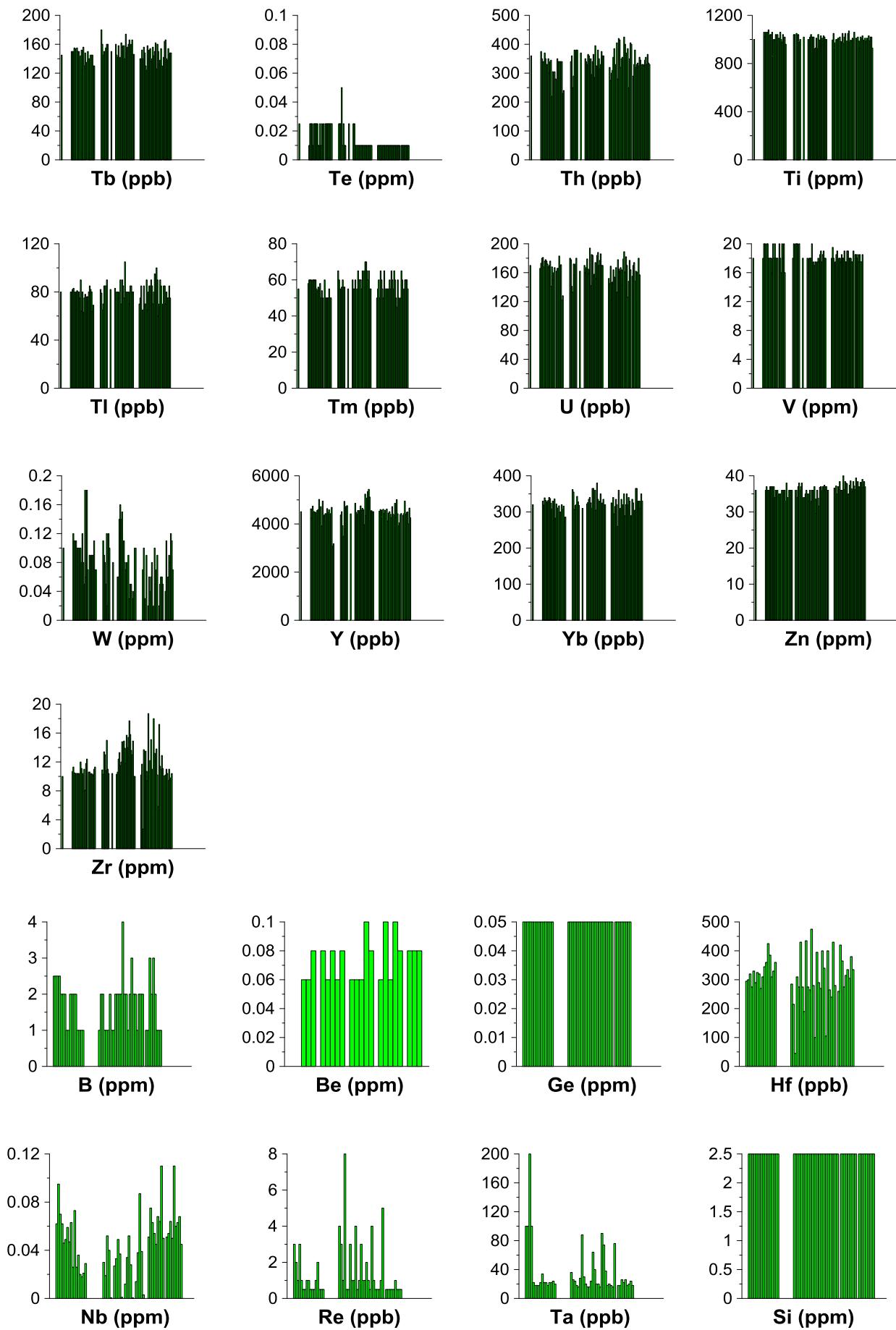
Appendix Figure 2: Internal CSIRO Mulga R1 standard replicates. Displayed are standard samples run for several biogeochemical projects including NE Yilgarn and NW Yilgarn data sets (continued).



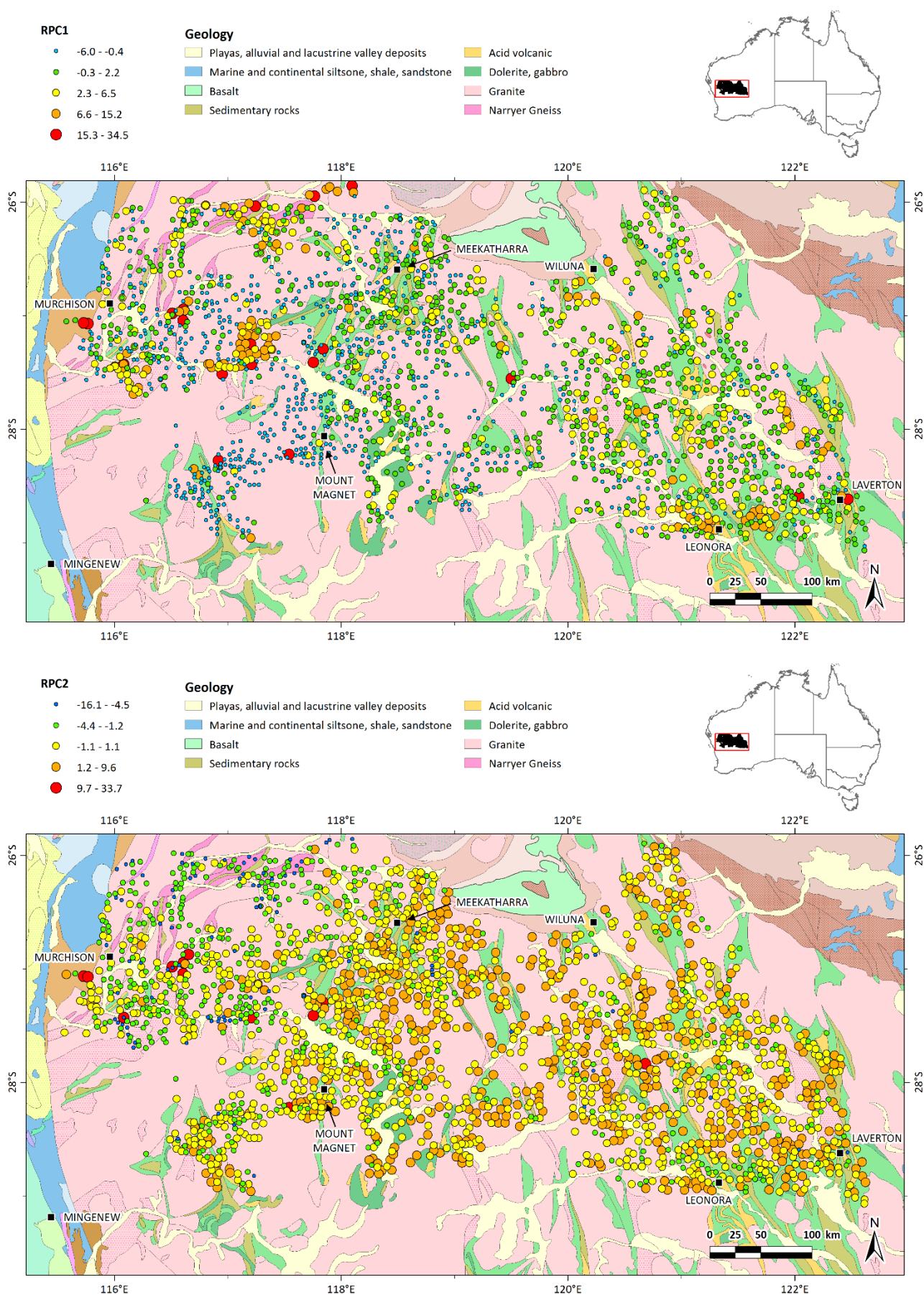
Appendix Figure 3: External (Bureau Veritas) S257 standard. Displayed are standard samples run for sthis project and previous projects.



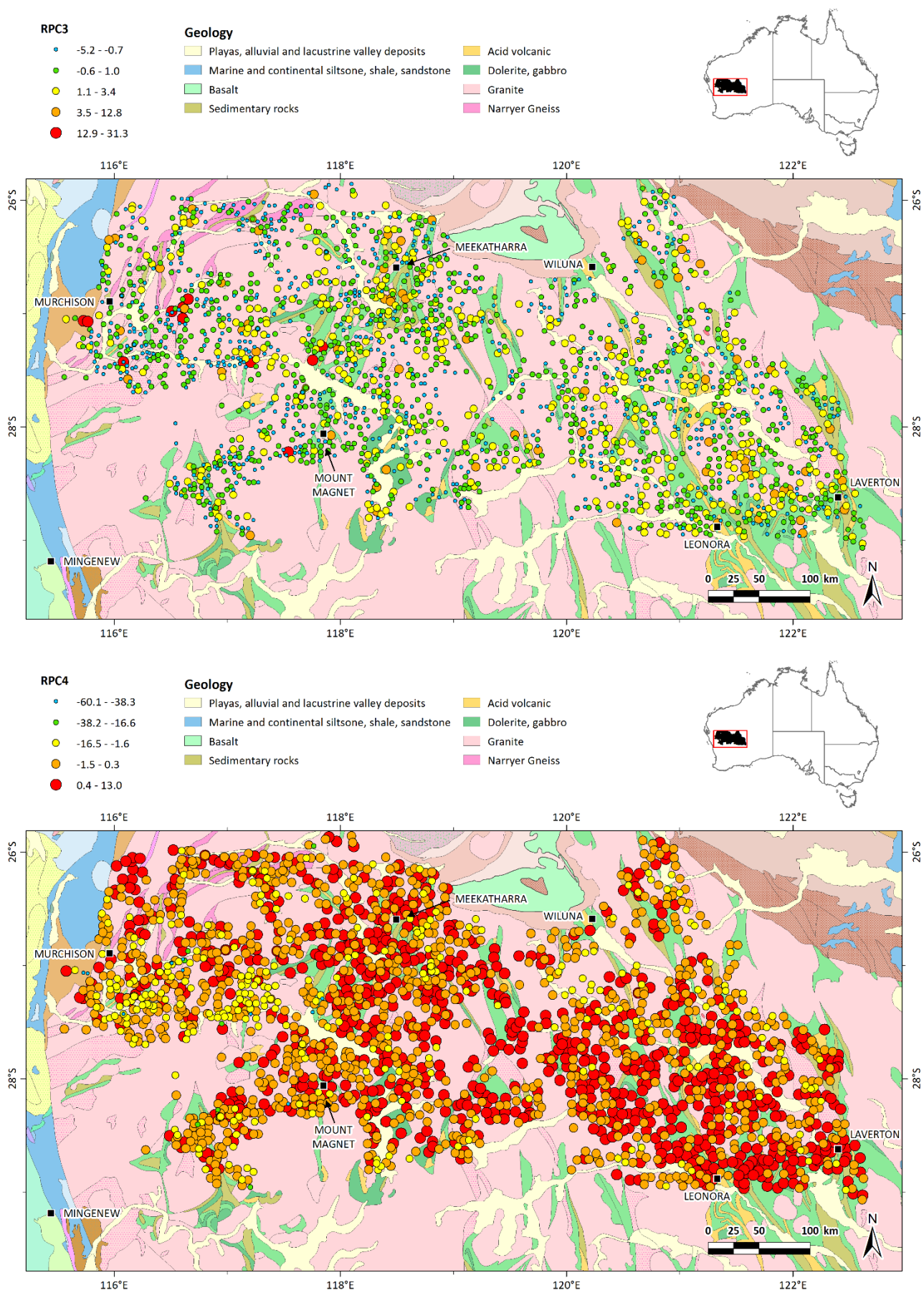
Appendix Figure 3: External (Bureau Veritas) S257 standard run for this project and previous projects (continued).



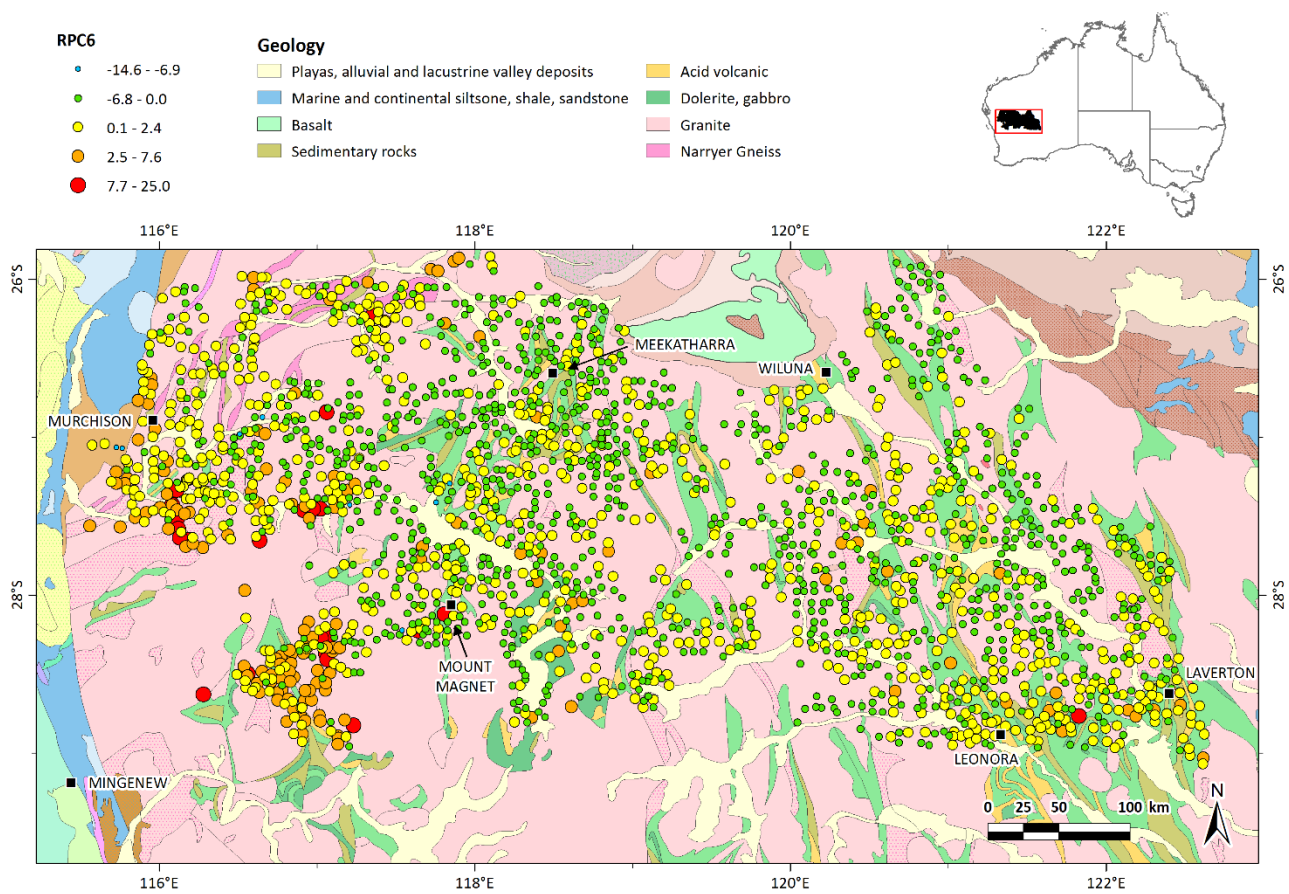
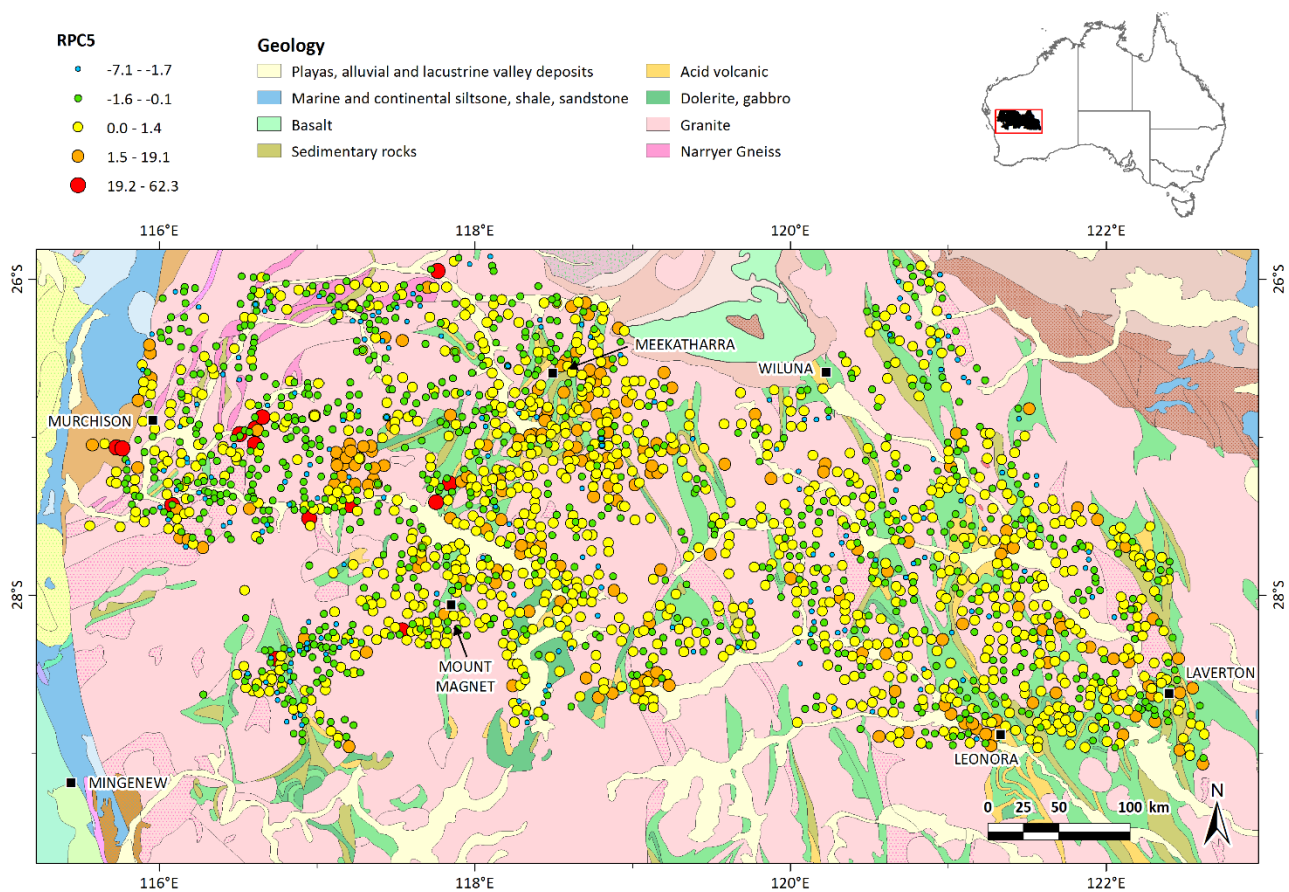
Appendix Figure 3: External (Bureau Veritas) S257 standard run for this project and previous projects (continued).



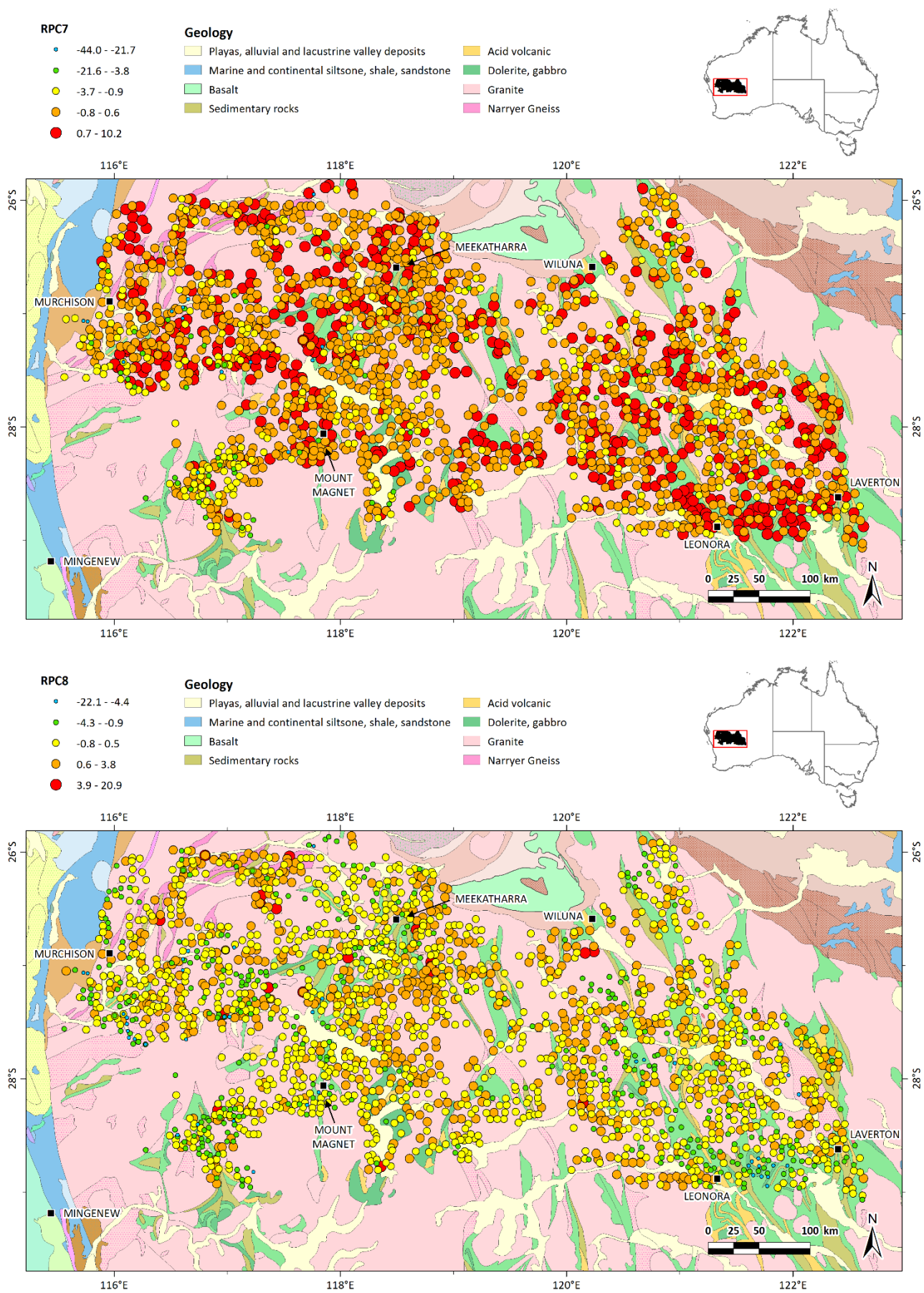
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12.



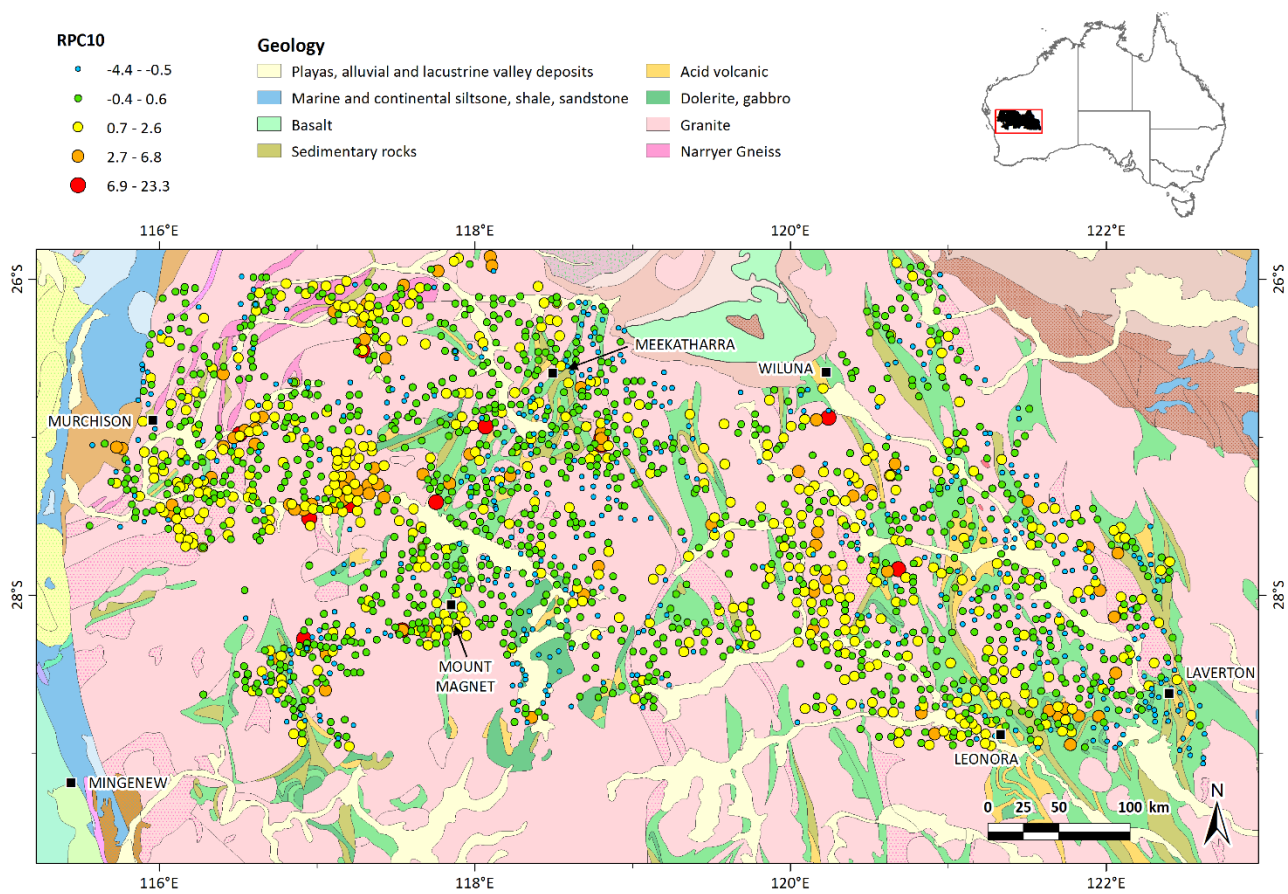
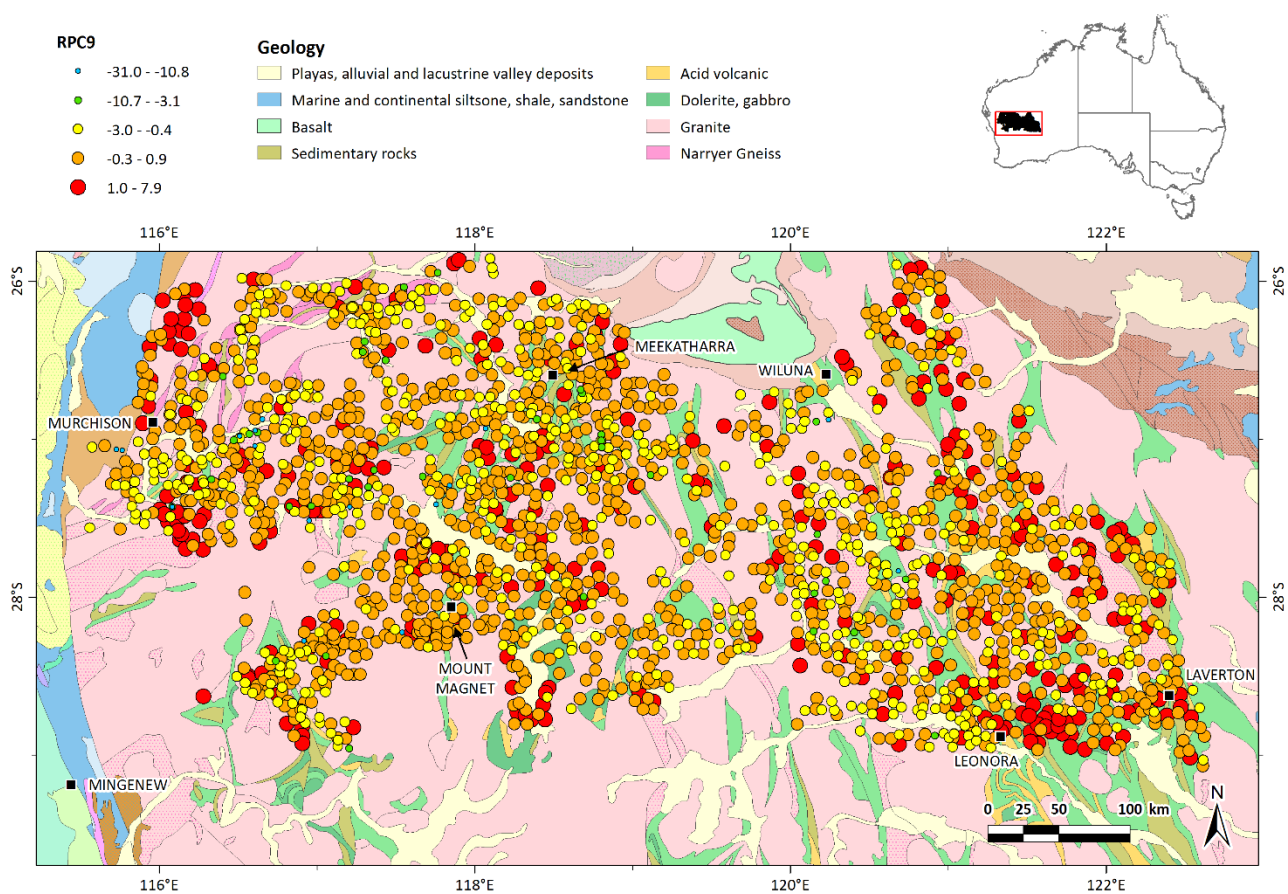
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12 (continued).



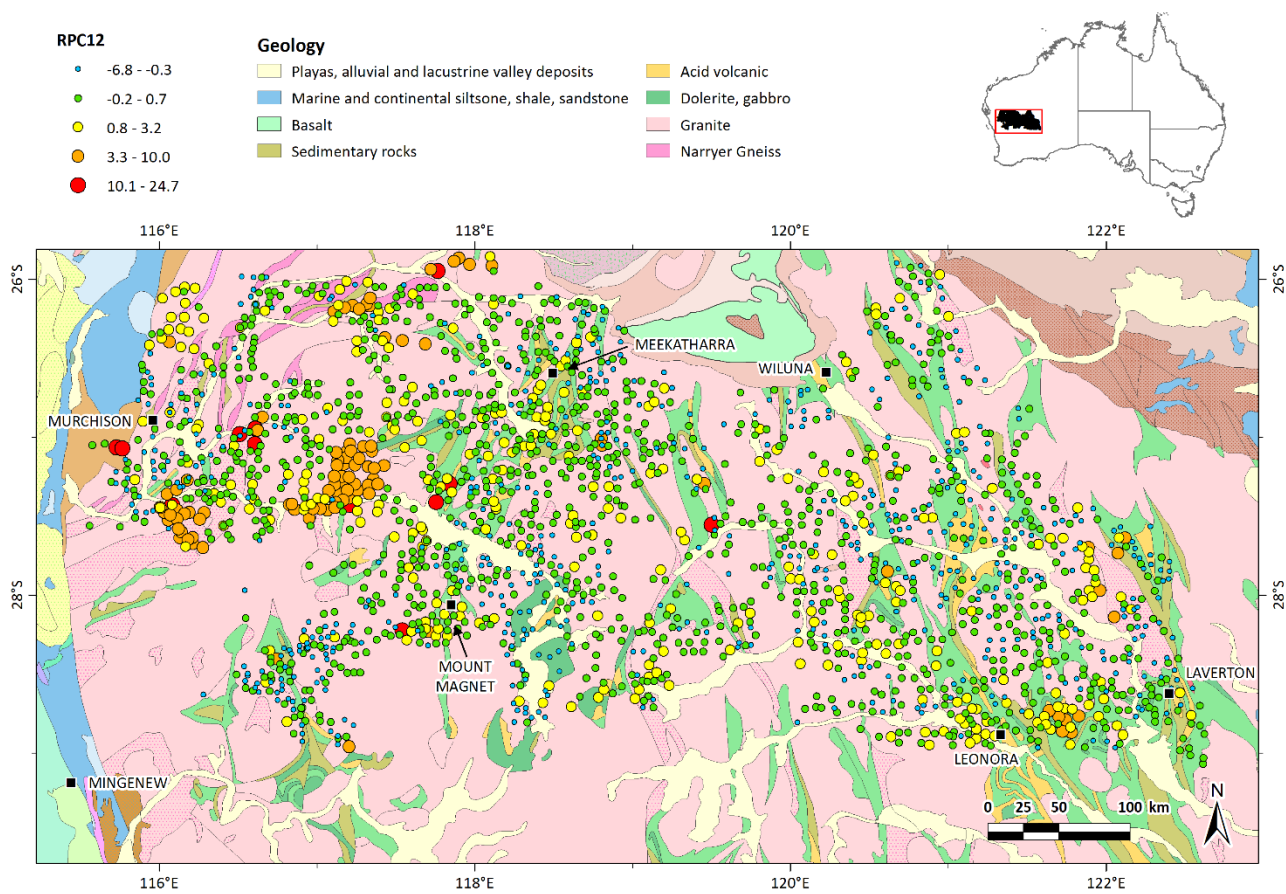
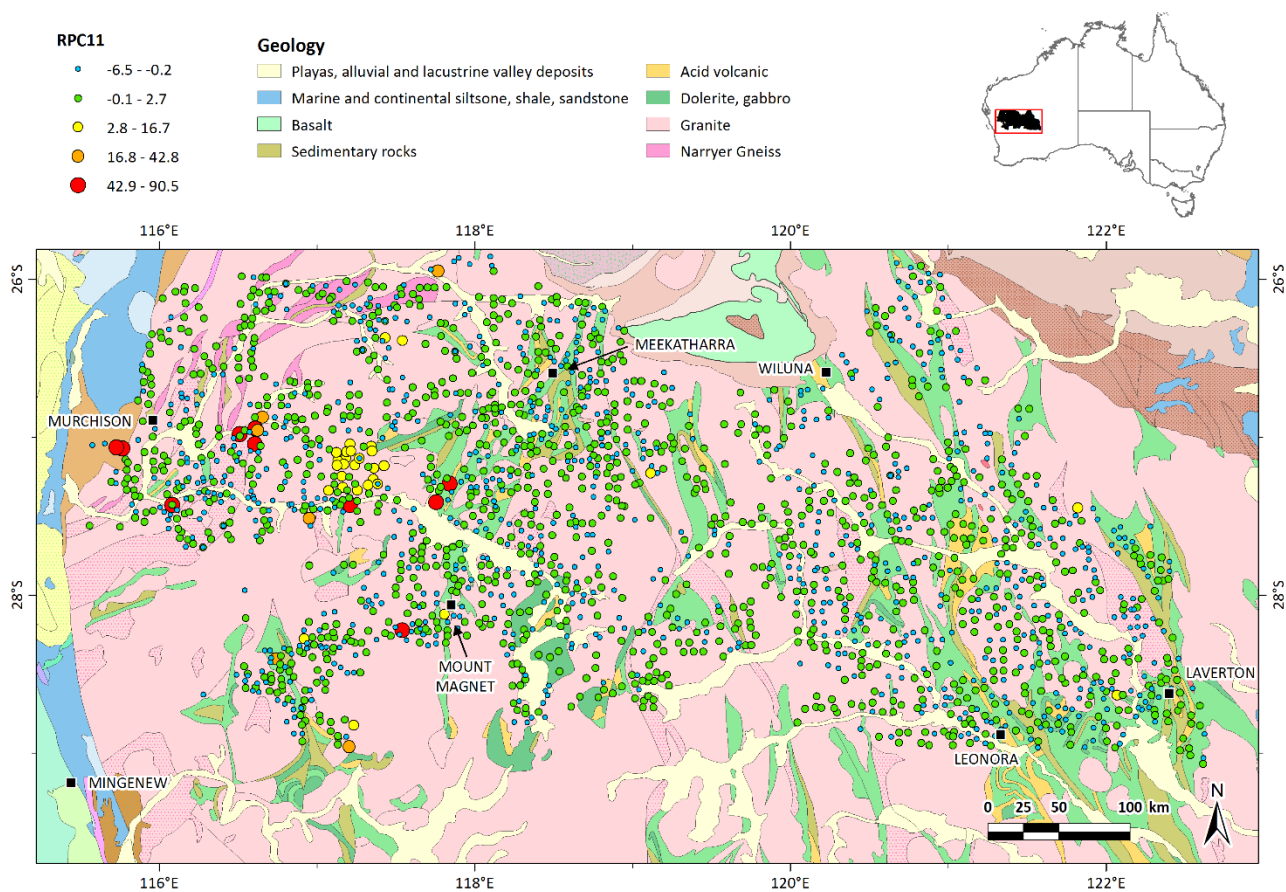
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12 (continued).



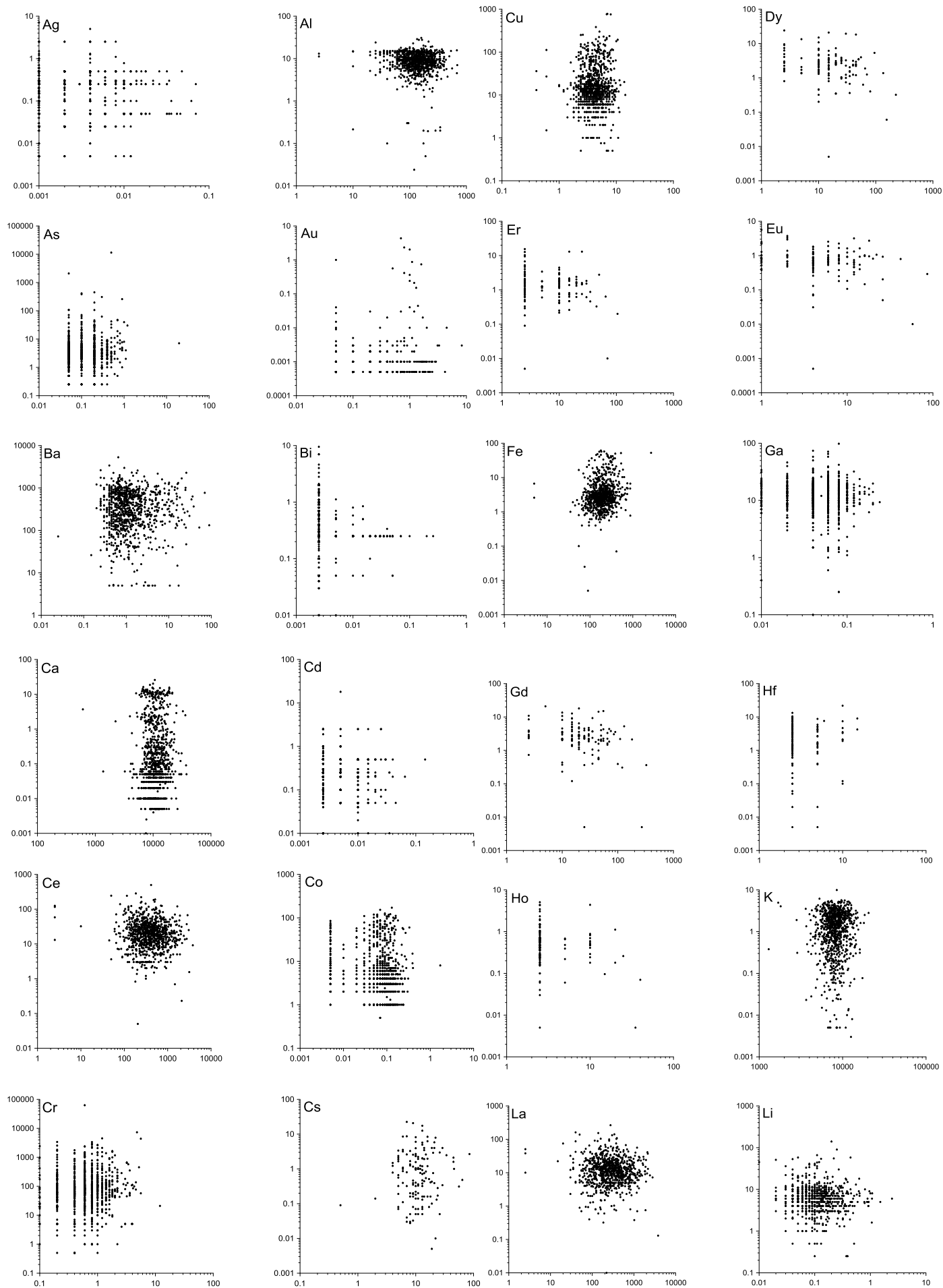
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12 (continued).



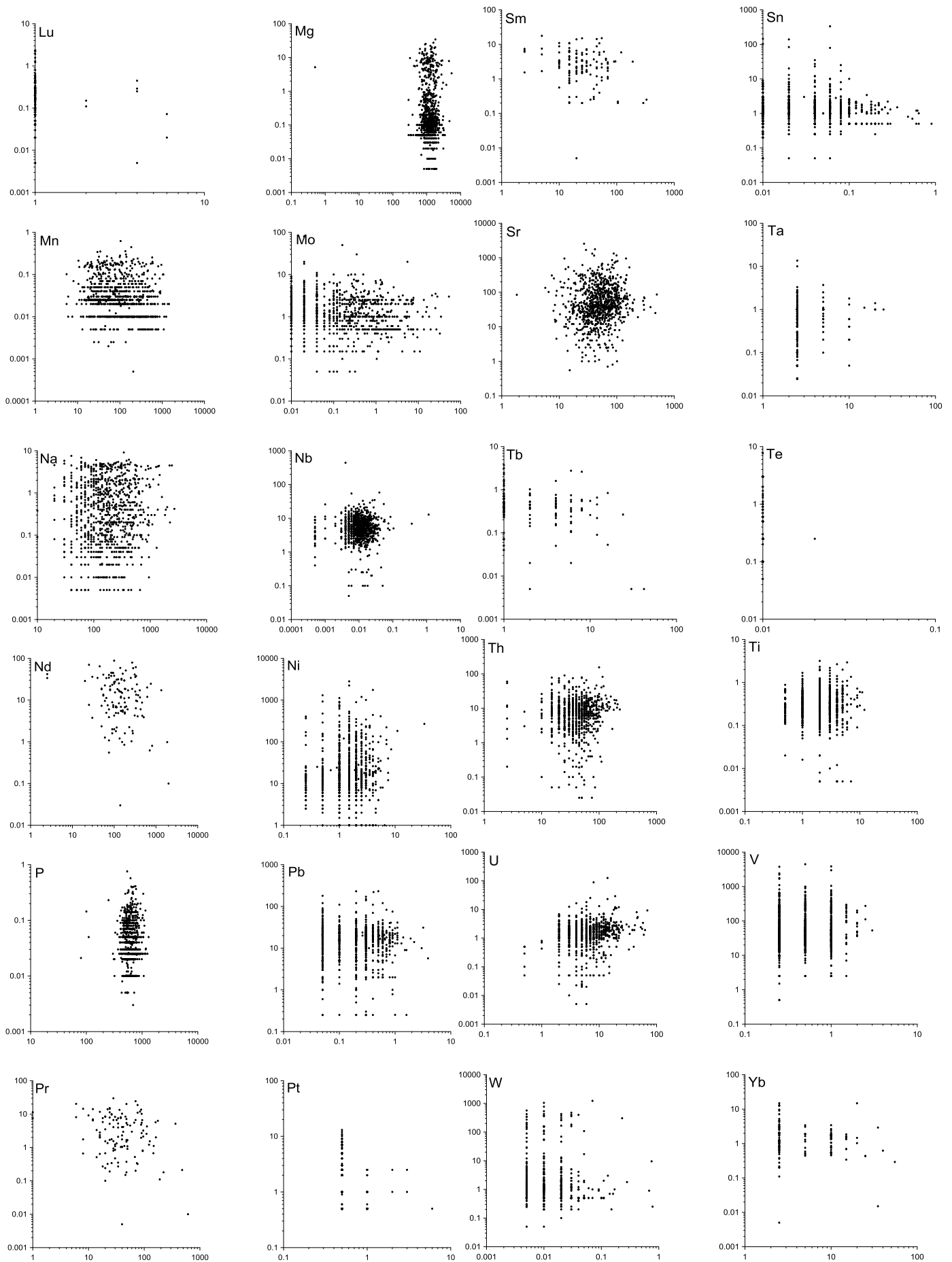
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12 (continued).



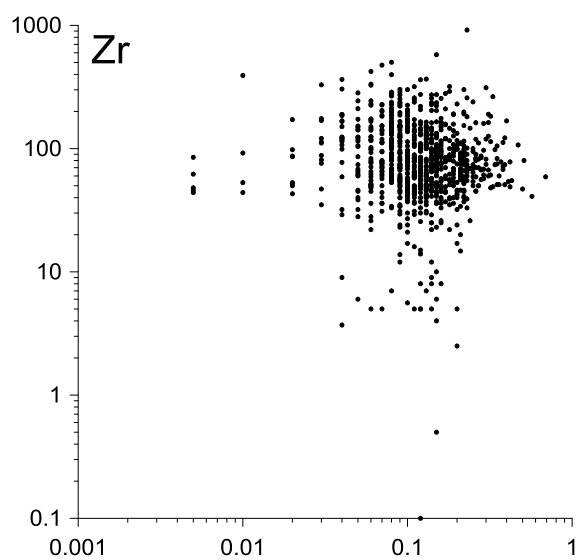
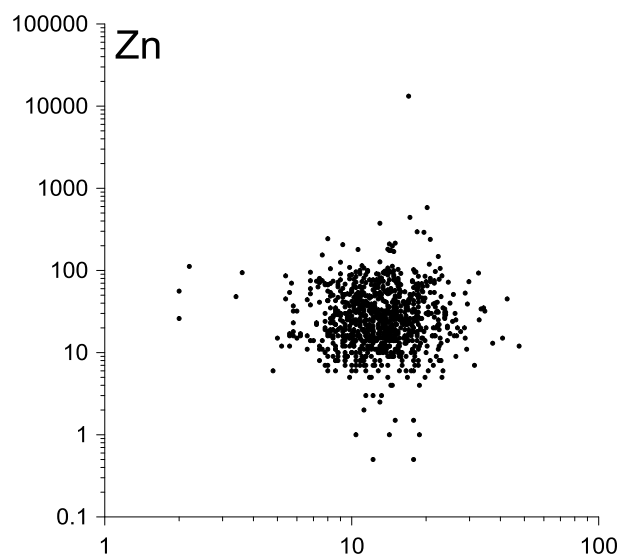
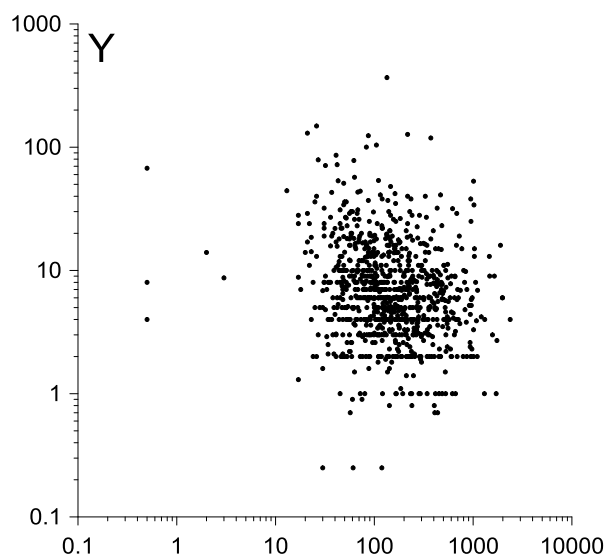
Appendix Figure 4: Robust Principal Component Analysis plotted scores for PC1-PC12 (continued).



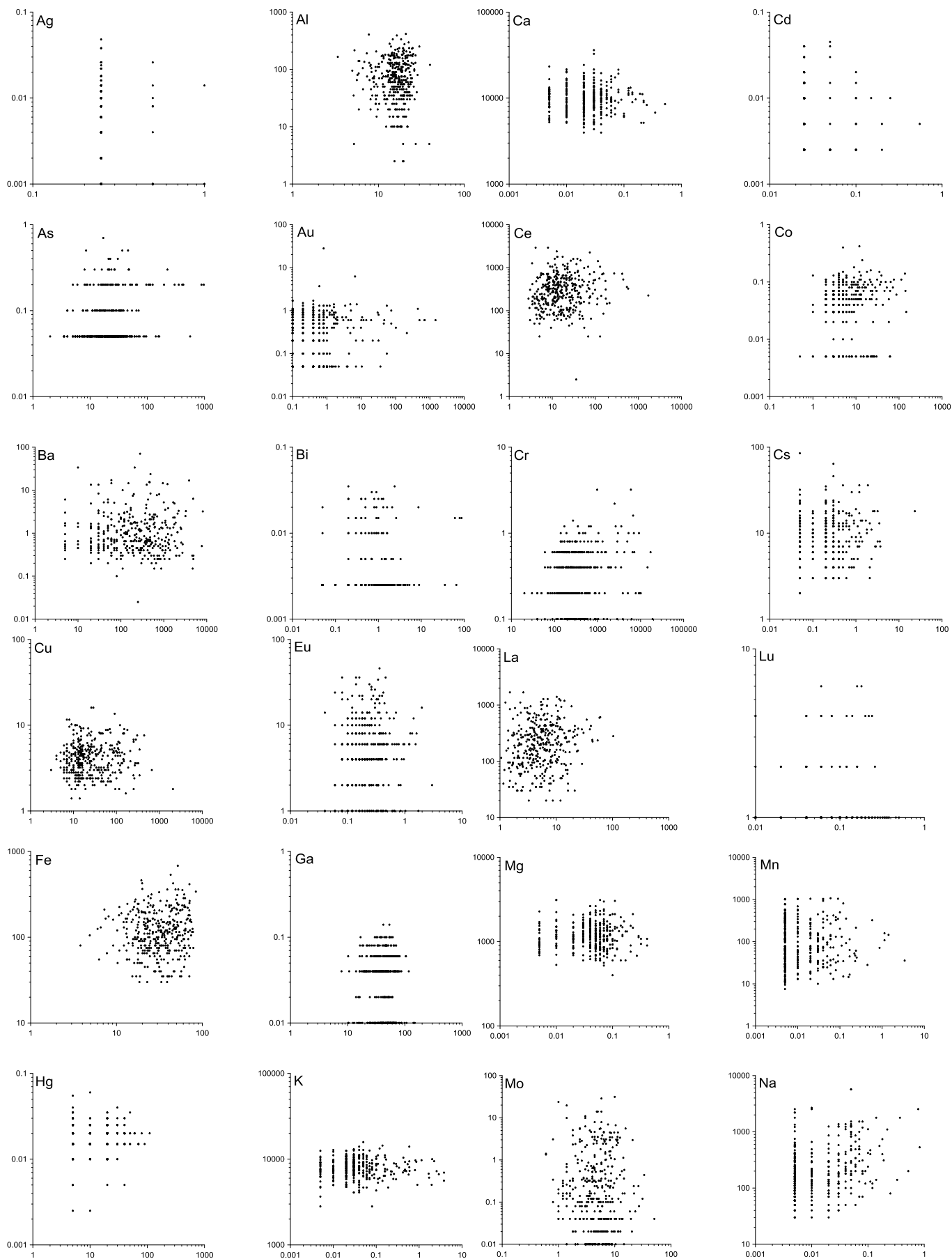
Appendix Figure 5: GSWA data vs biogeochemistry data for north Yilgarn.



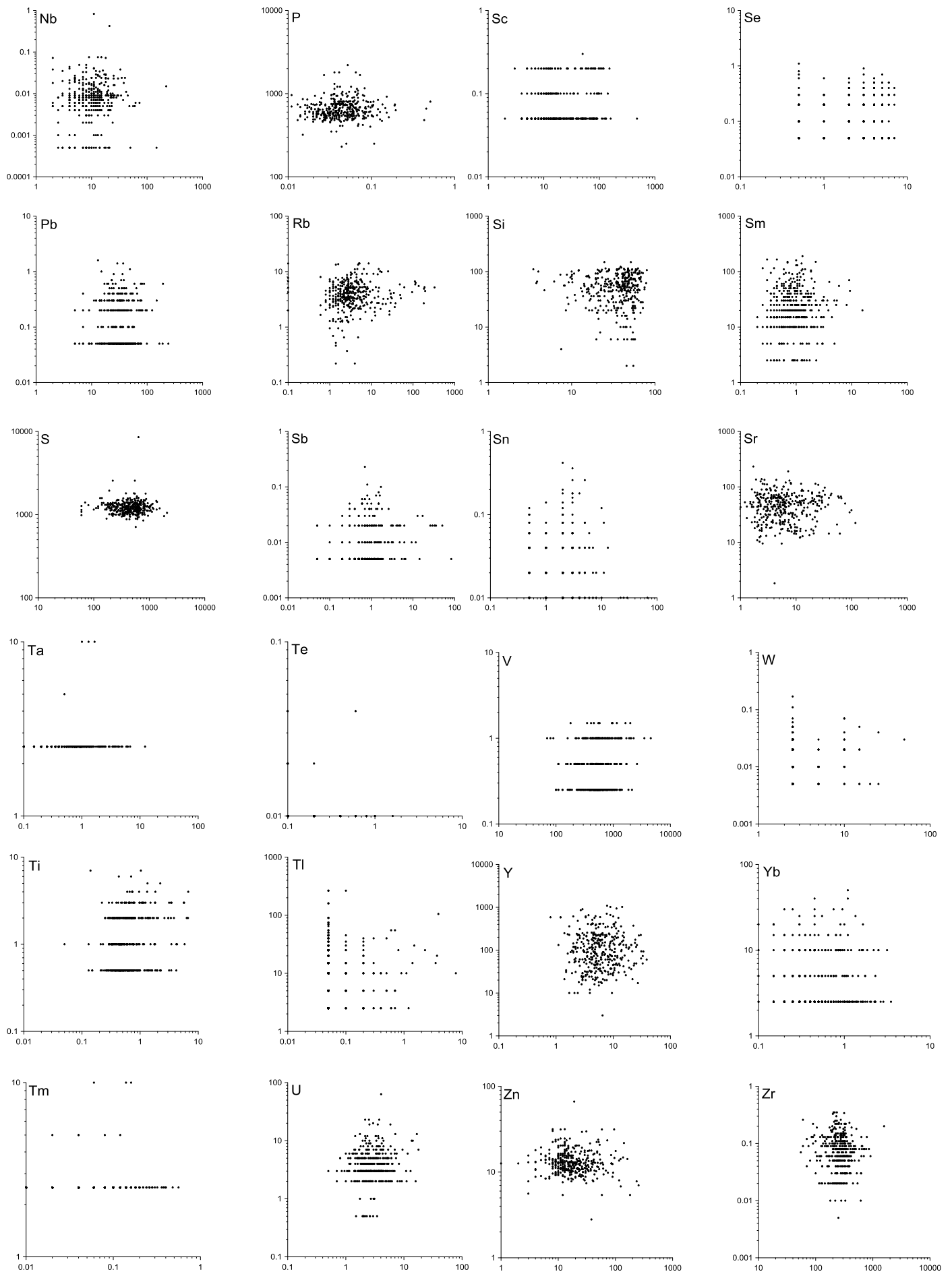
Appendix Figure 5: GSWA data vs biogeochemistry data for north Yilgarn (continued).



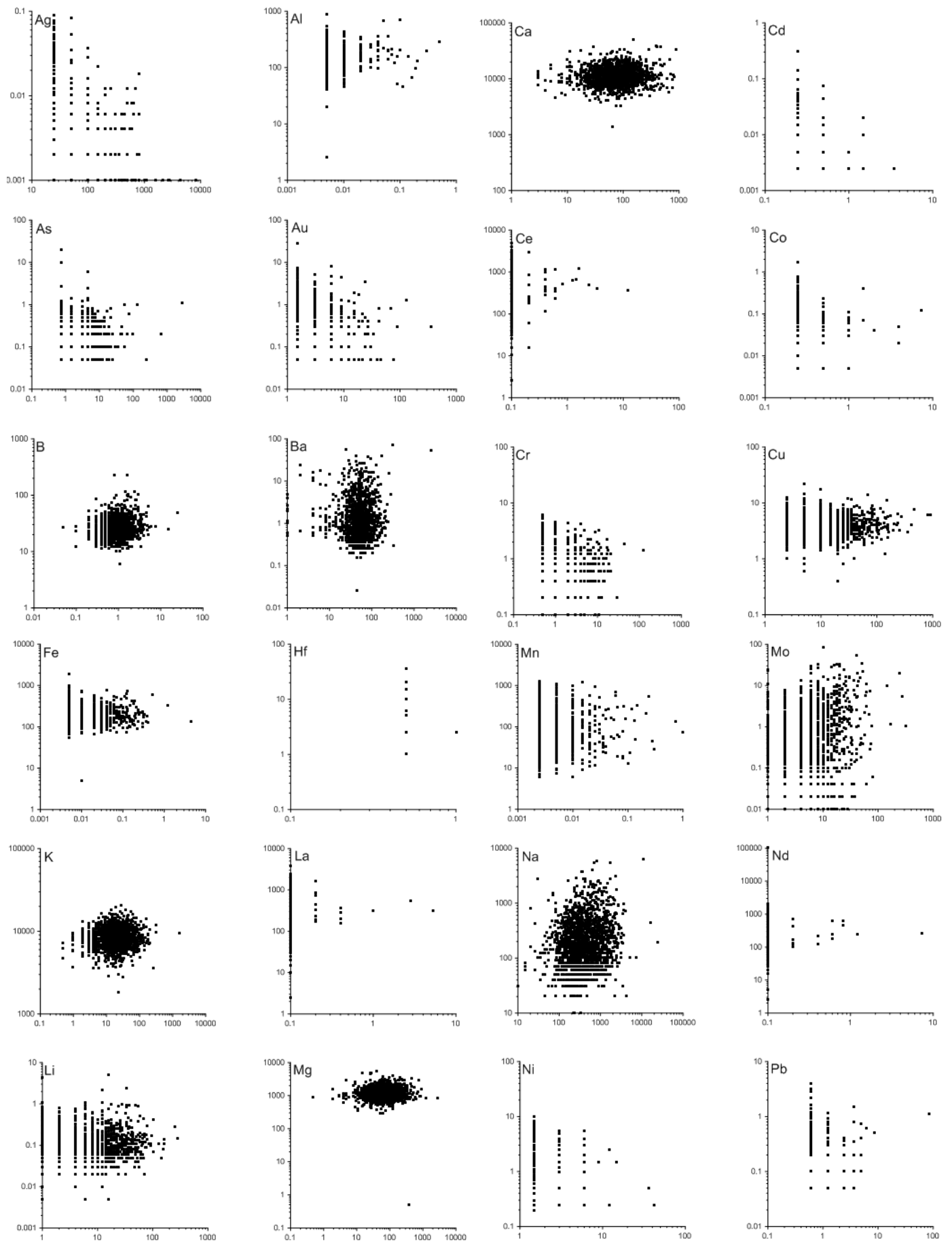
Appendix Figure 5: GSWA data vs biogeochemistry data for north Yilgarn (continued).



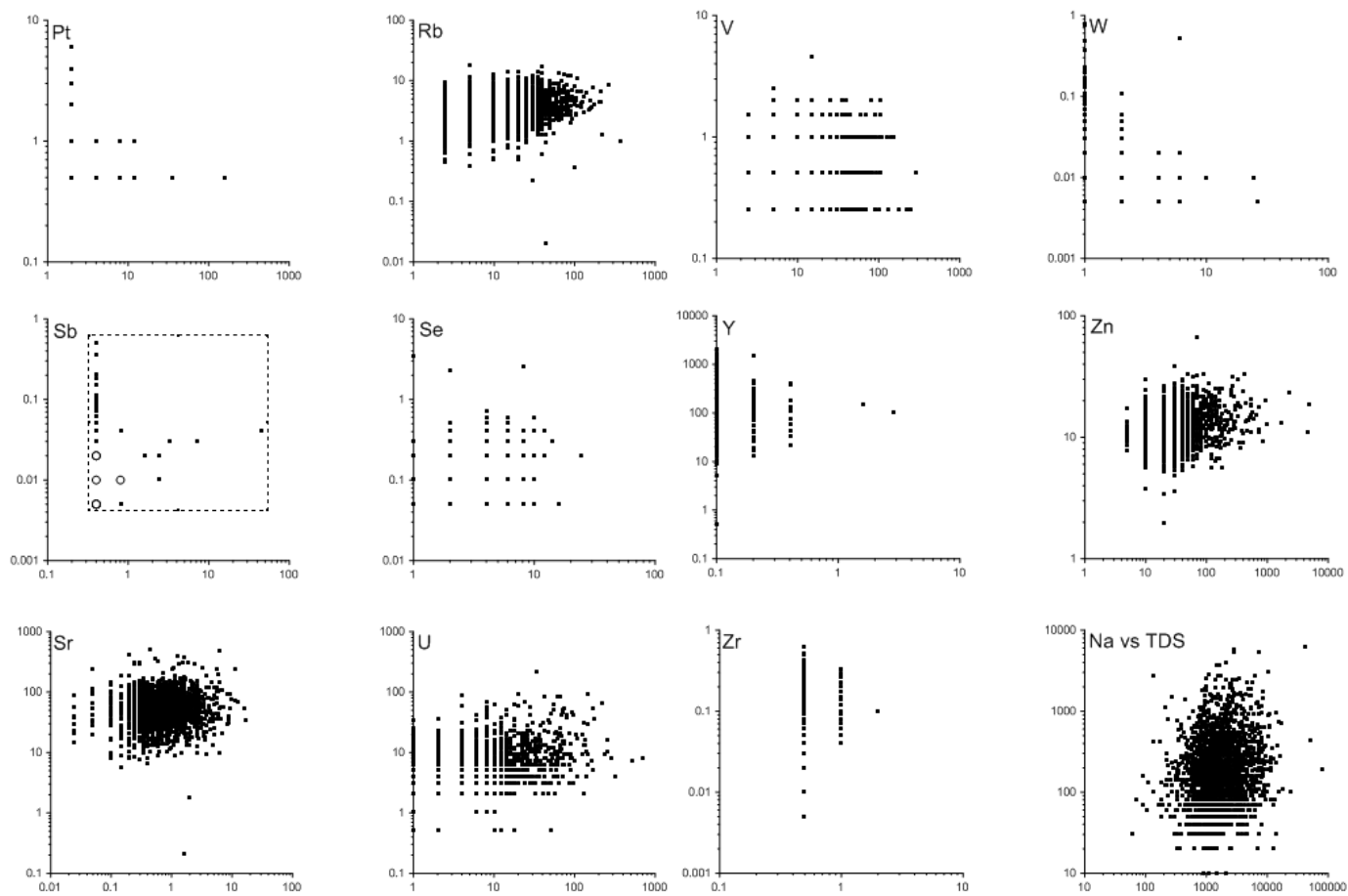
Appendix Figure 6: Yilgarn atlas data vs biogeochemistry data



Appendix Figure 6: Yilgarn atlas data vs biogeochemistry data (continued).



Appendix Figure 7: Hydrogeochemistry data vs biogeochemistry data.



Appendix Figure 7: Hydrogeochemistry data vs biogeochemistry data (continued).

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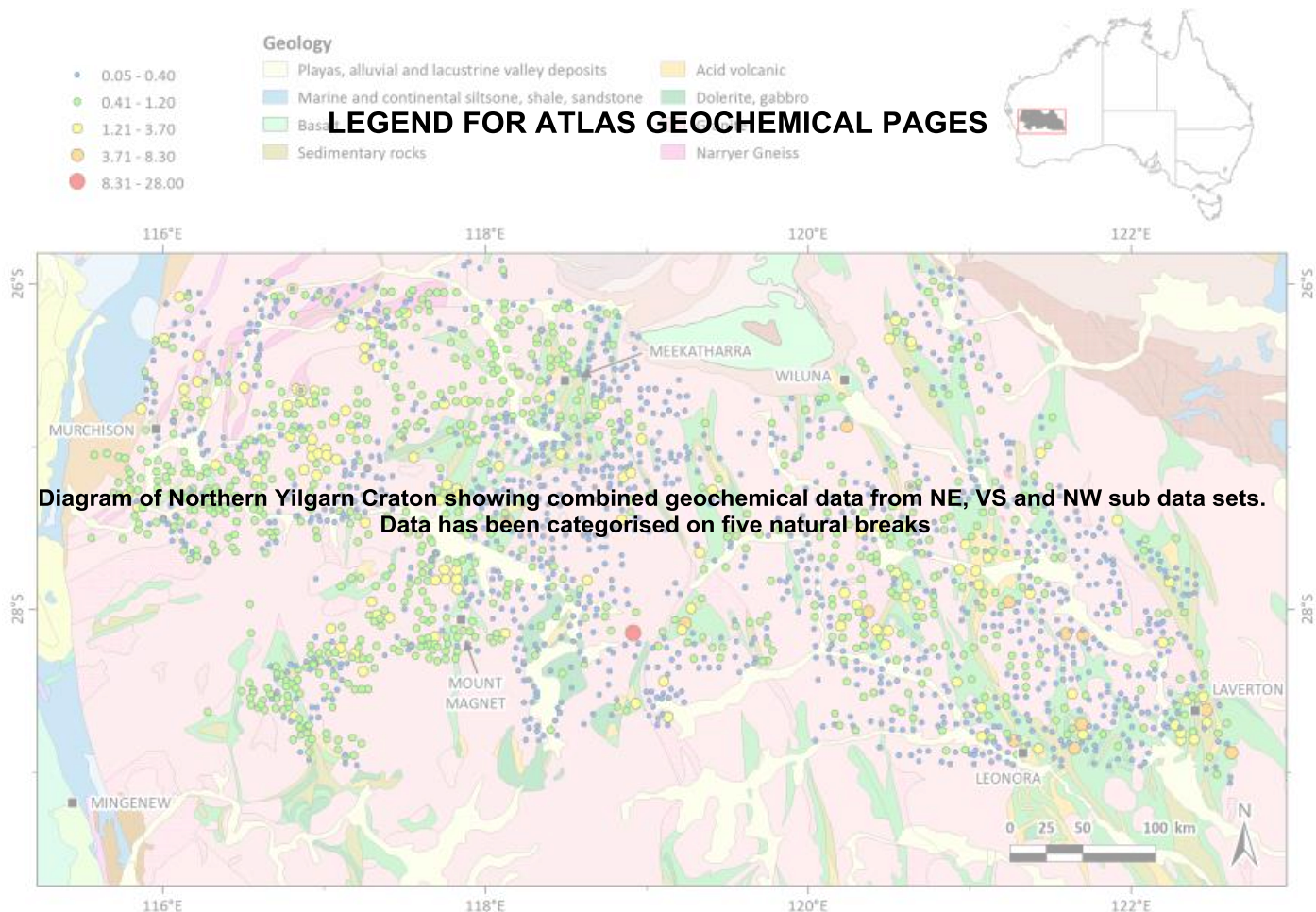
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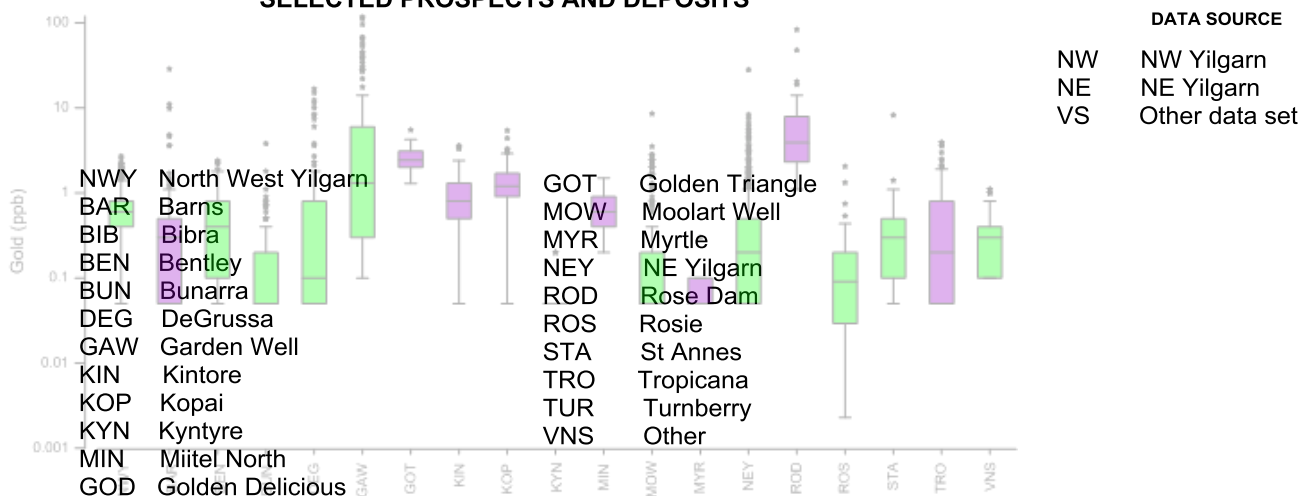
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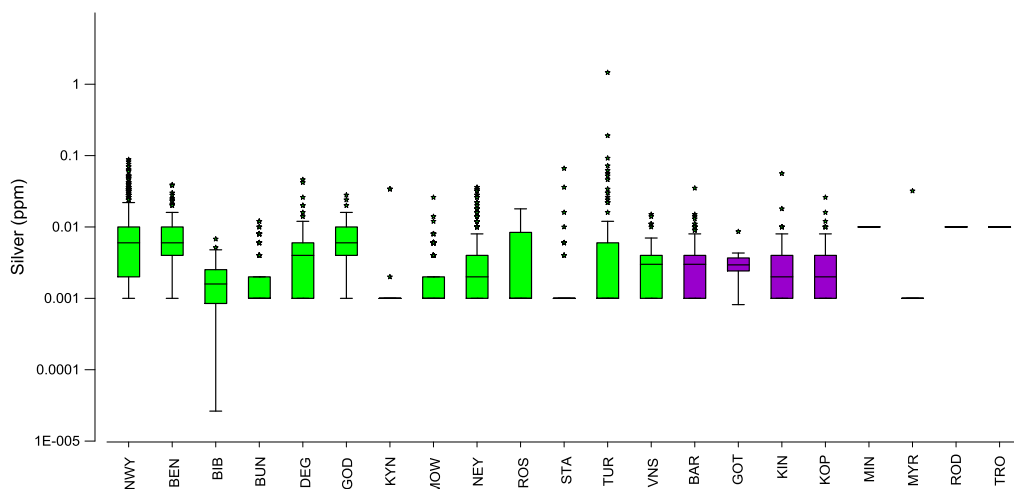
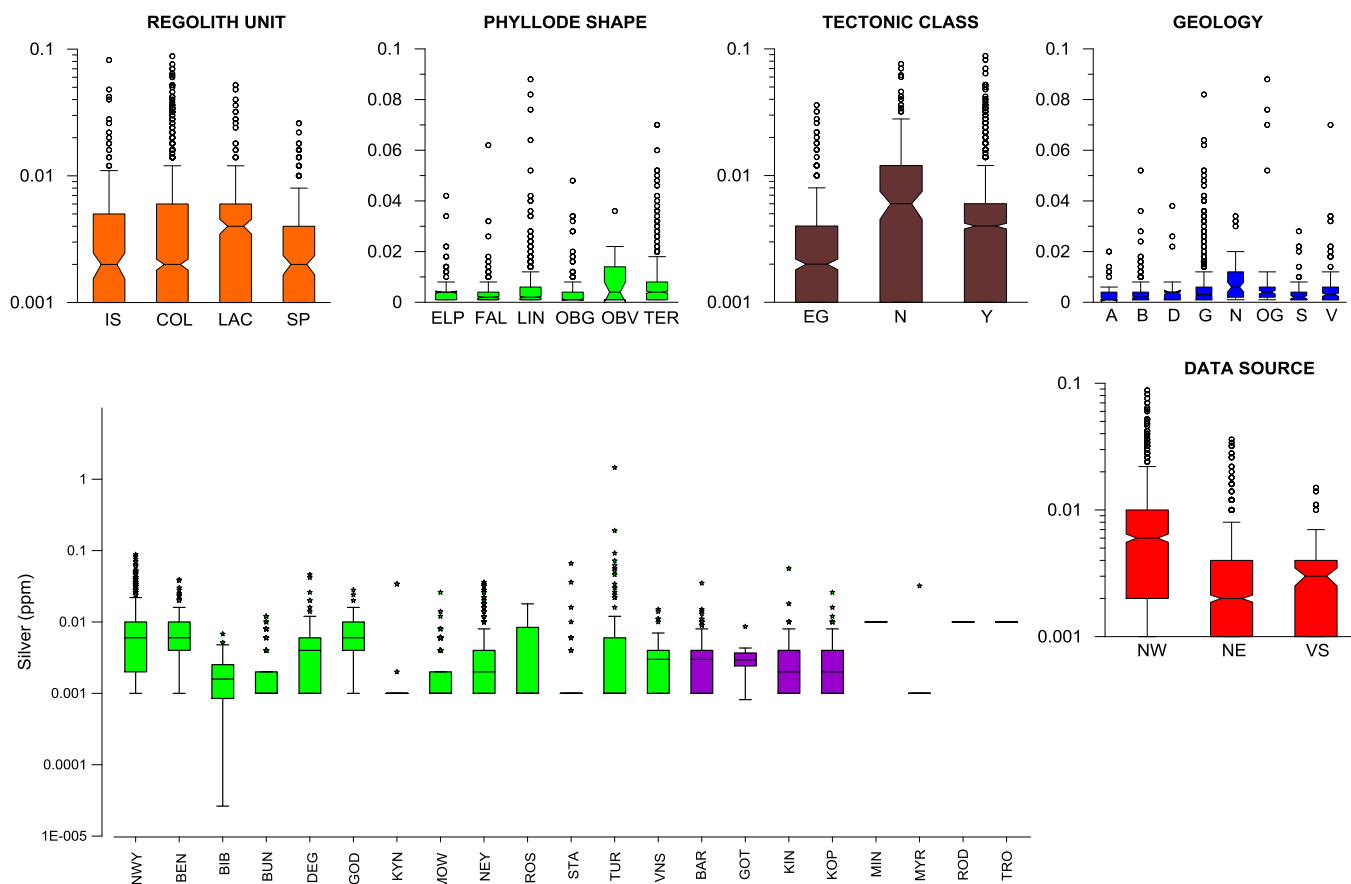
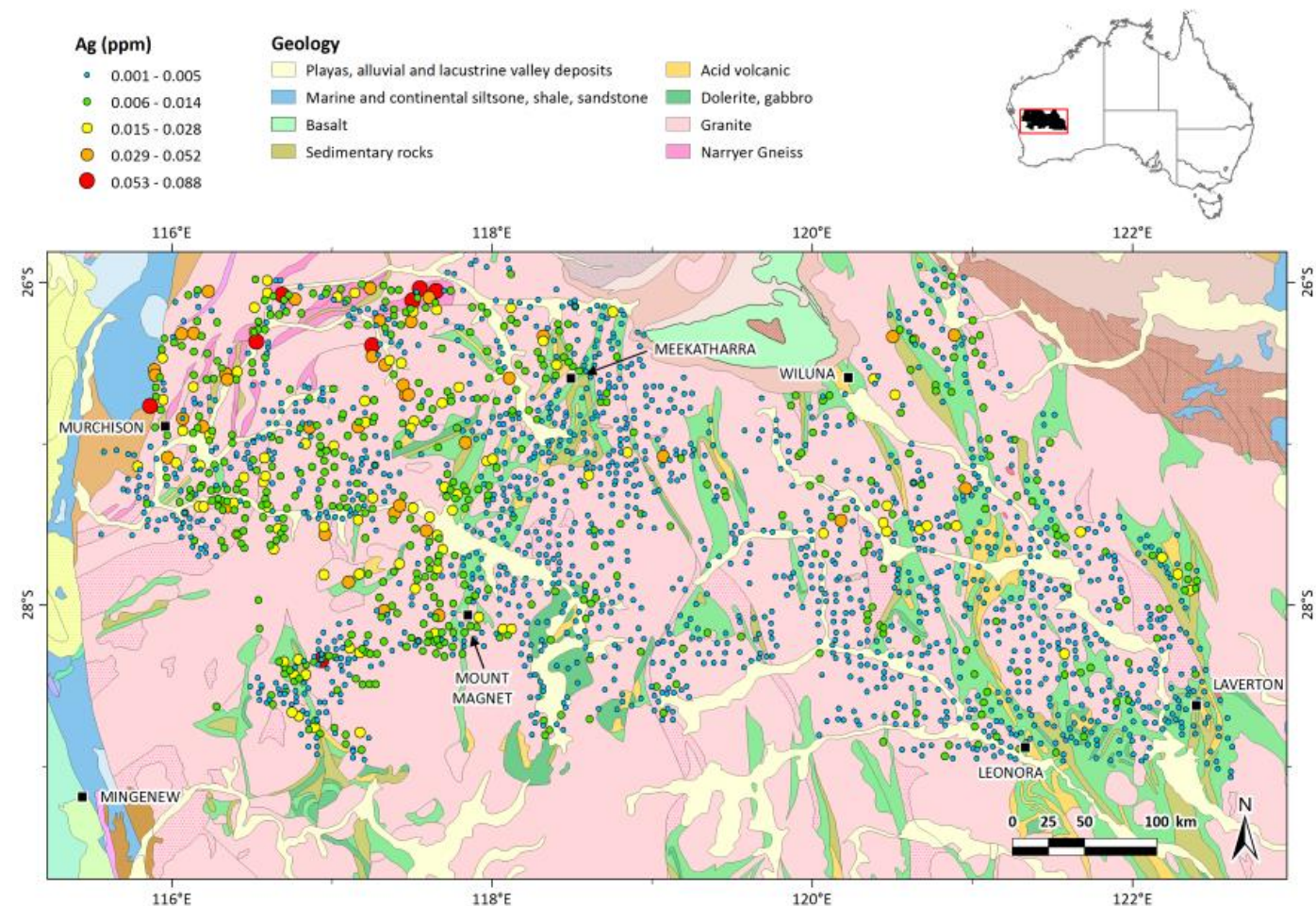


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IS	In situ	ELP	Elliptical	EG	Eastern Goldfields	A	Acid Volcanic
COL	Colluvium	FAL	Falcate	N	Narryer	B	Basalt
LAC	Lacustrine	LIN	Linear	Y	Youanmi	D	Dolerite-gabbro
	/calcrete	OBG	Oblong			G	Granite
SP	Sandplain	OBV	Obovate			N	Narryer Gneiss
		TER	Terete			OG	Other Gneiss
						S	Sedimentary rocks
						V	Valley Fill

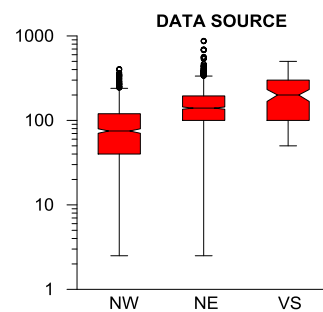
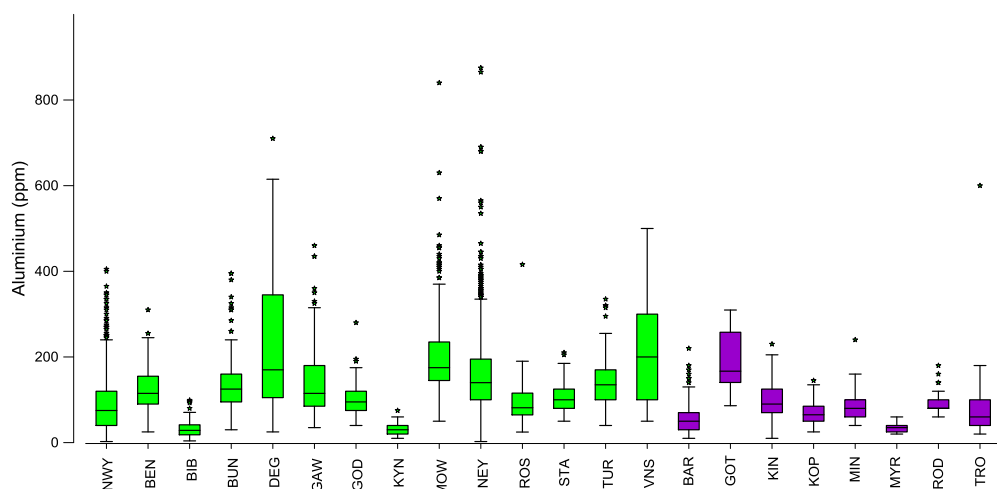
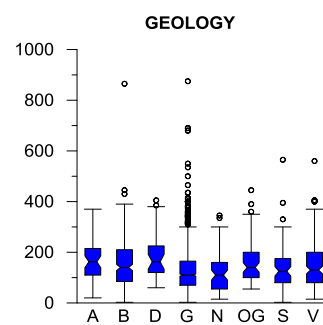
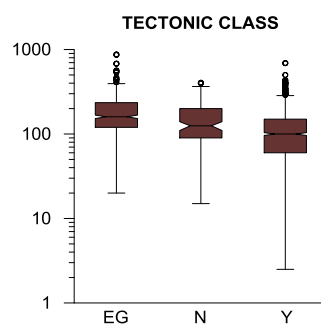
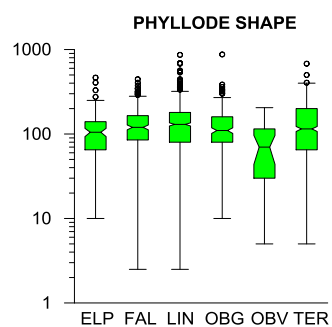
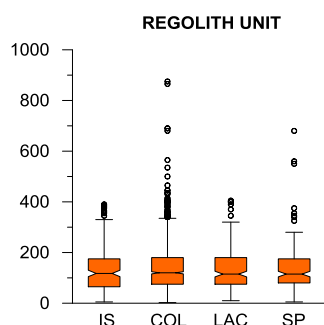
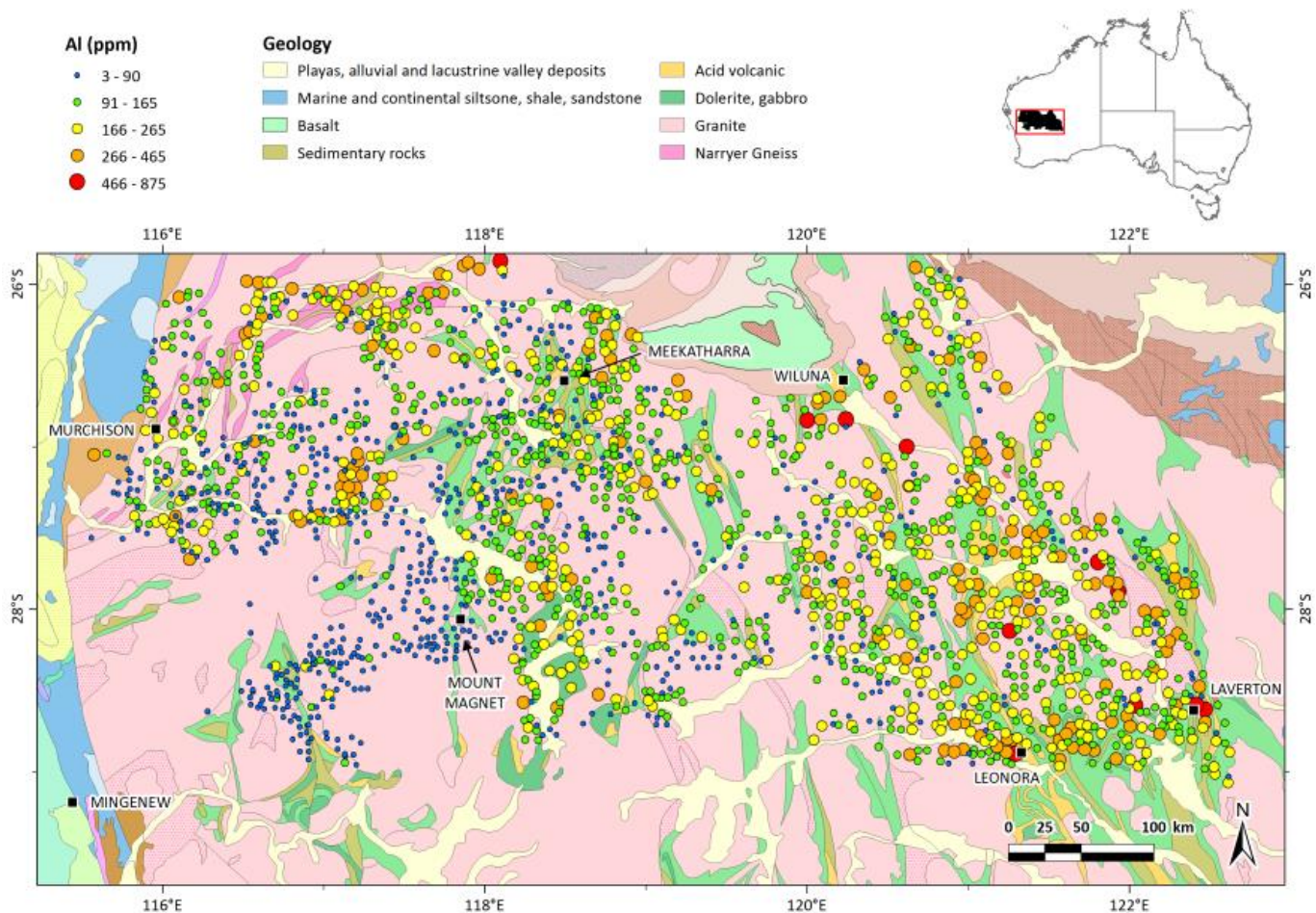
COMPARATIVE HISTOGRAMS OF GEOCHEMISTRY FROM SELECTED PROSPECTS AND DEPOSITS



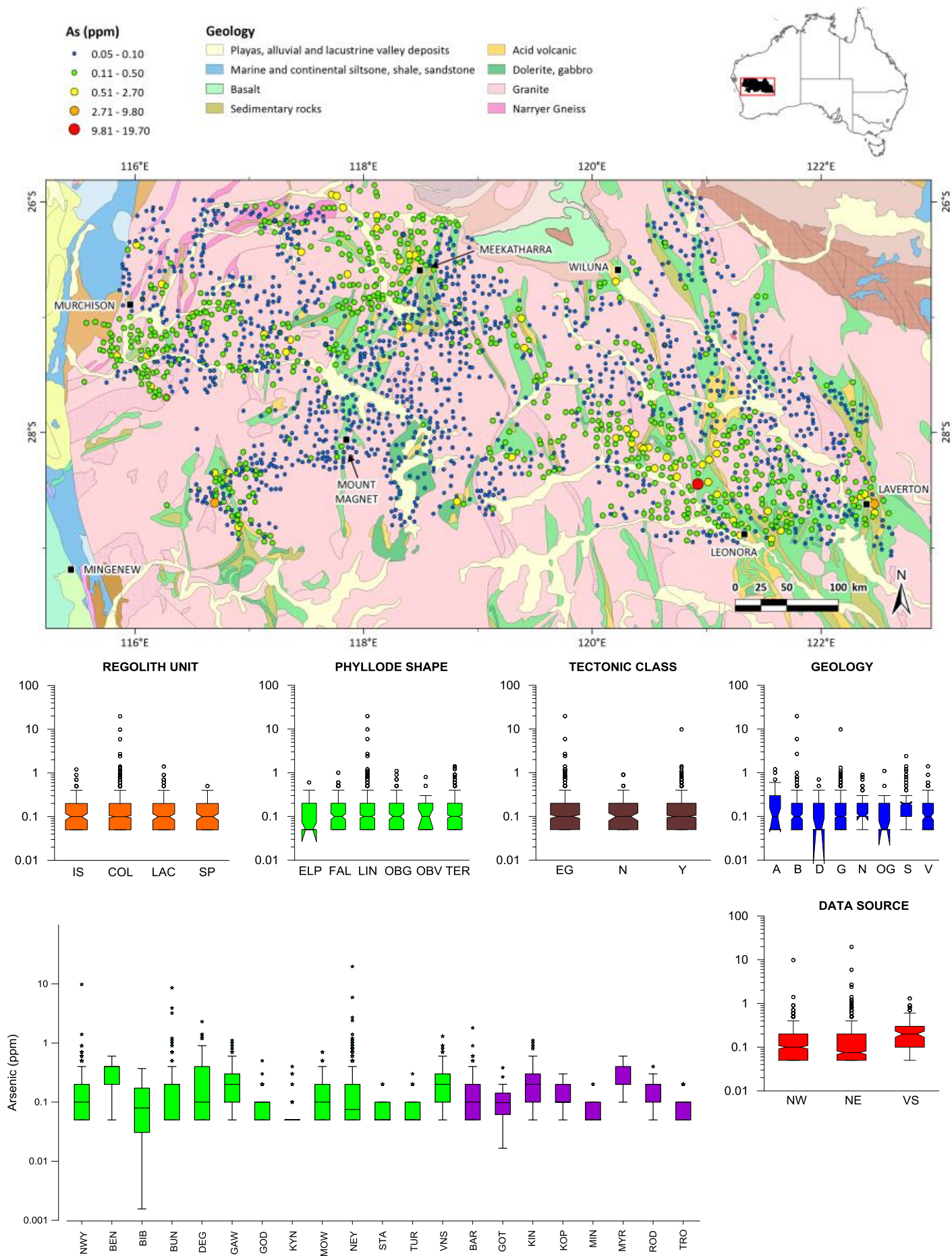
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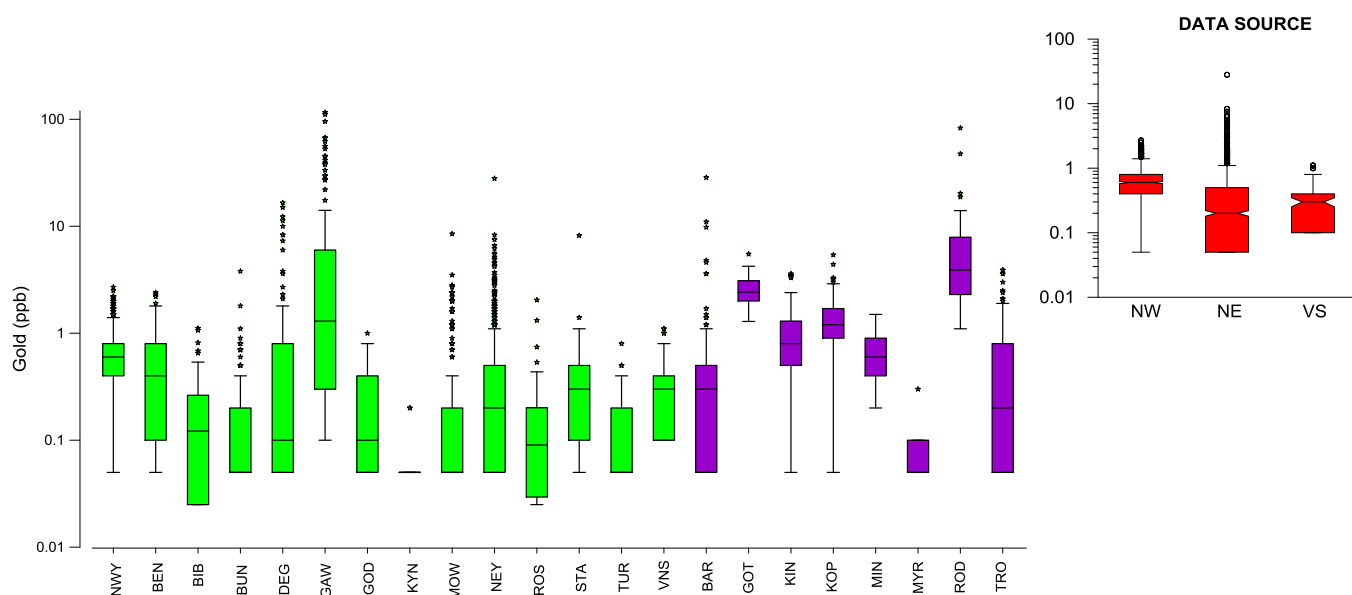
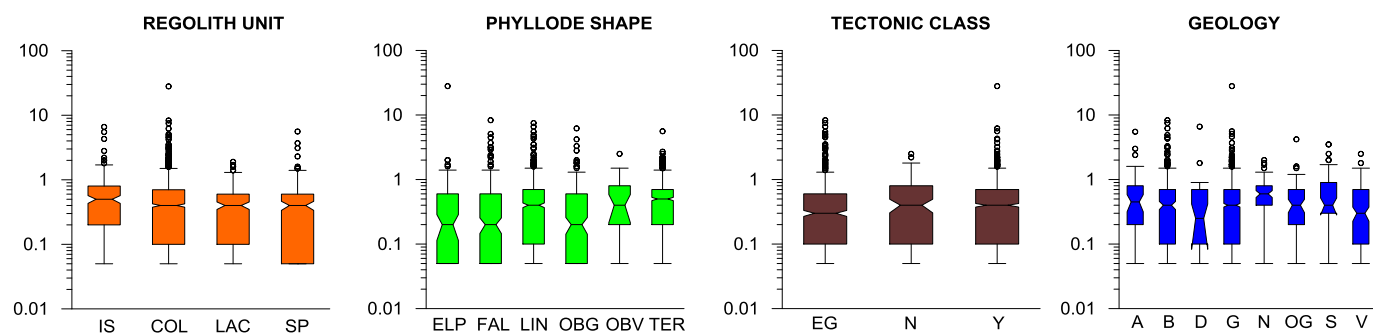
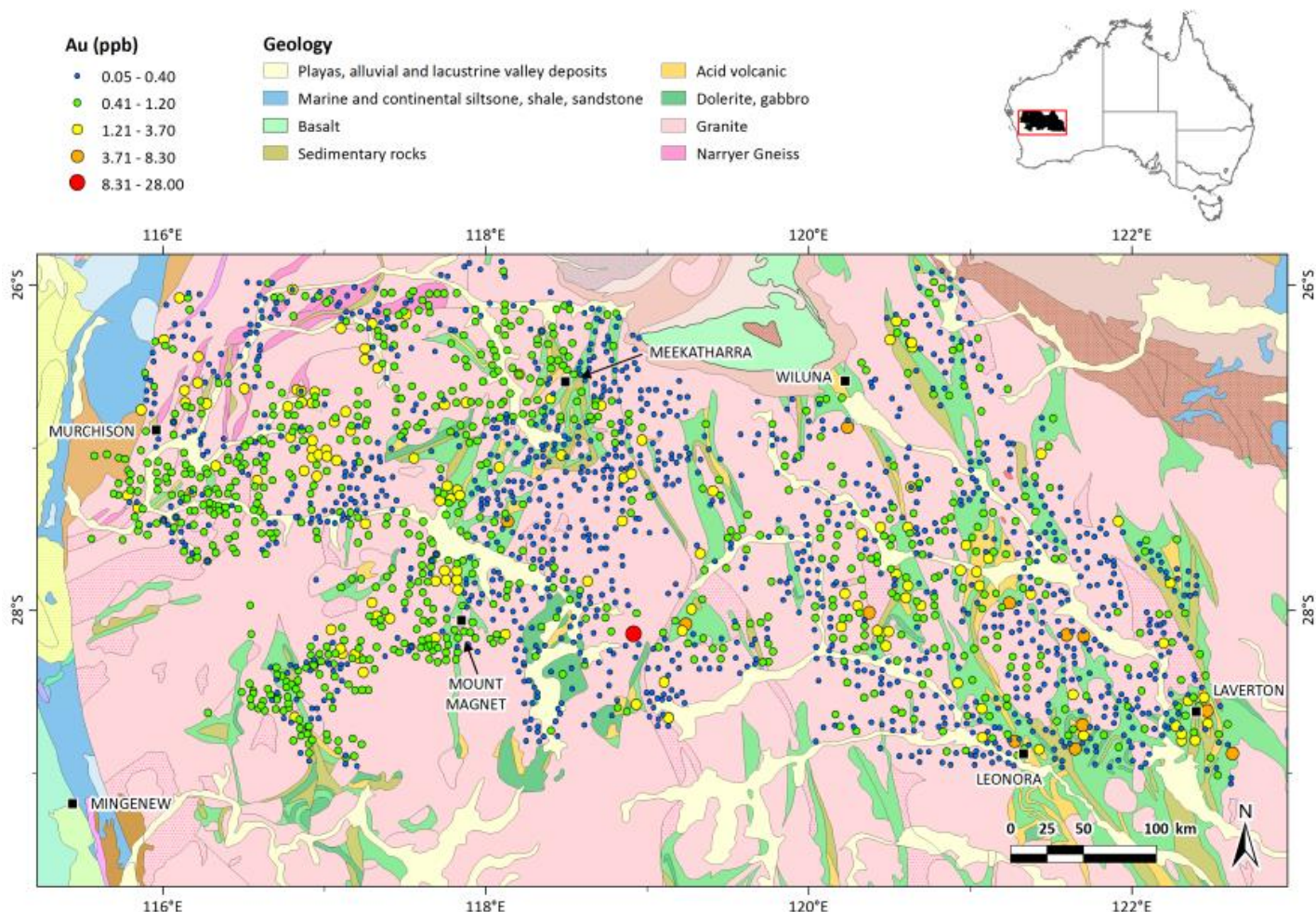
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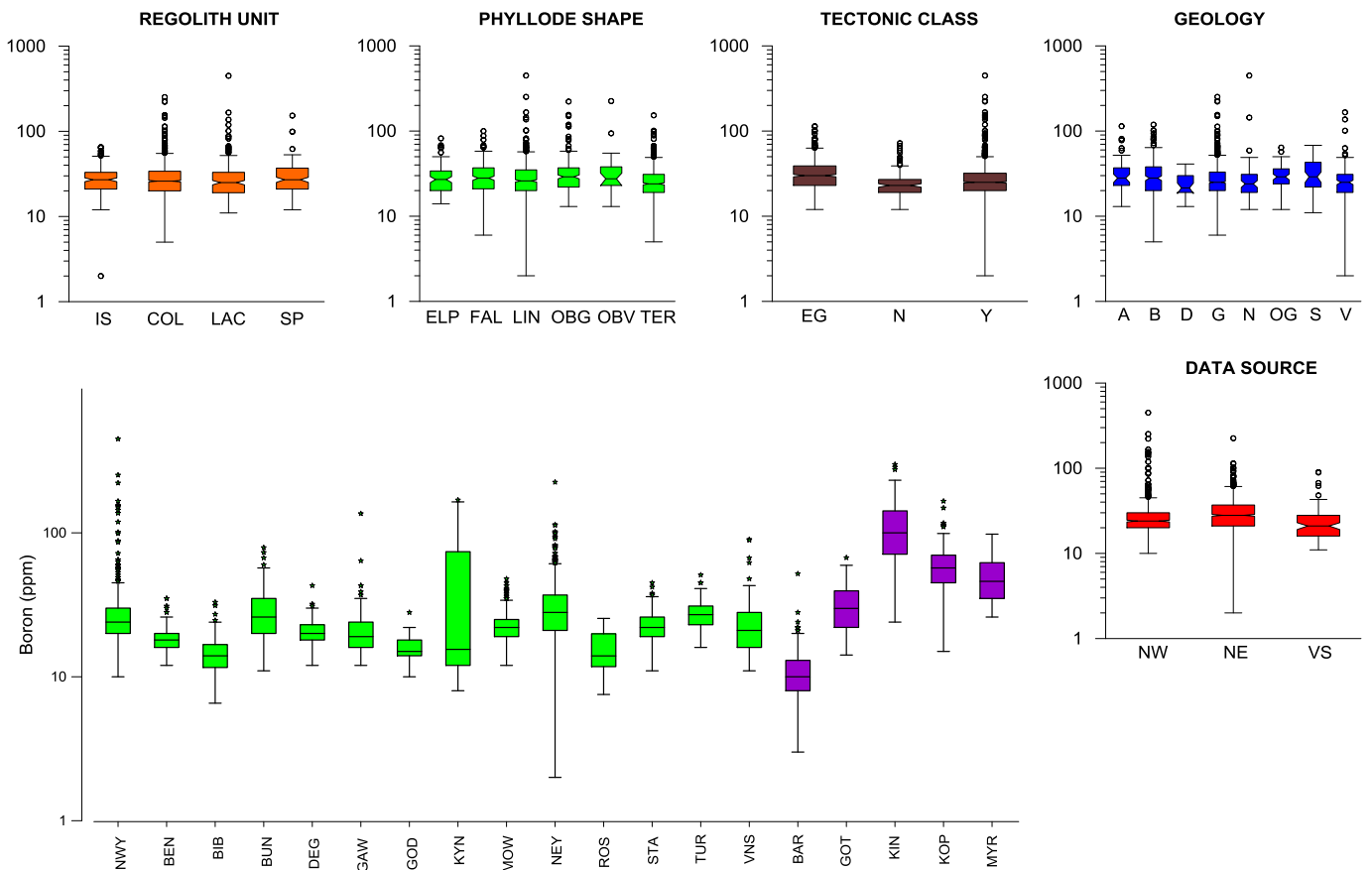
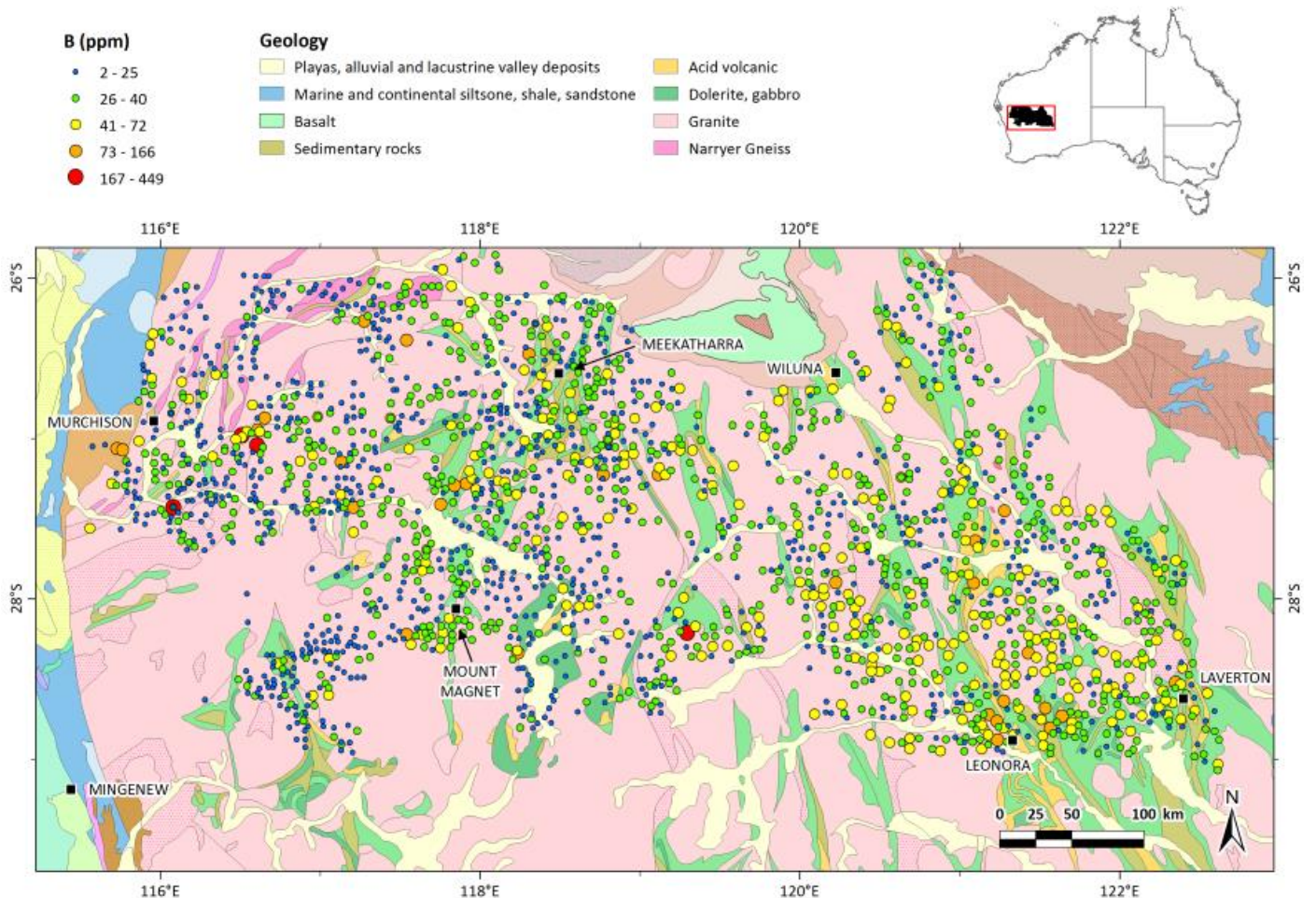
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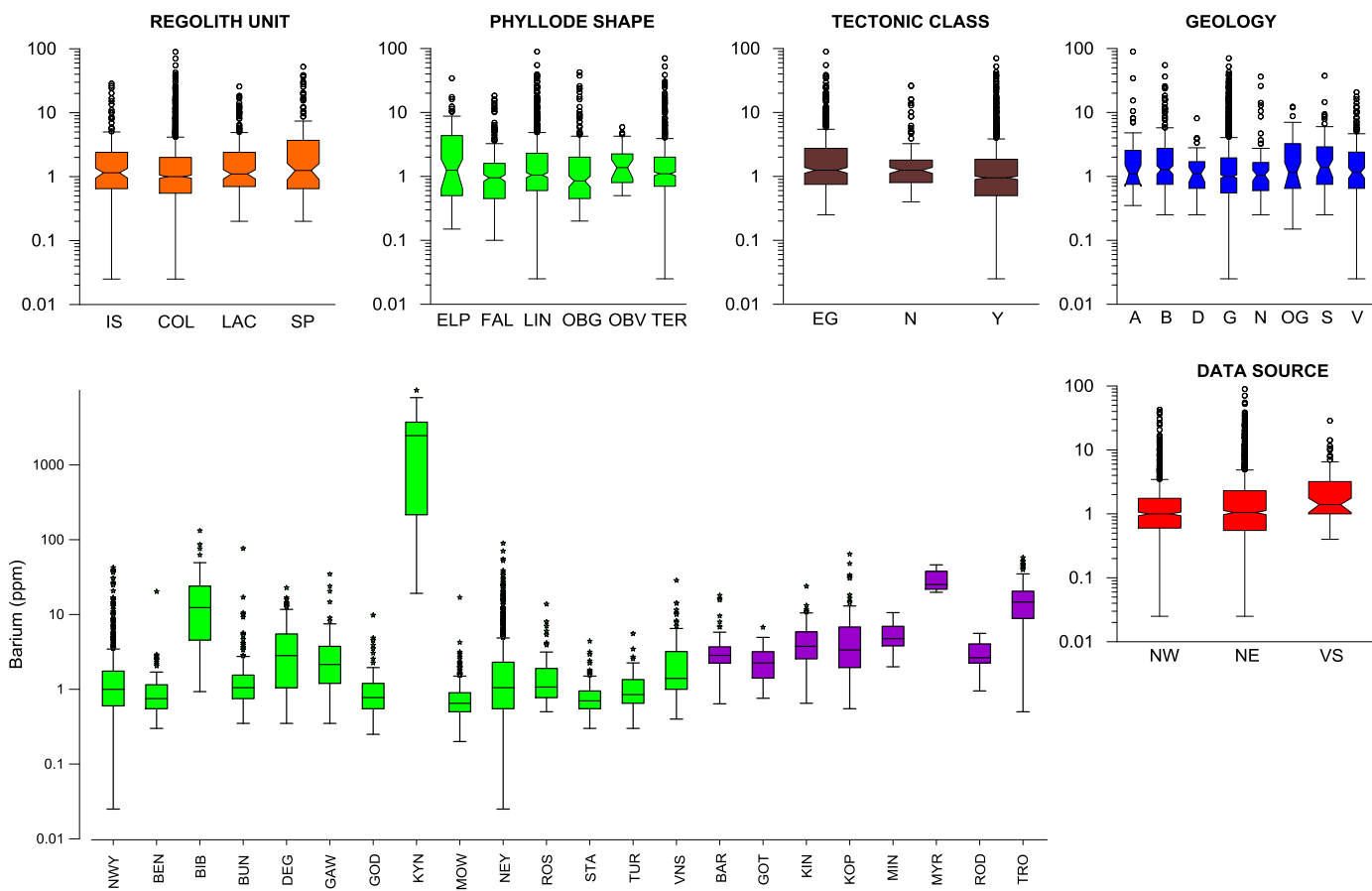
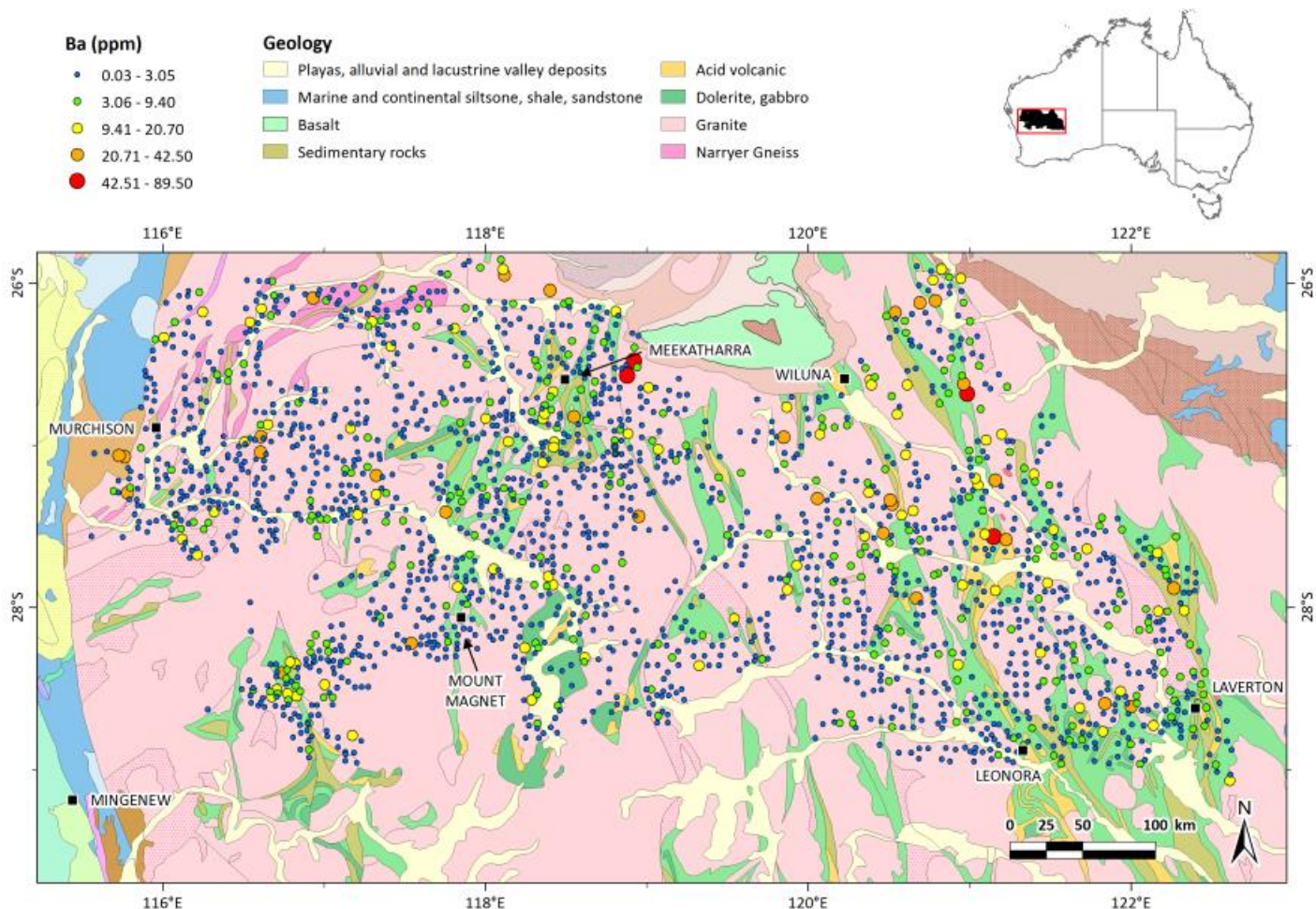
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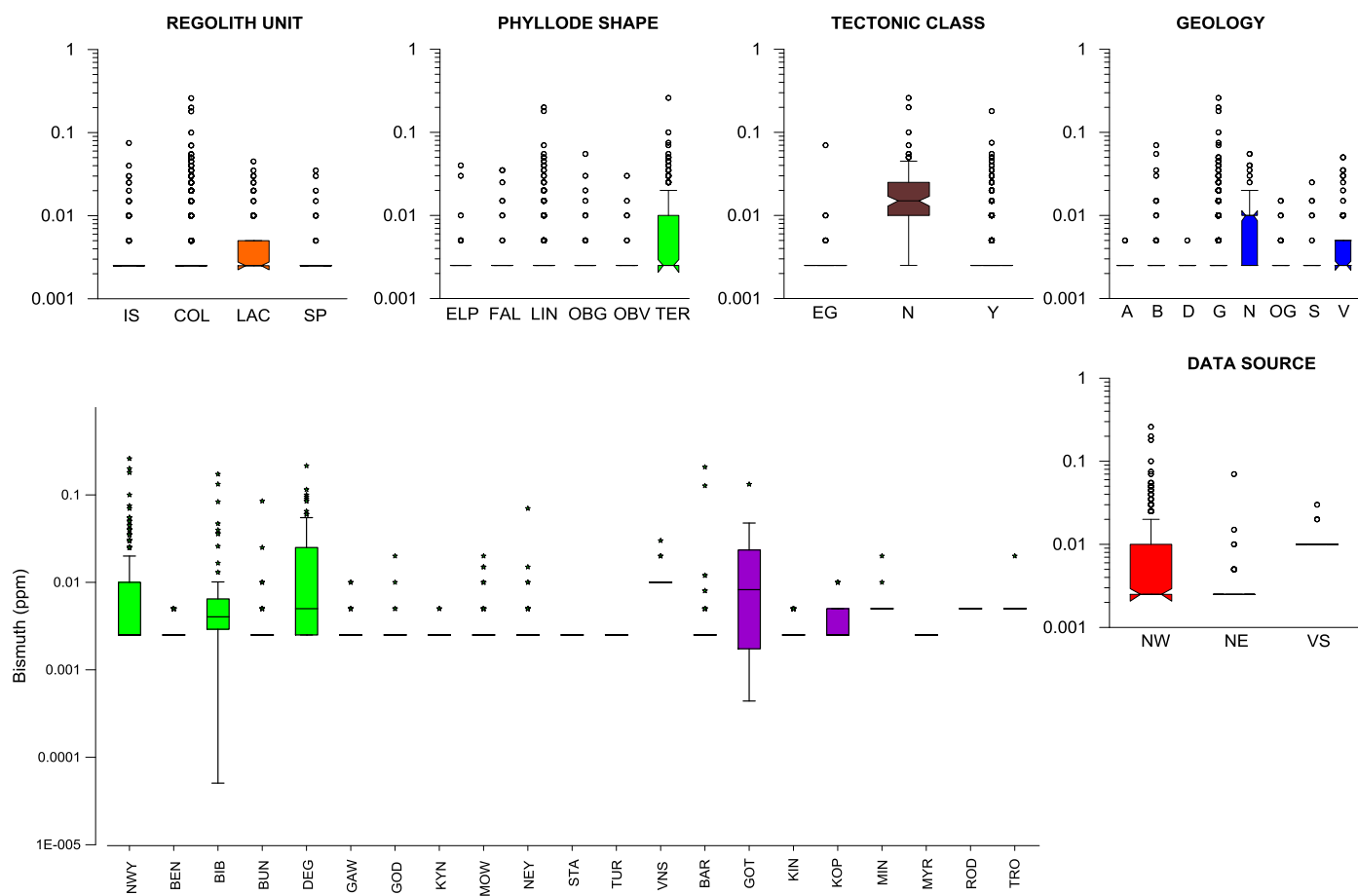
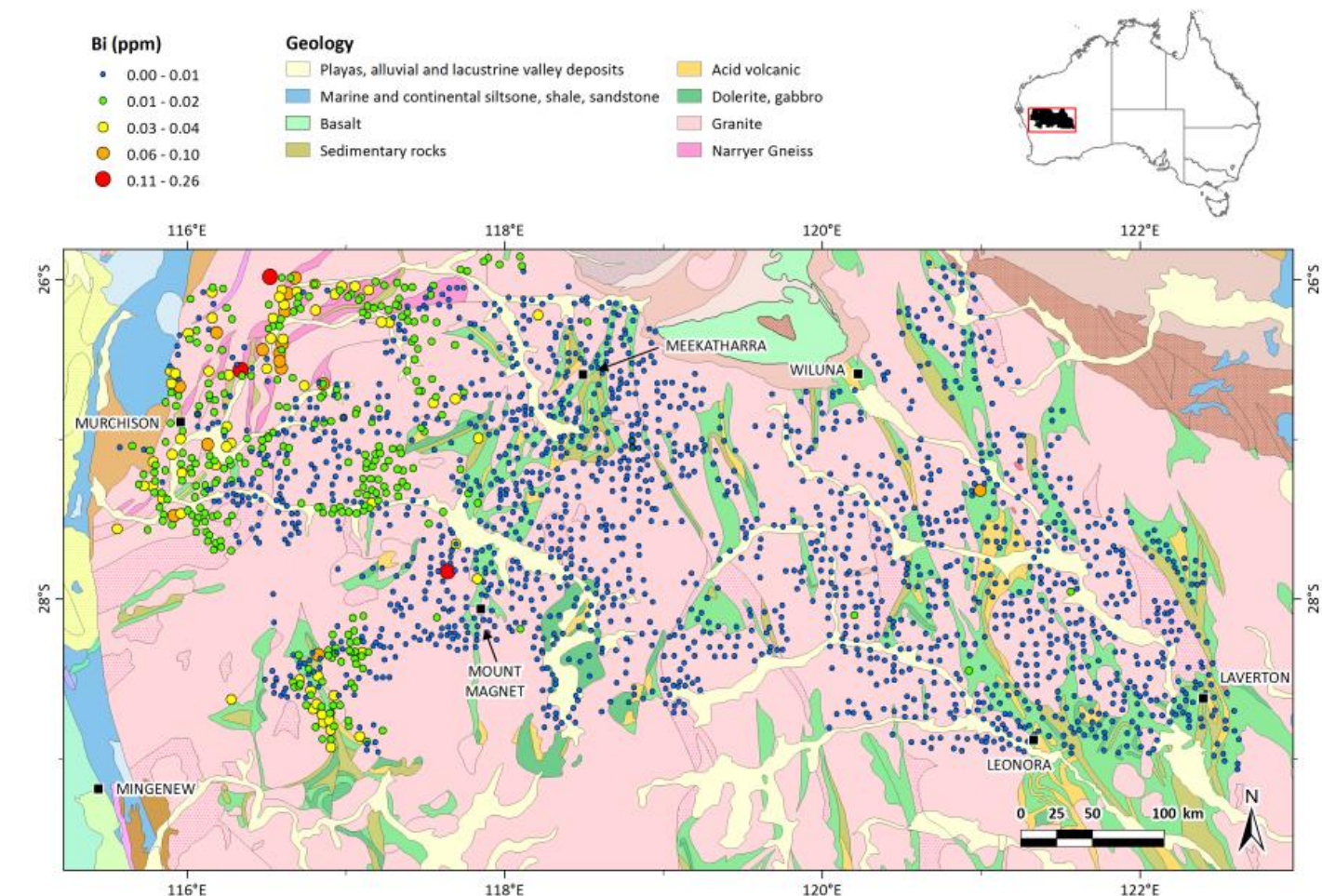
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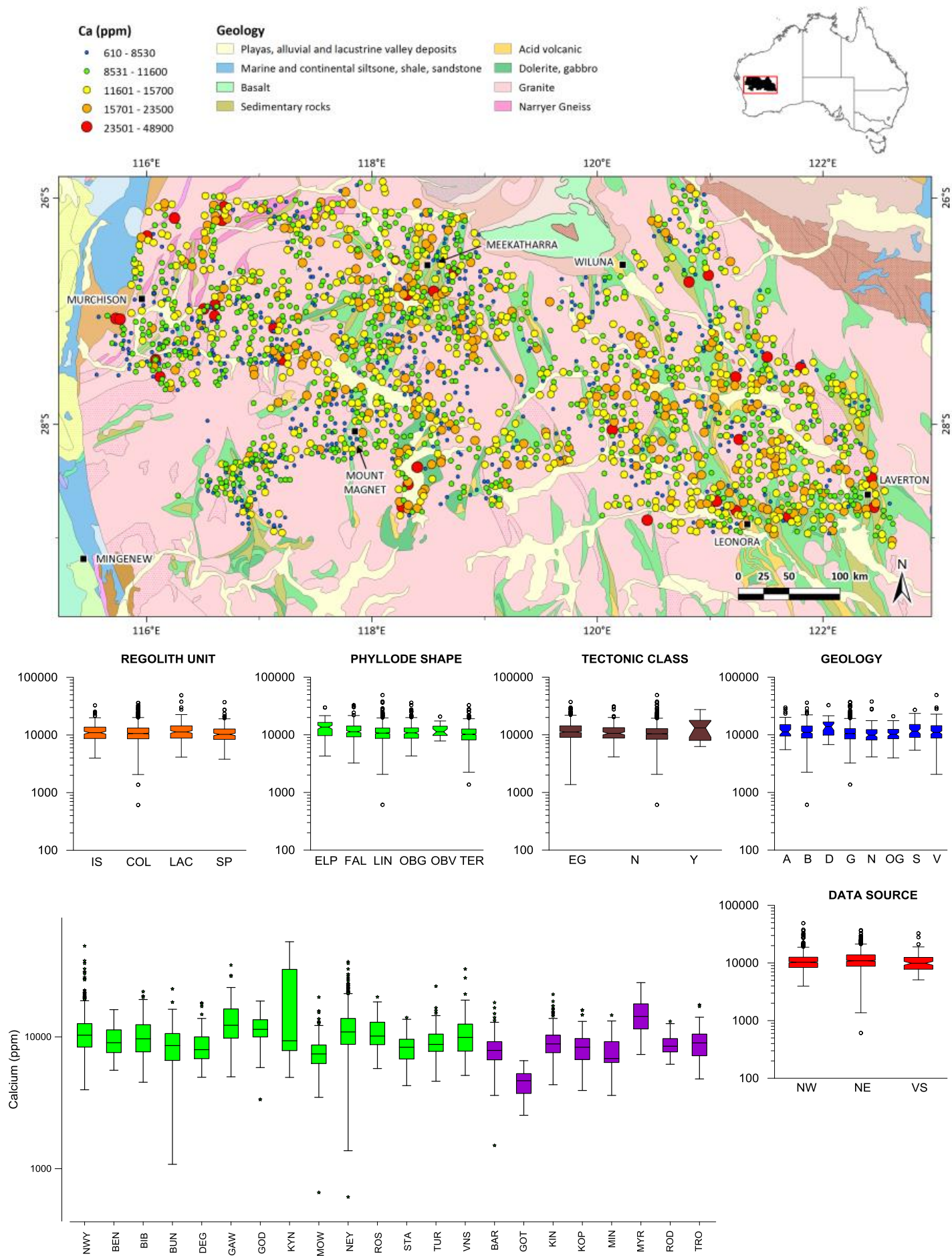
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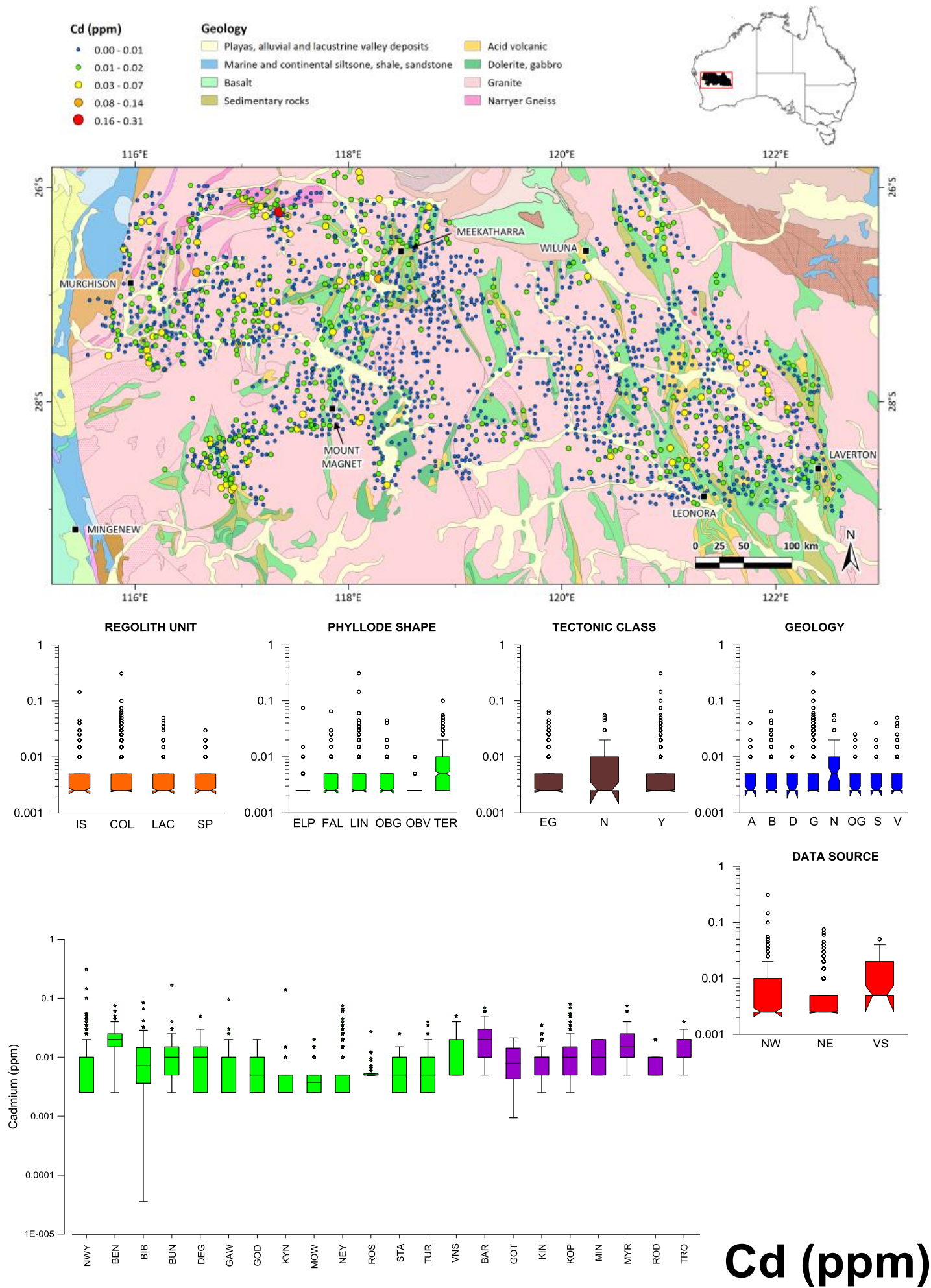
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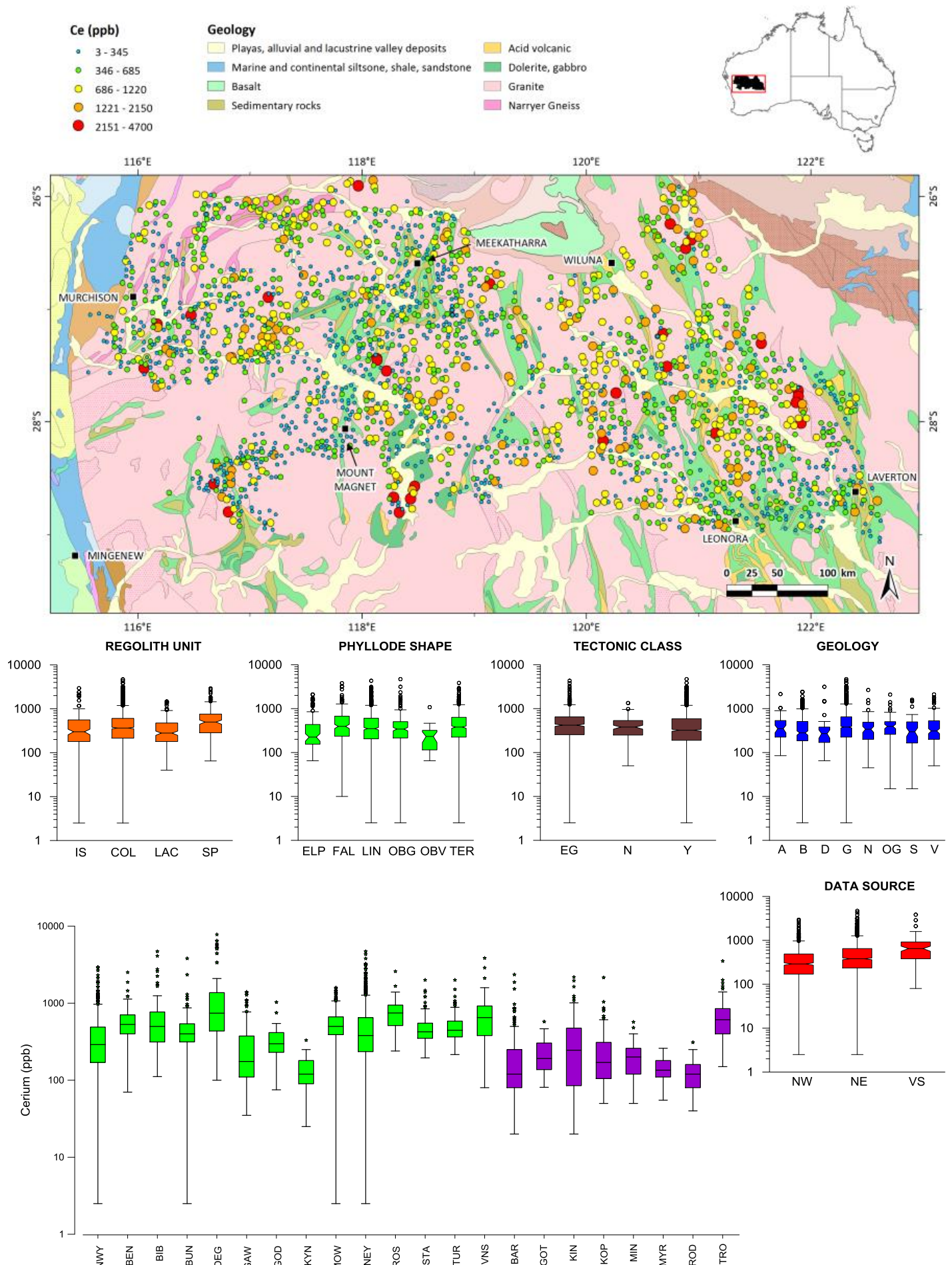


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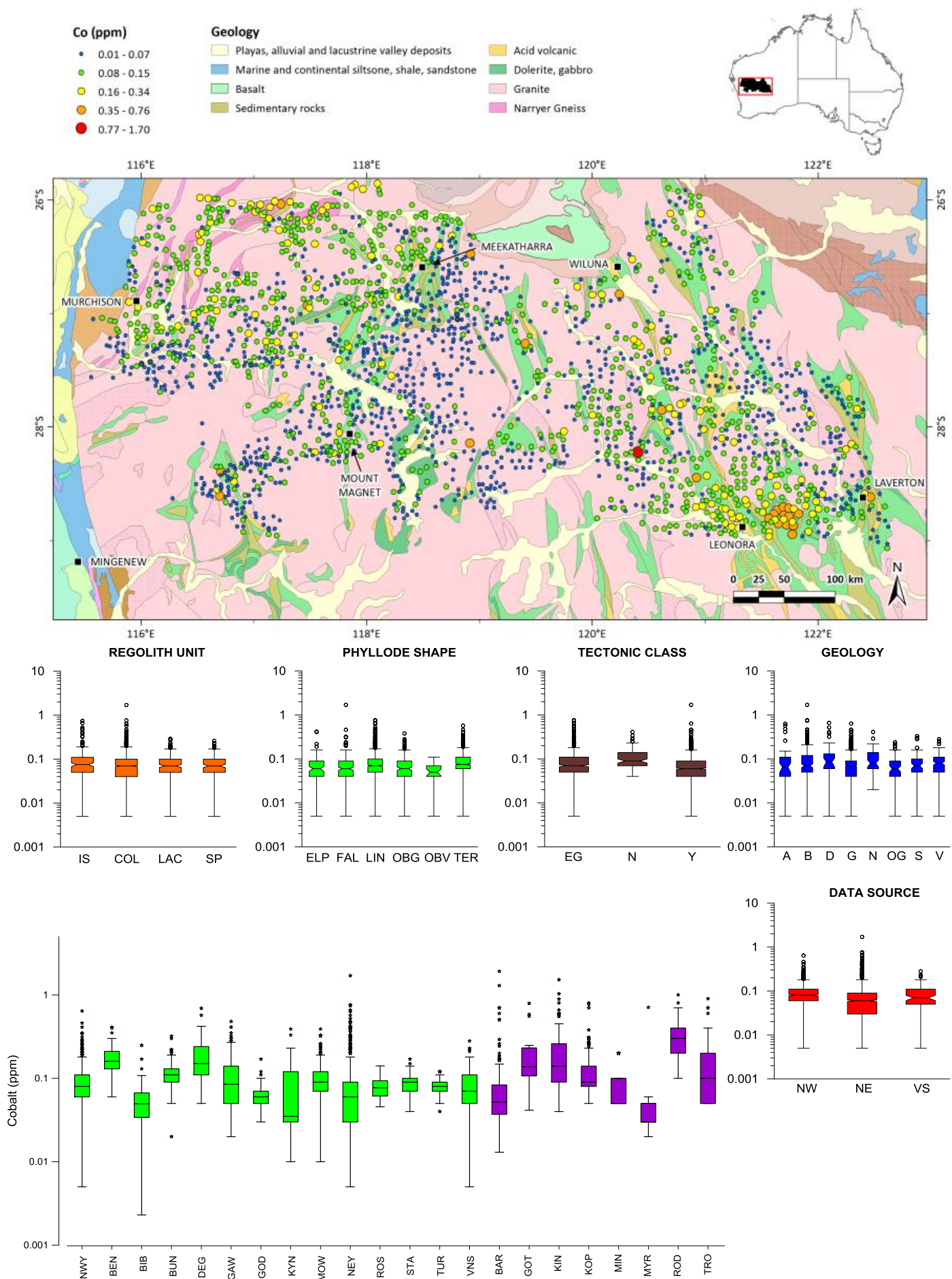


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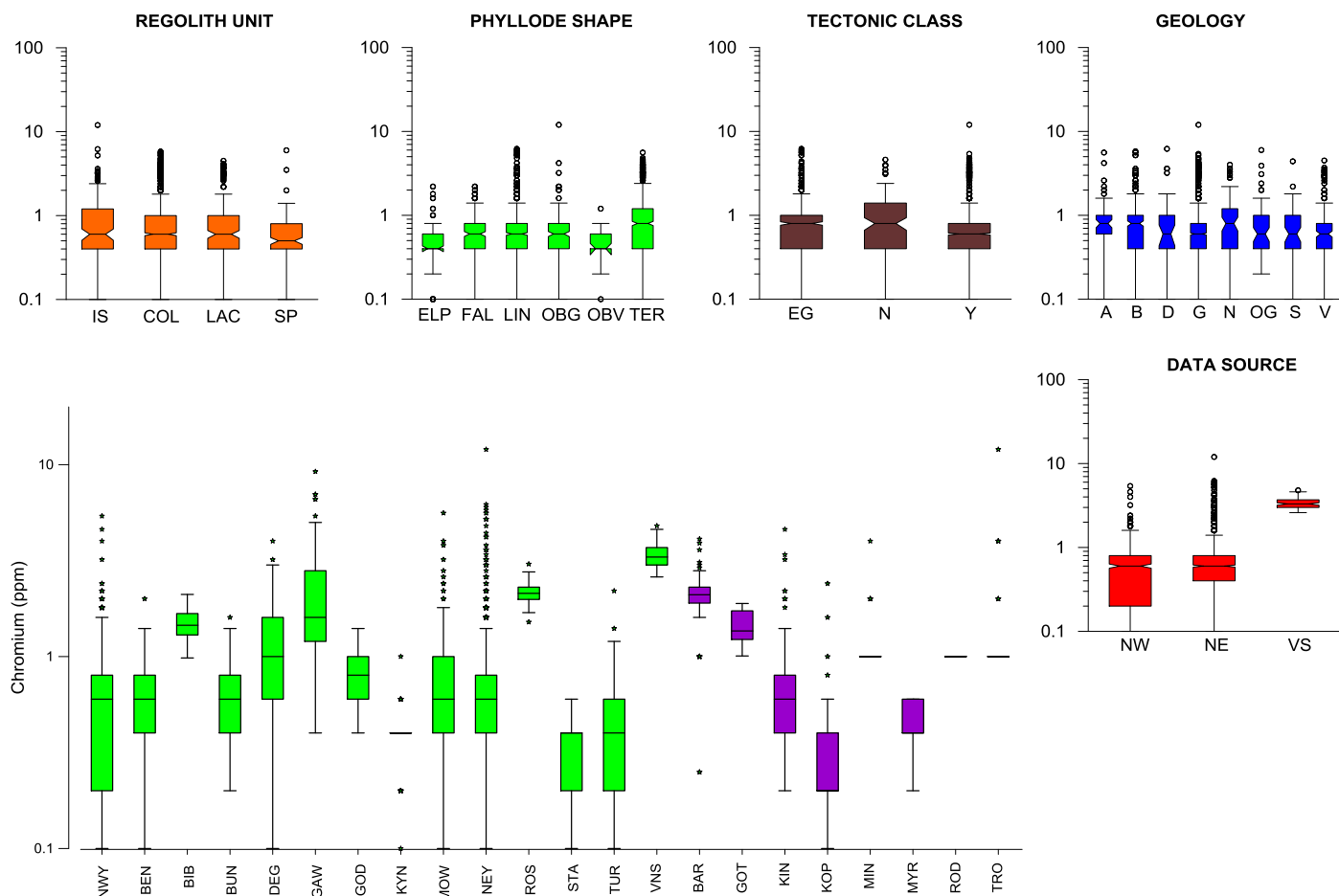
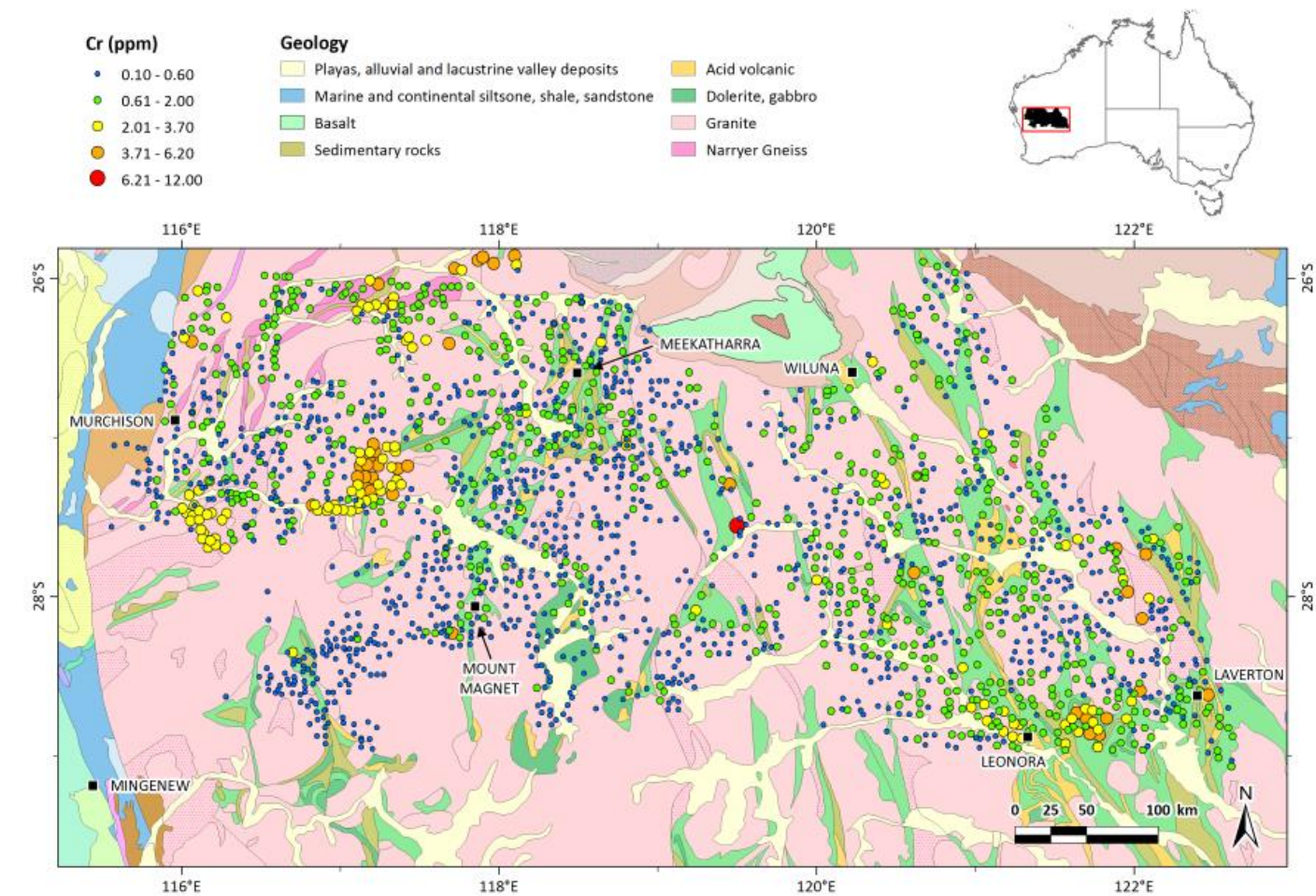




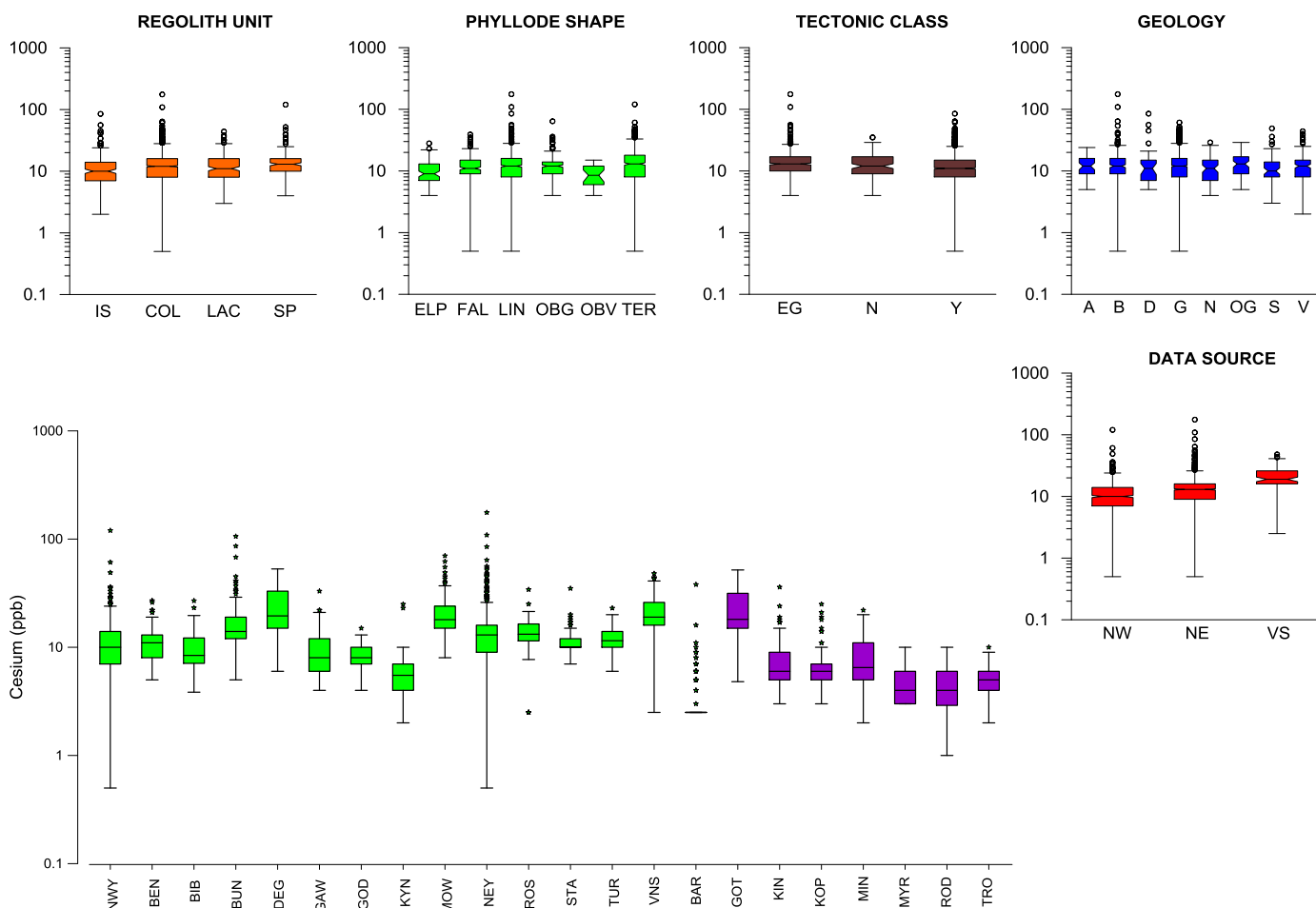
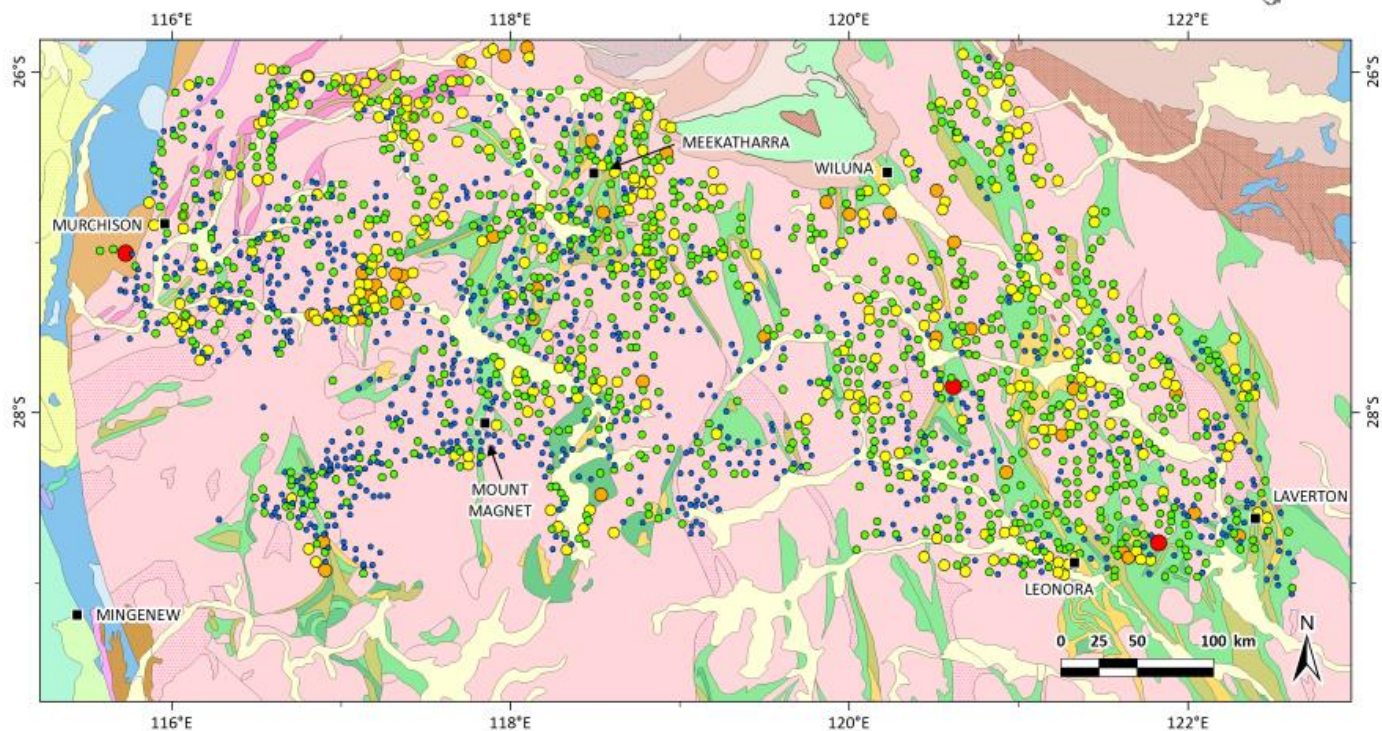
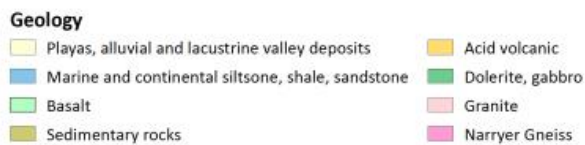
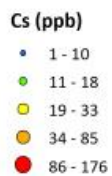
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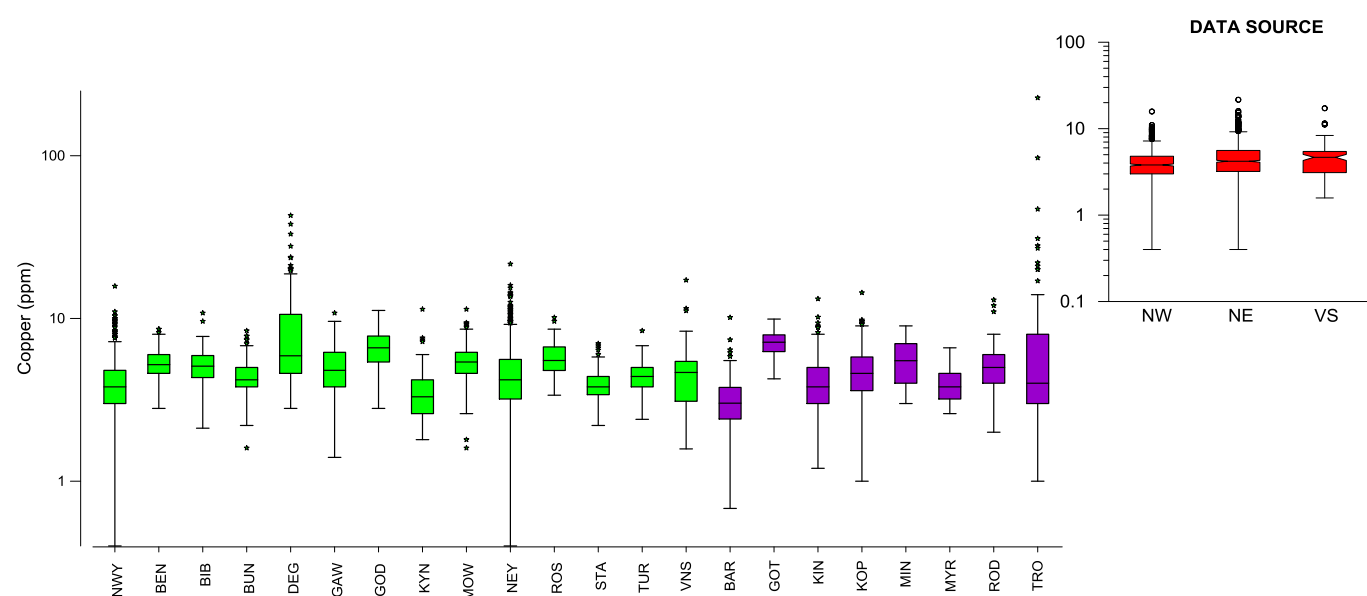
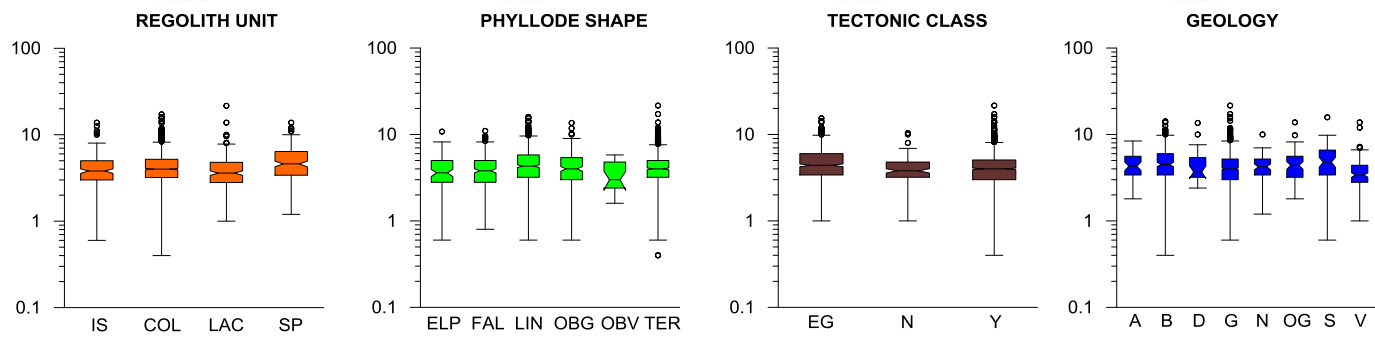
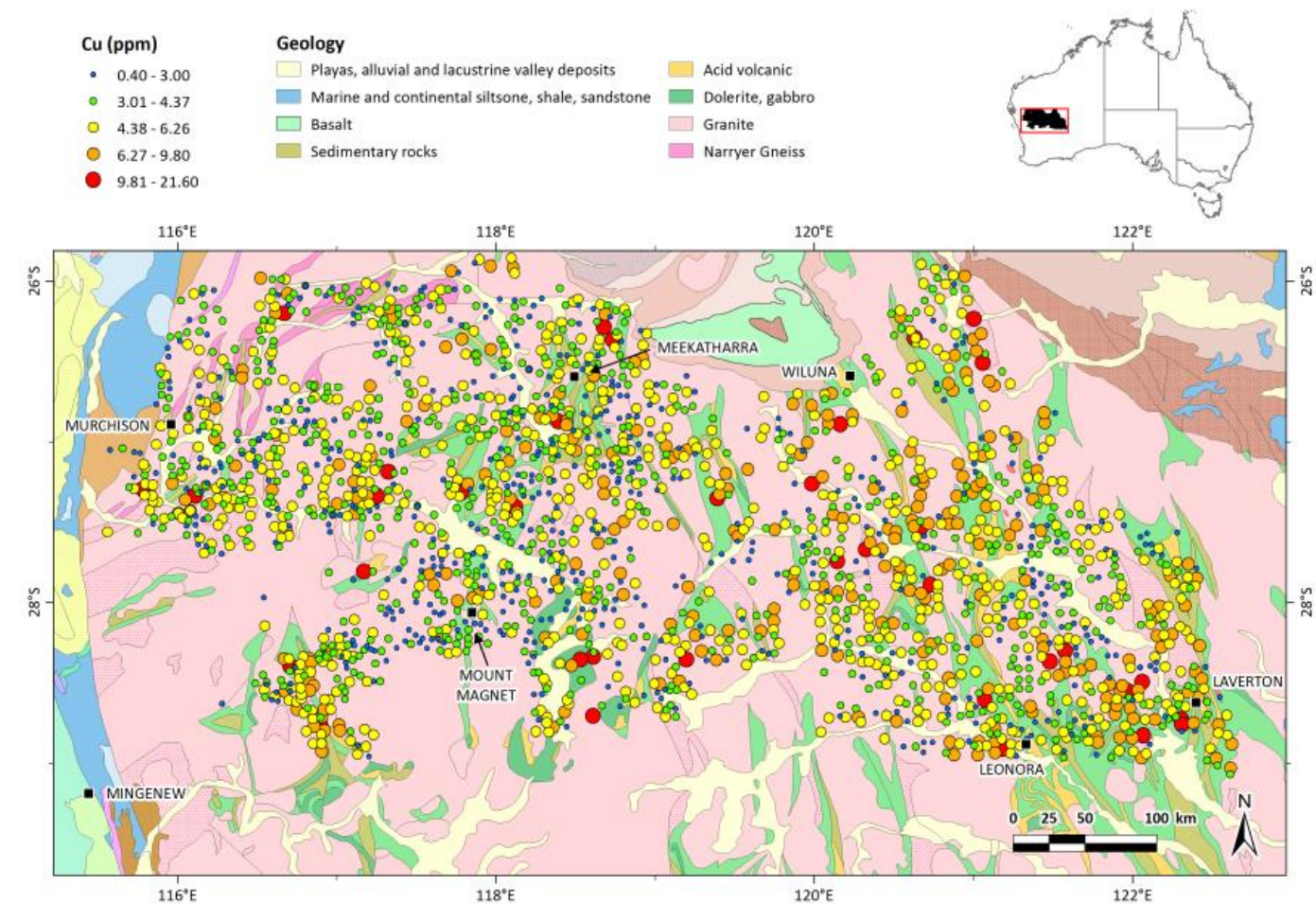
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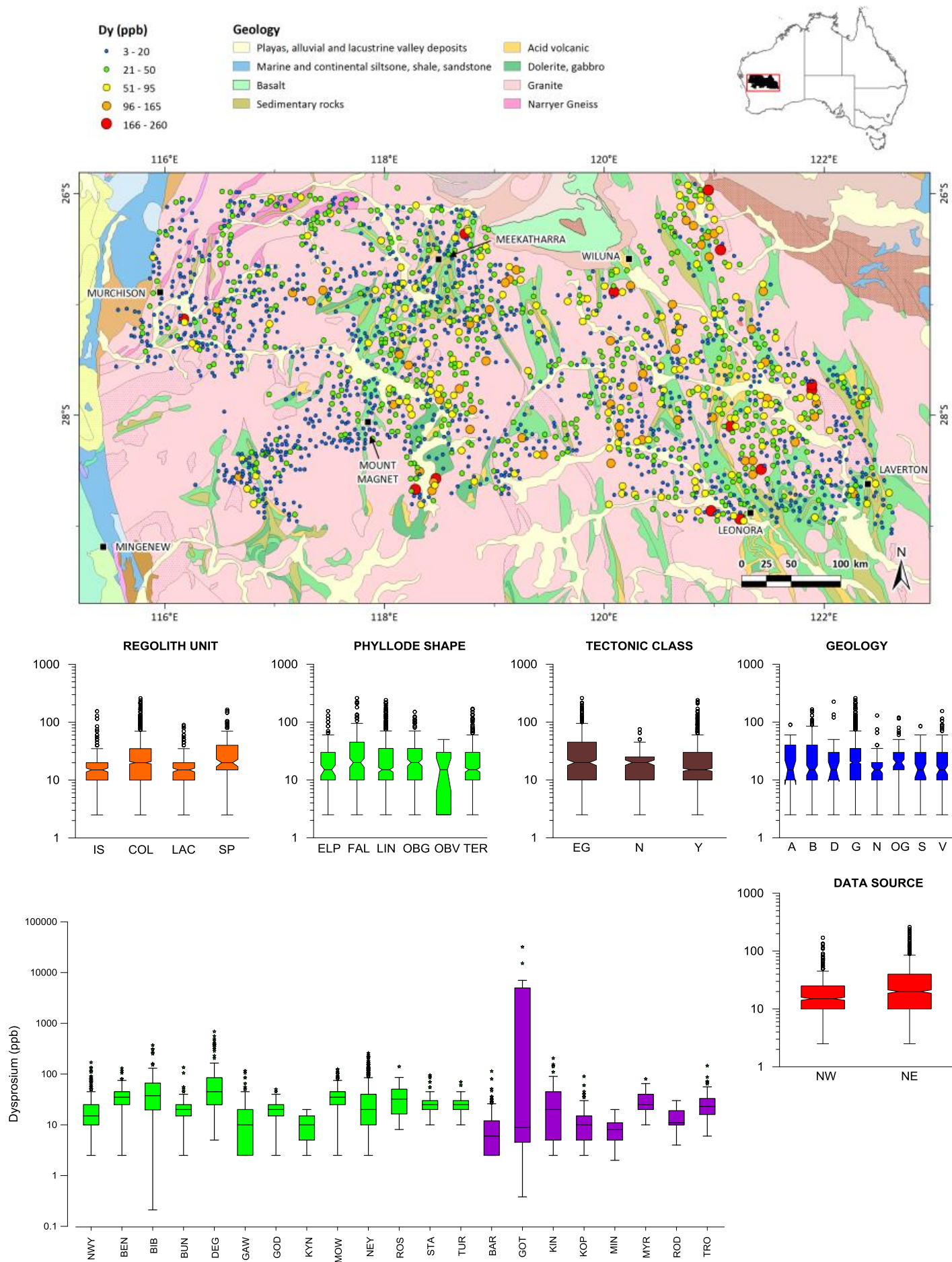
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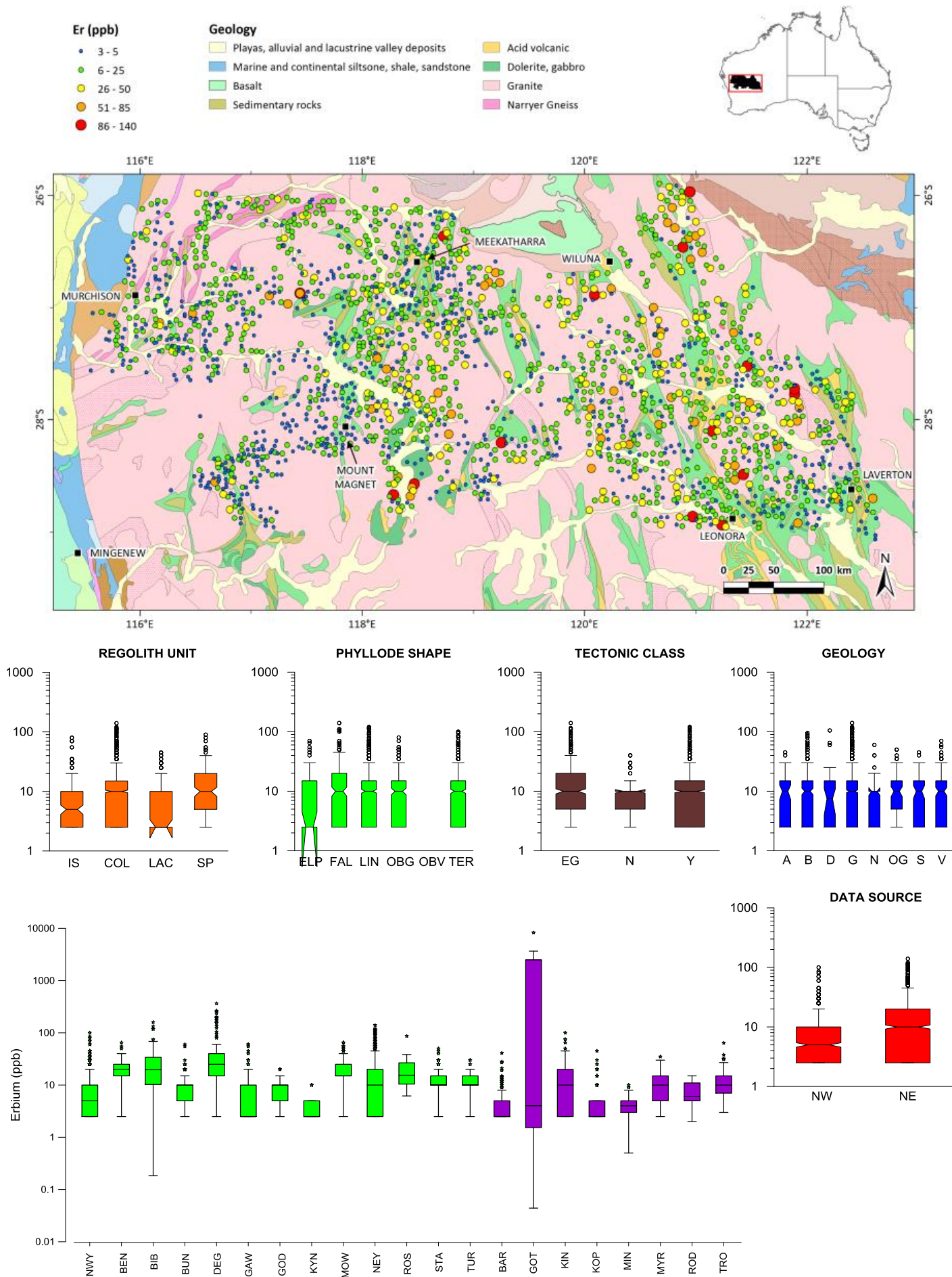
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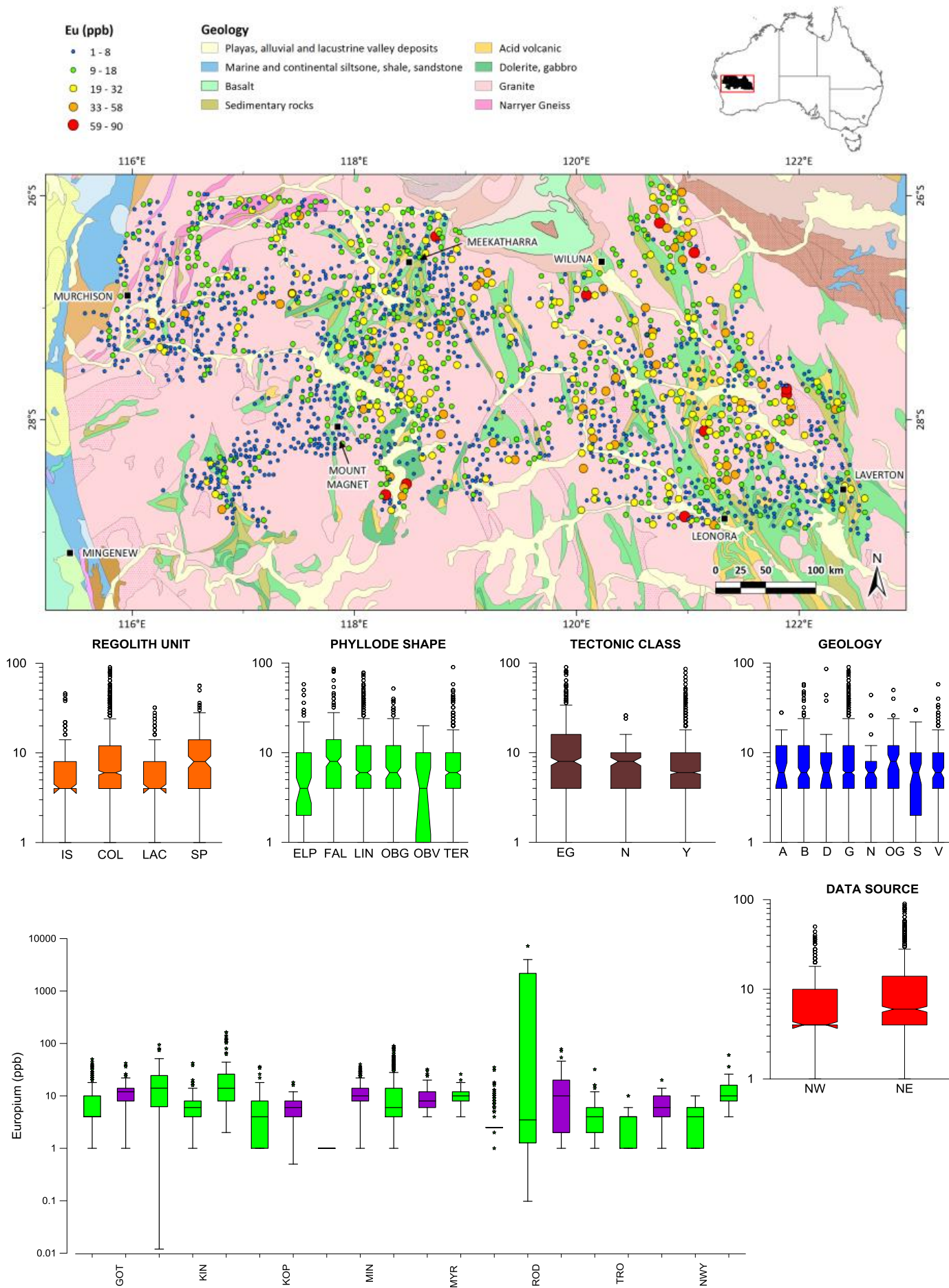
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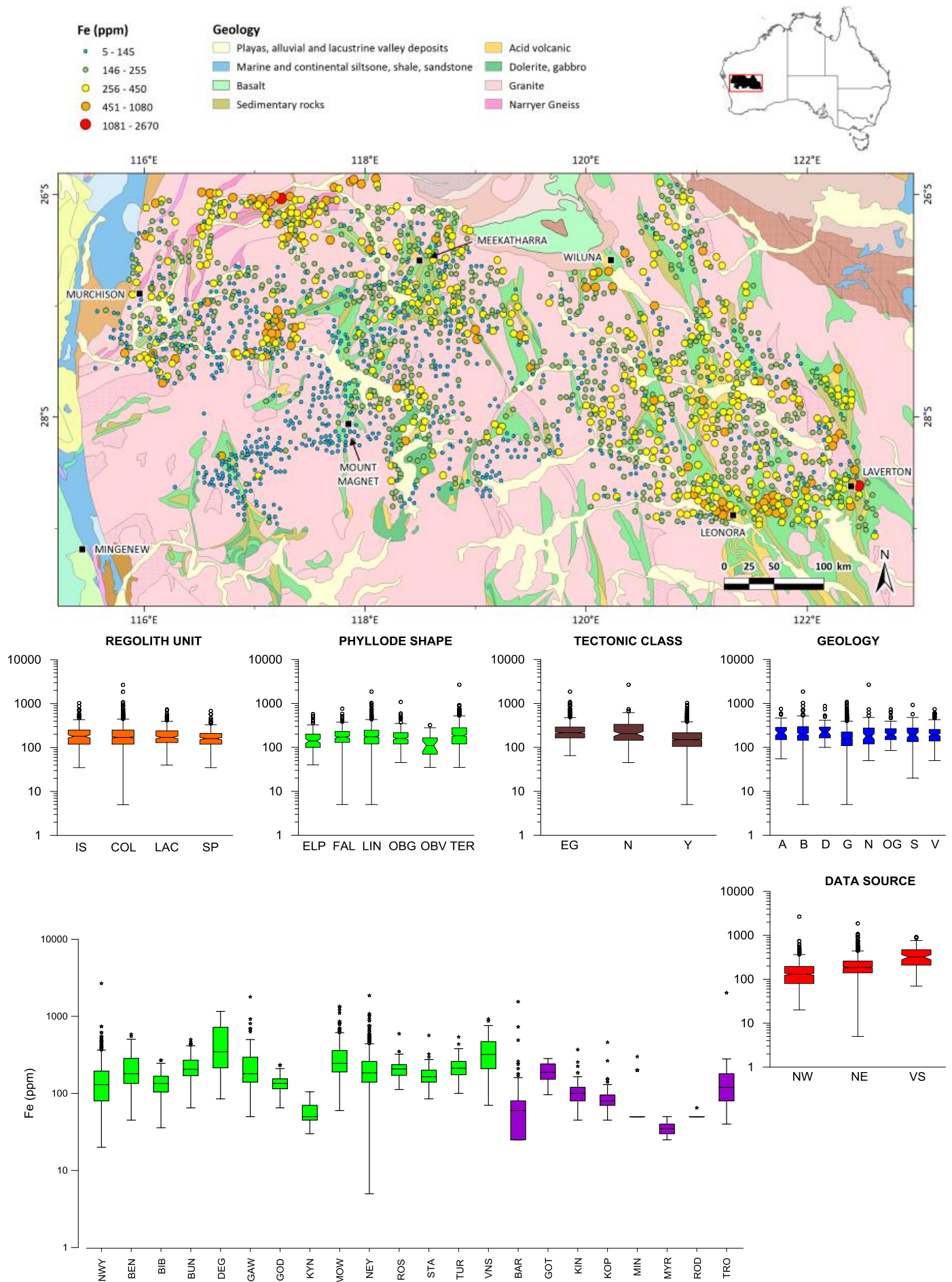
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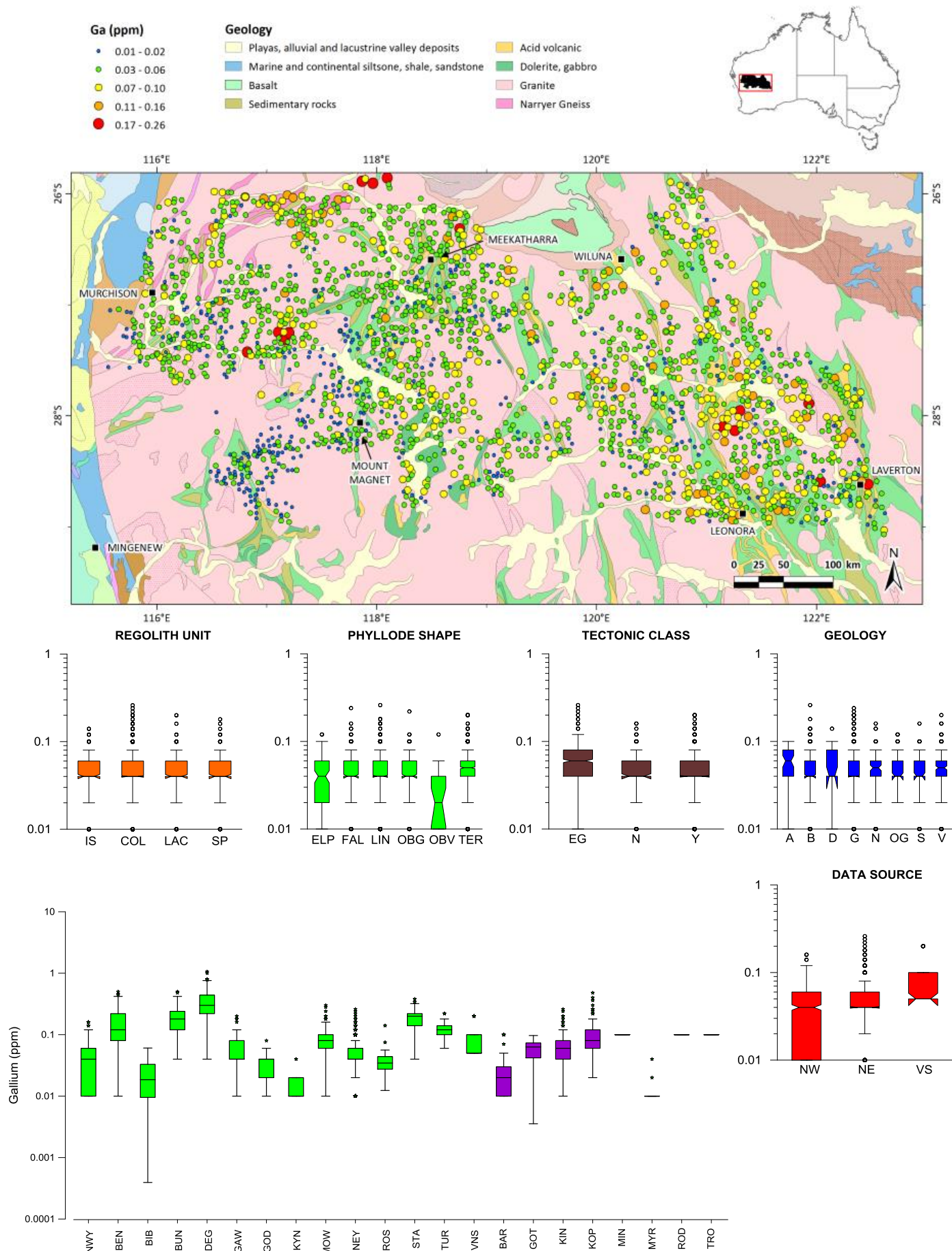
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Eu (ppb)

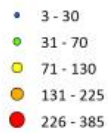


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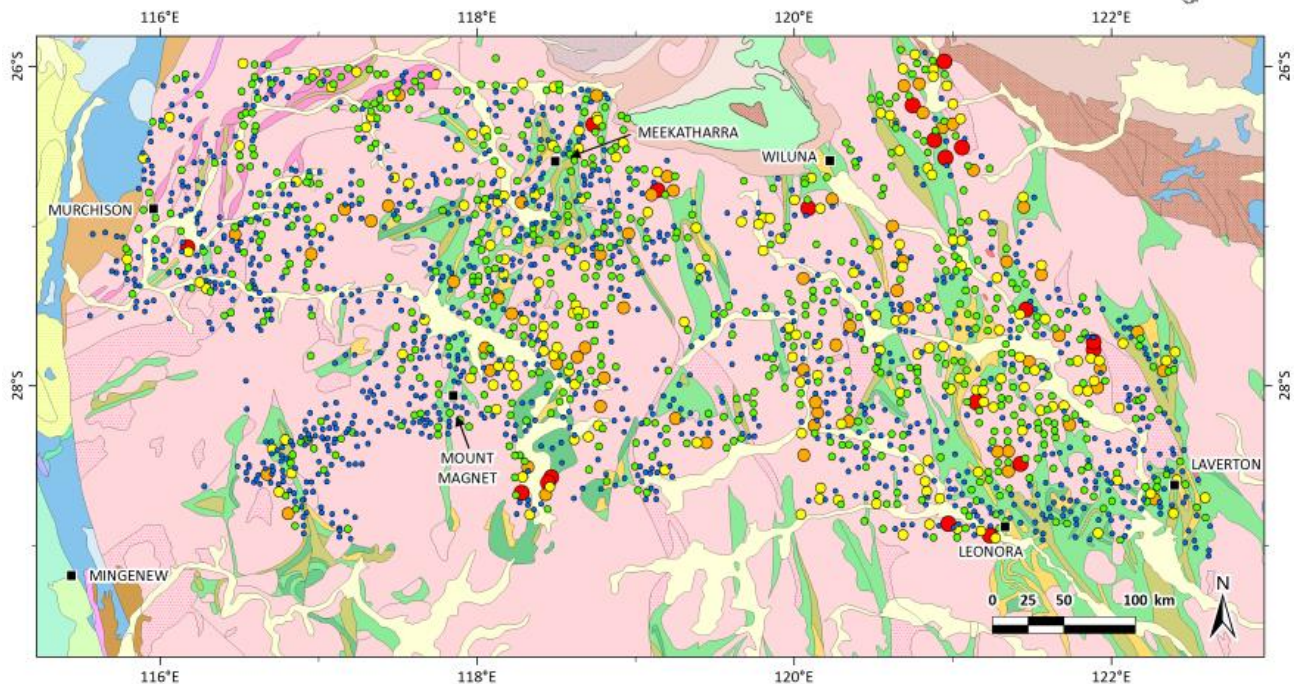
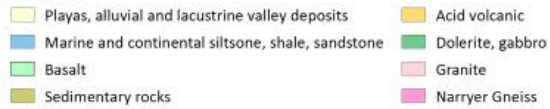


Ga (ppm)

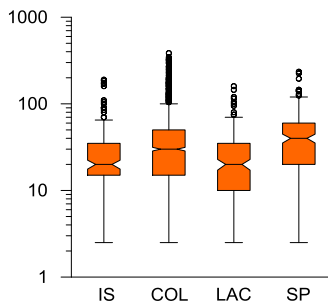
Gd (ppm)



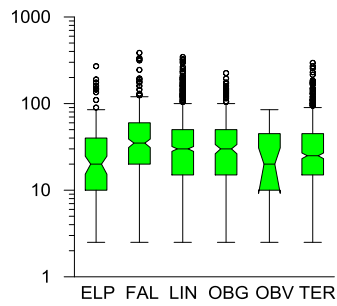
Geology



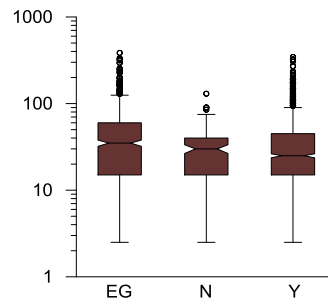
REGOLITH UNIT



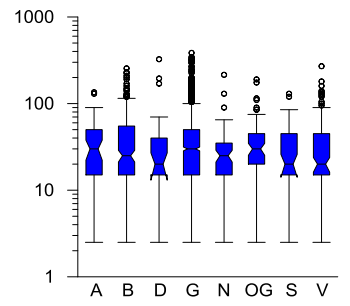
PHYLLITE SHAPE



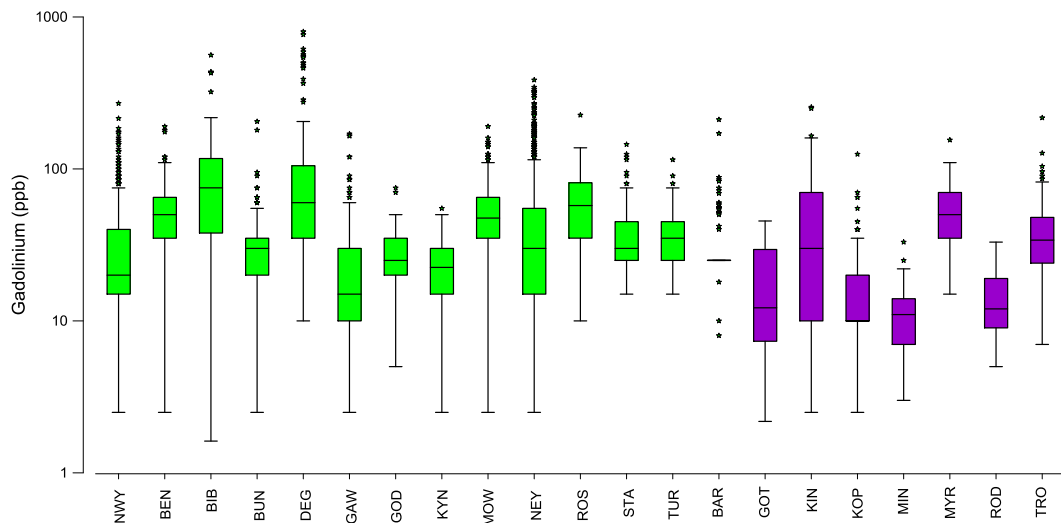
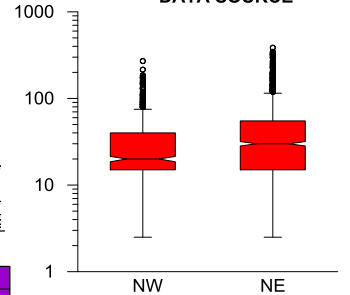
TECTONIC CLASS



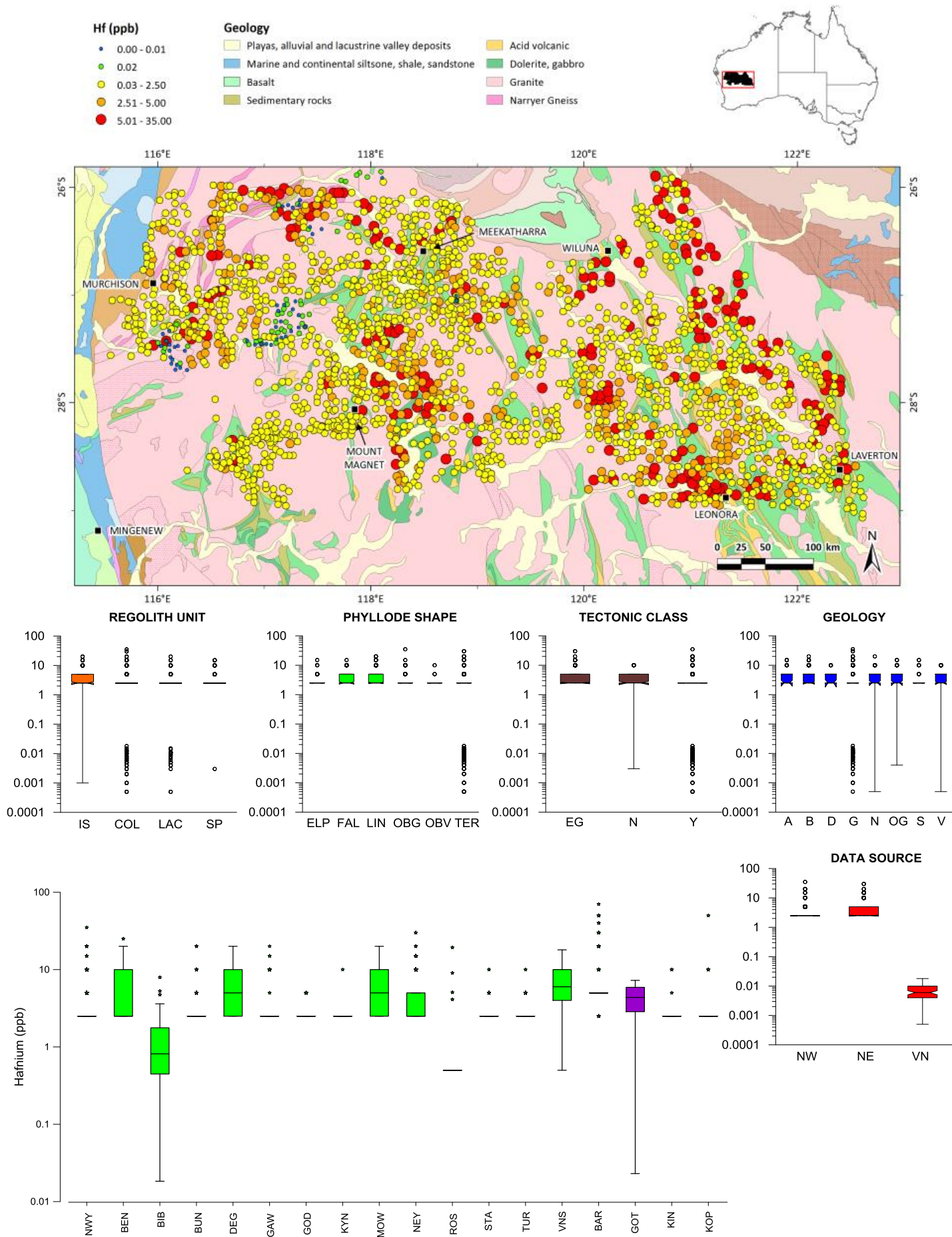
GEOLOGY



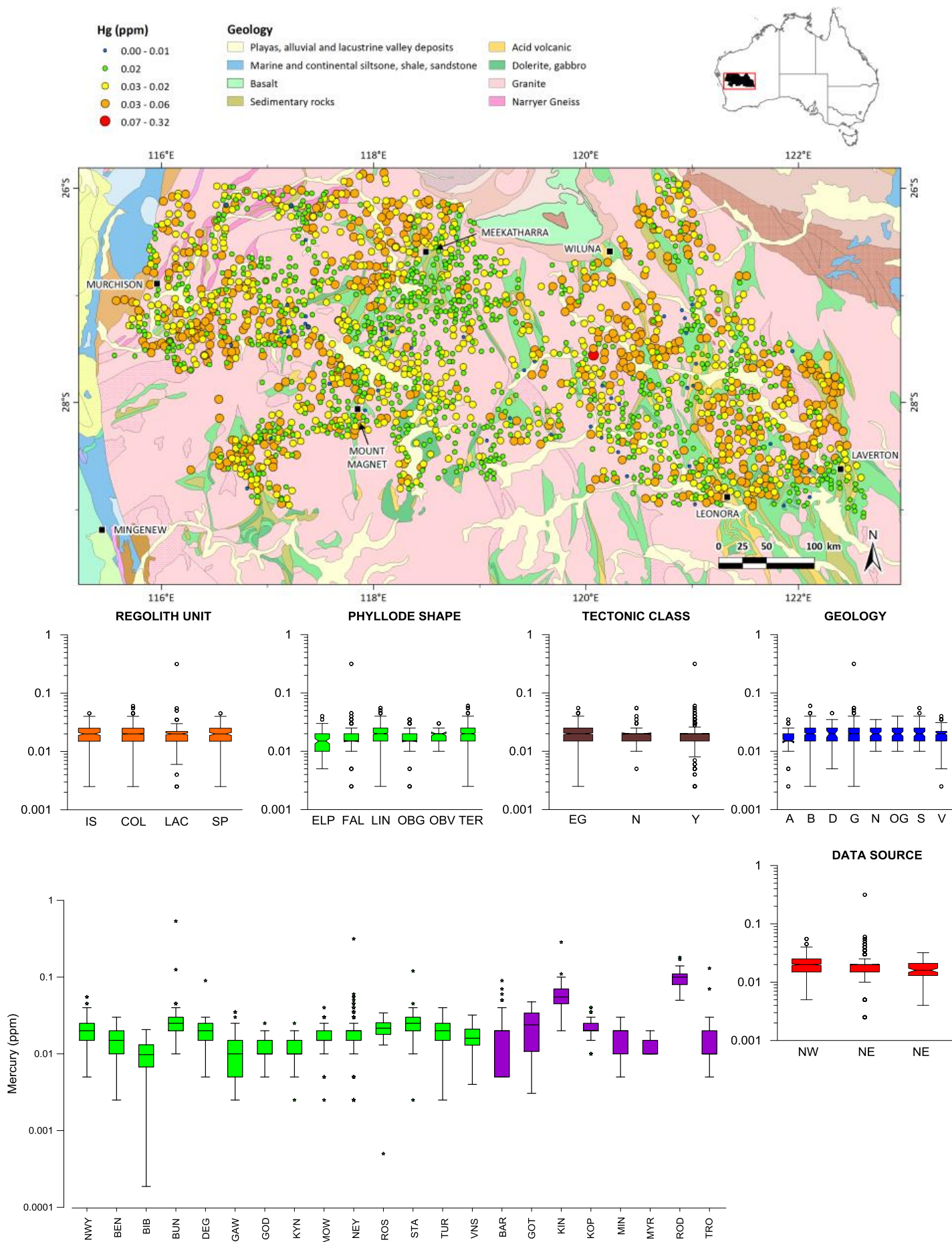
DATA SOURCE



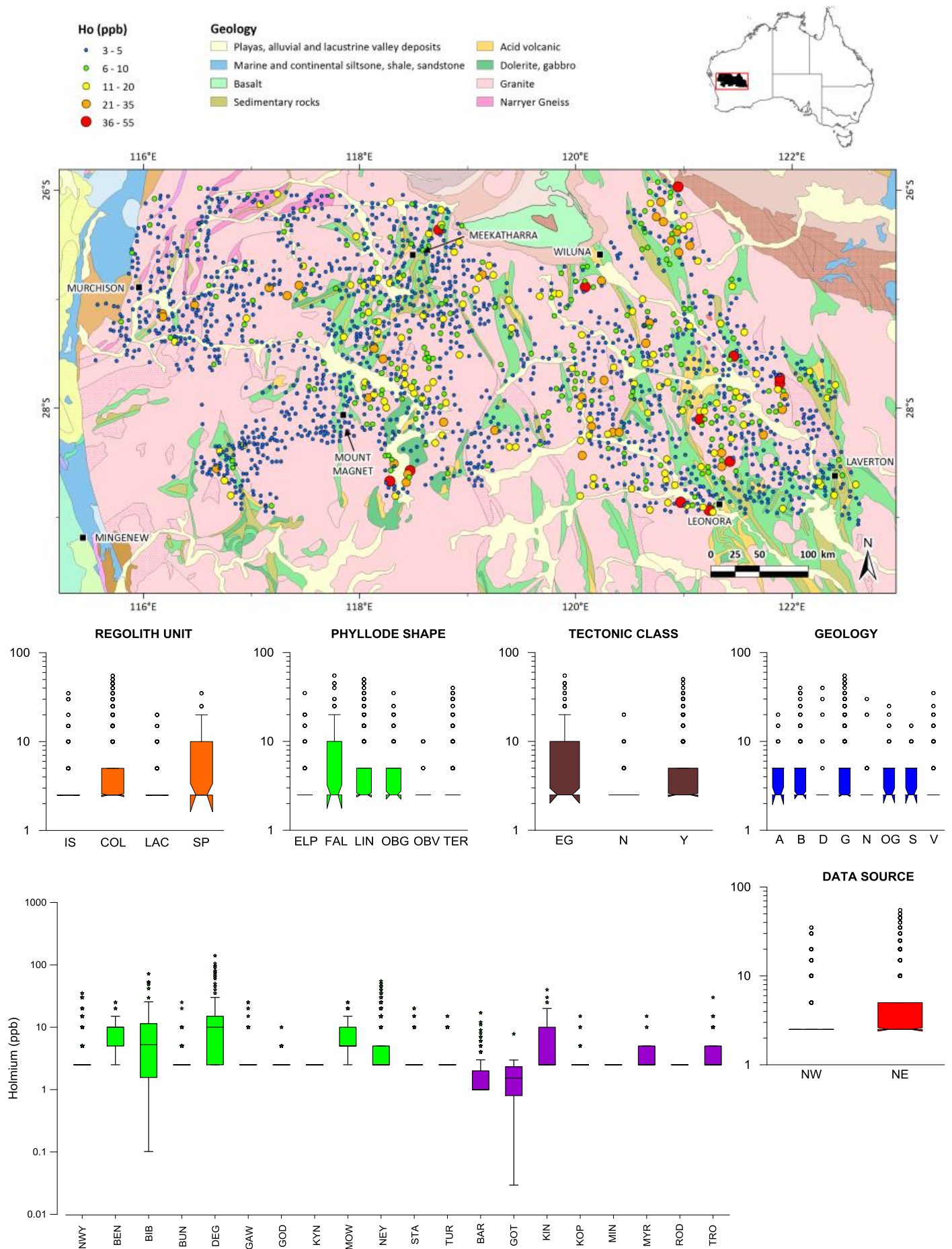
Gd (ppb)



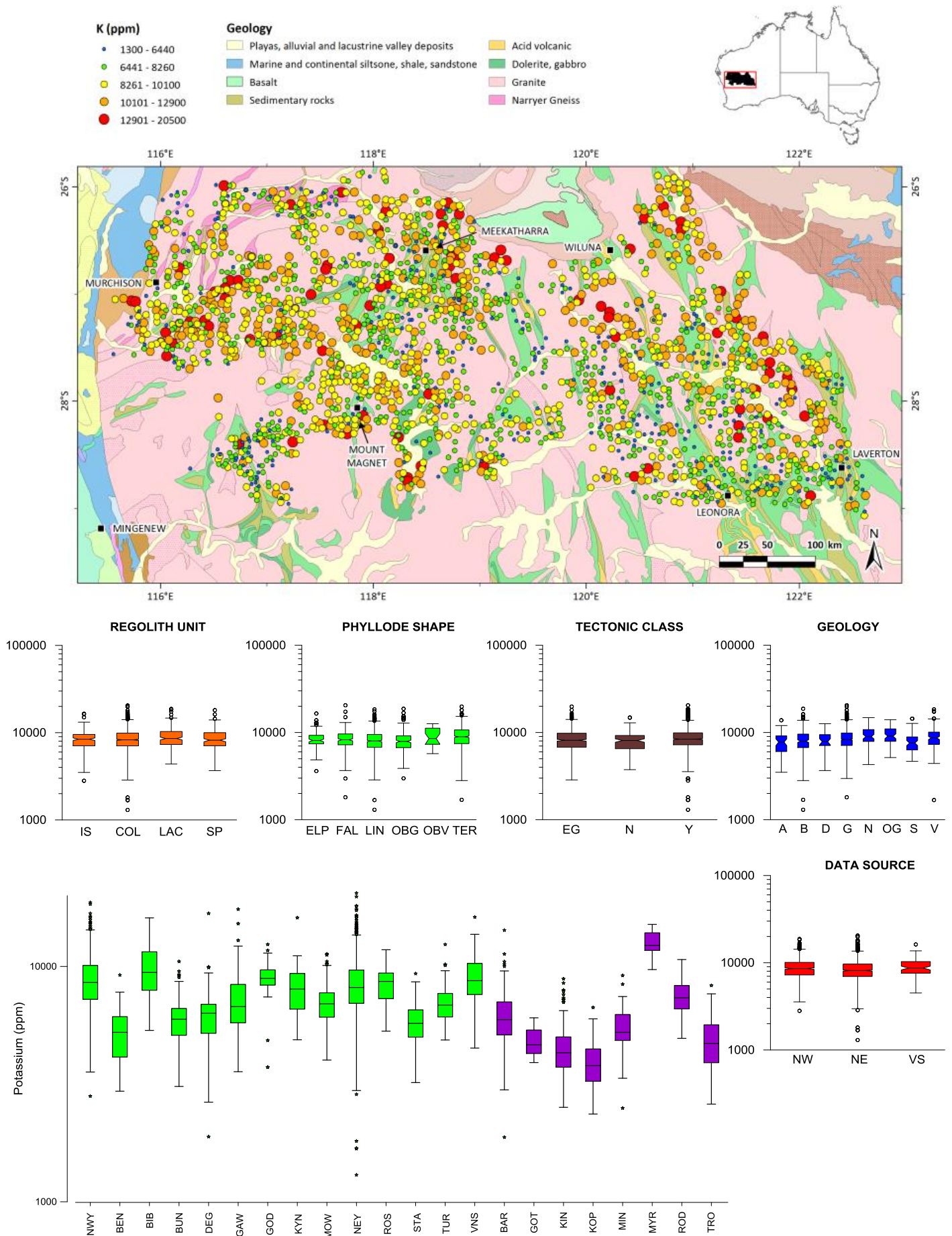
Hf (ppb)



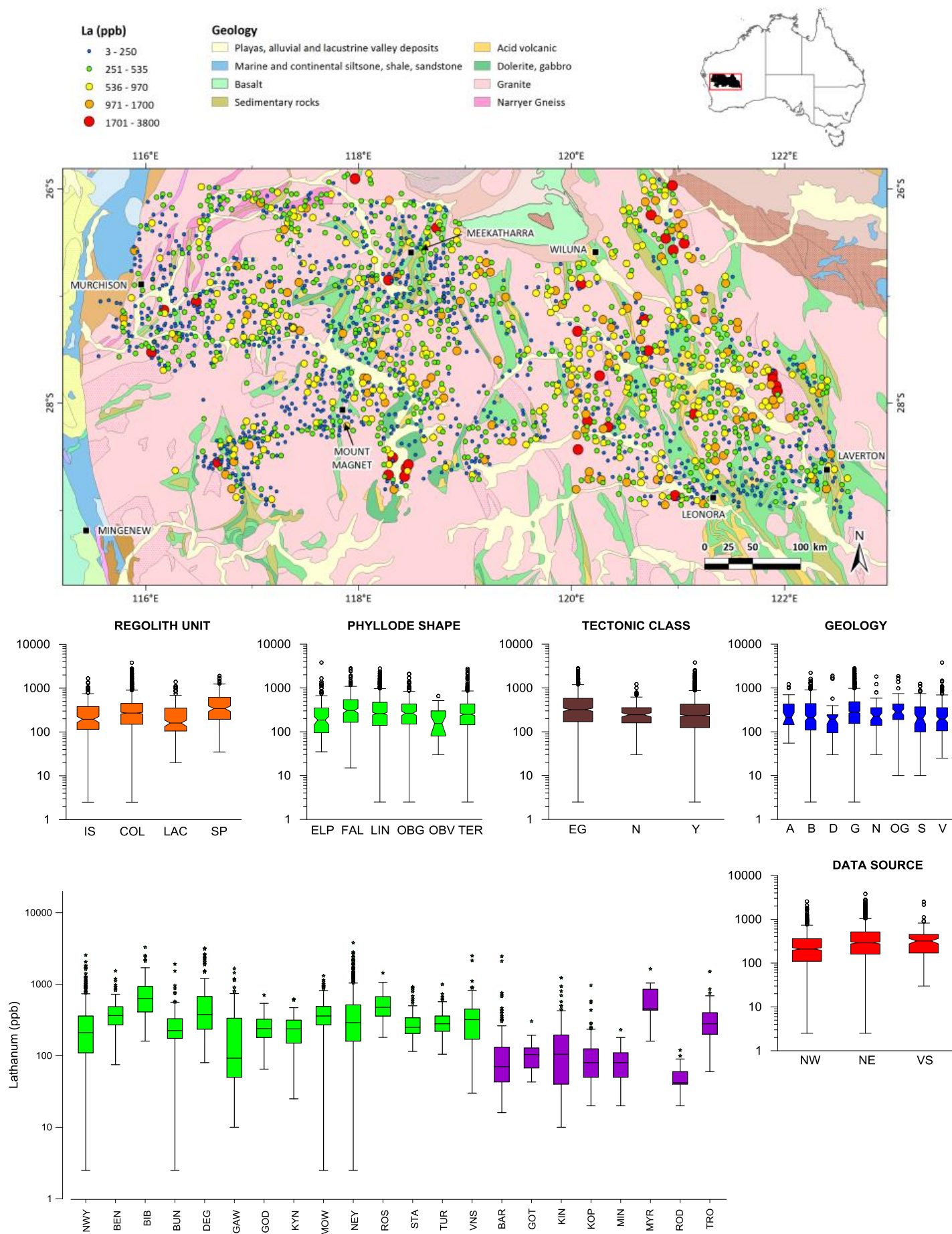
Hg (ppm)



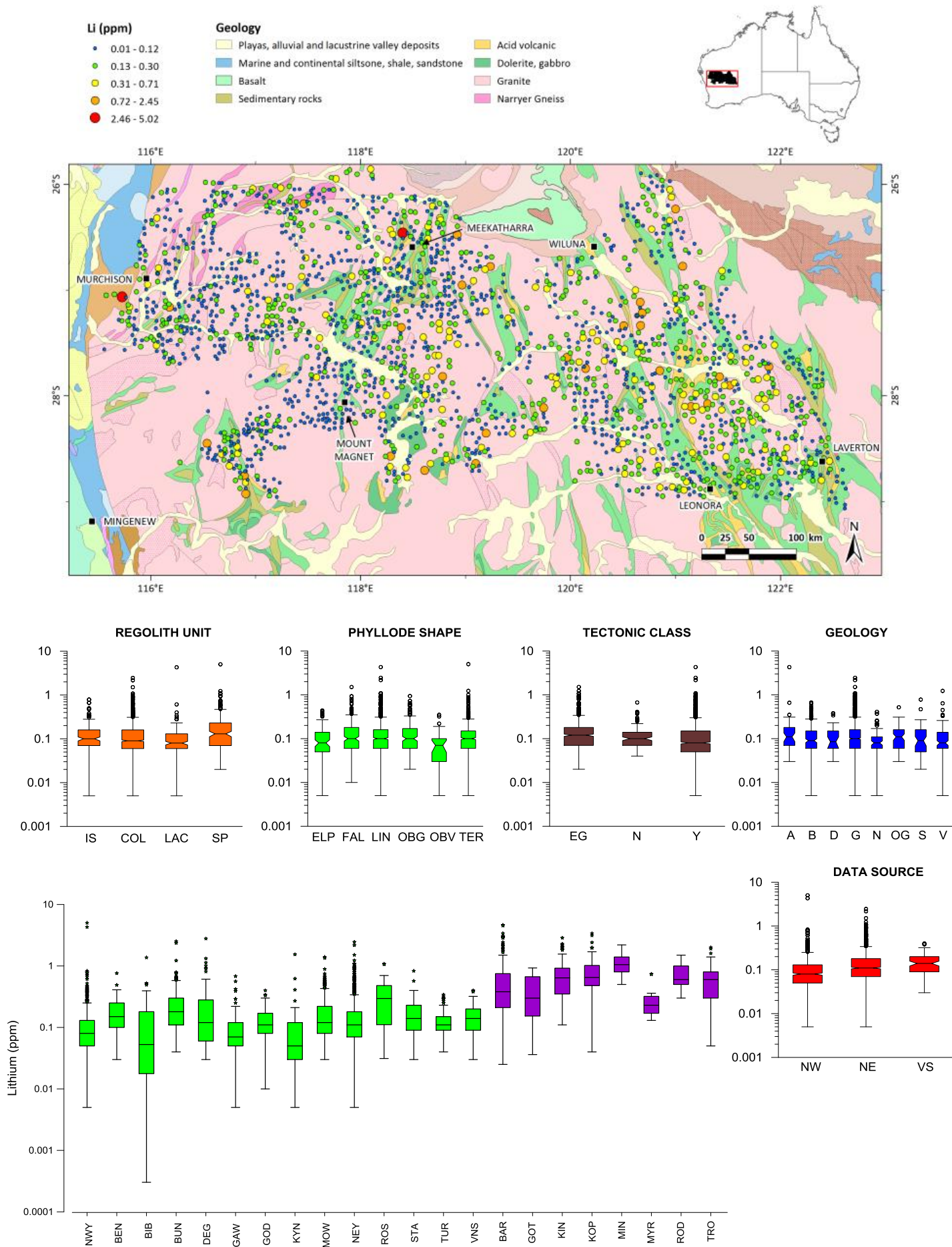
Ho (ppb)



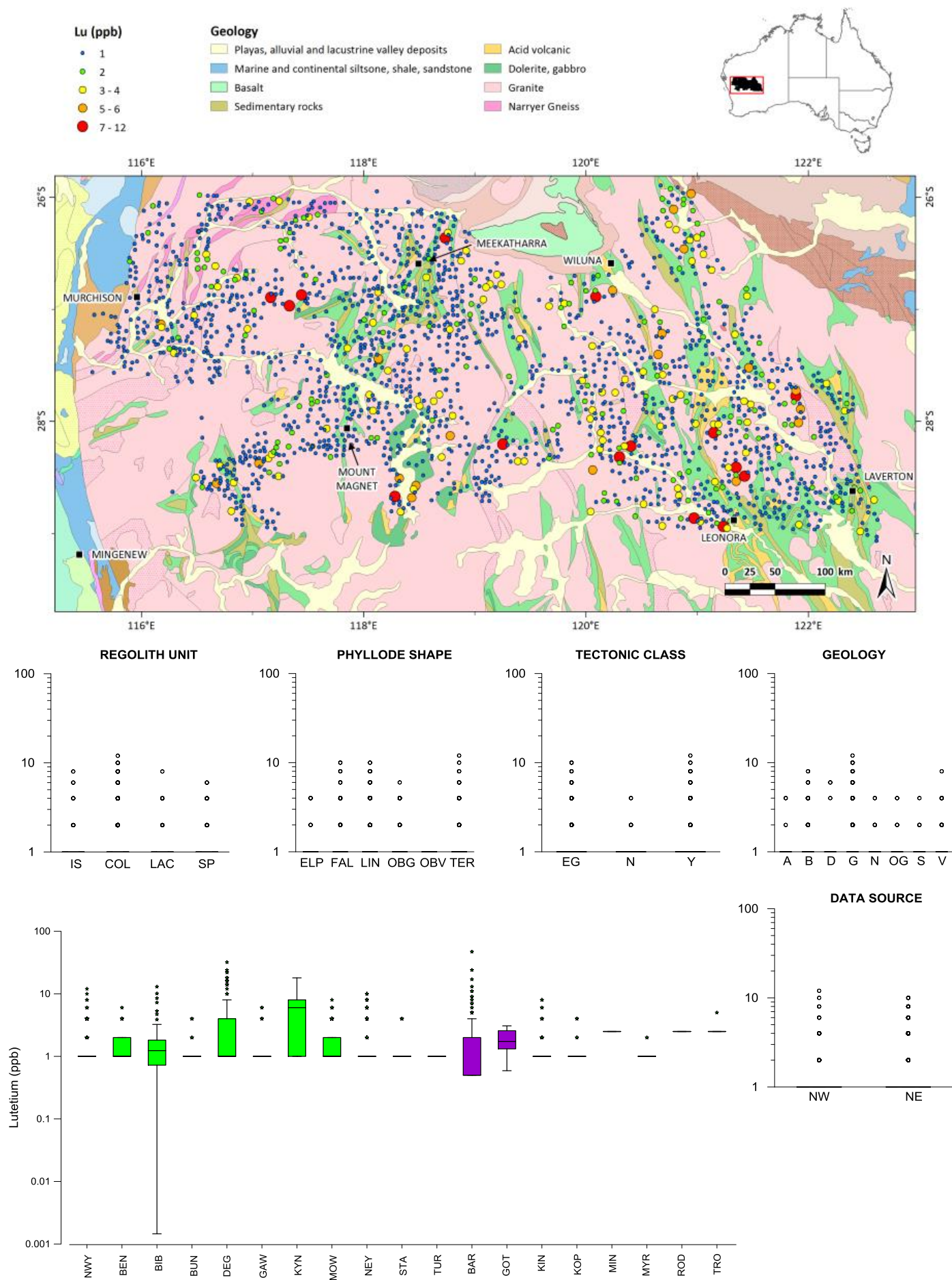
K (ppm)



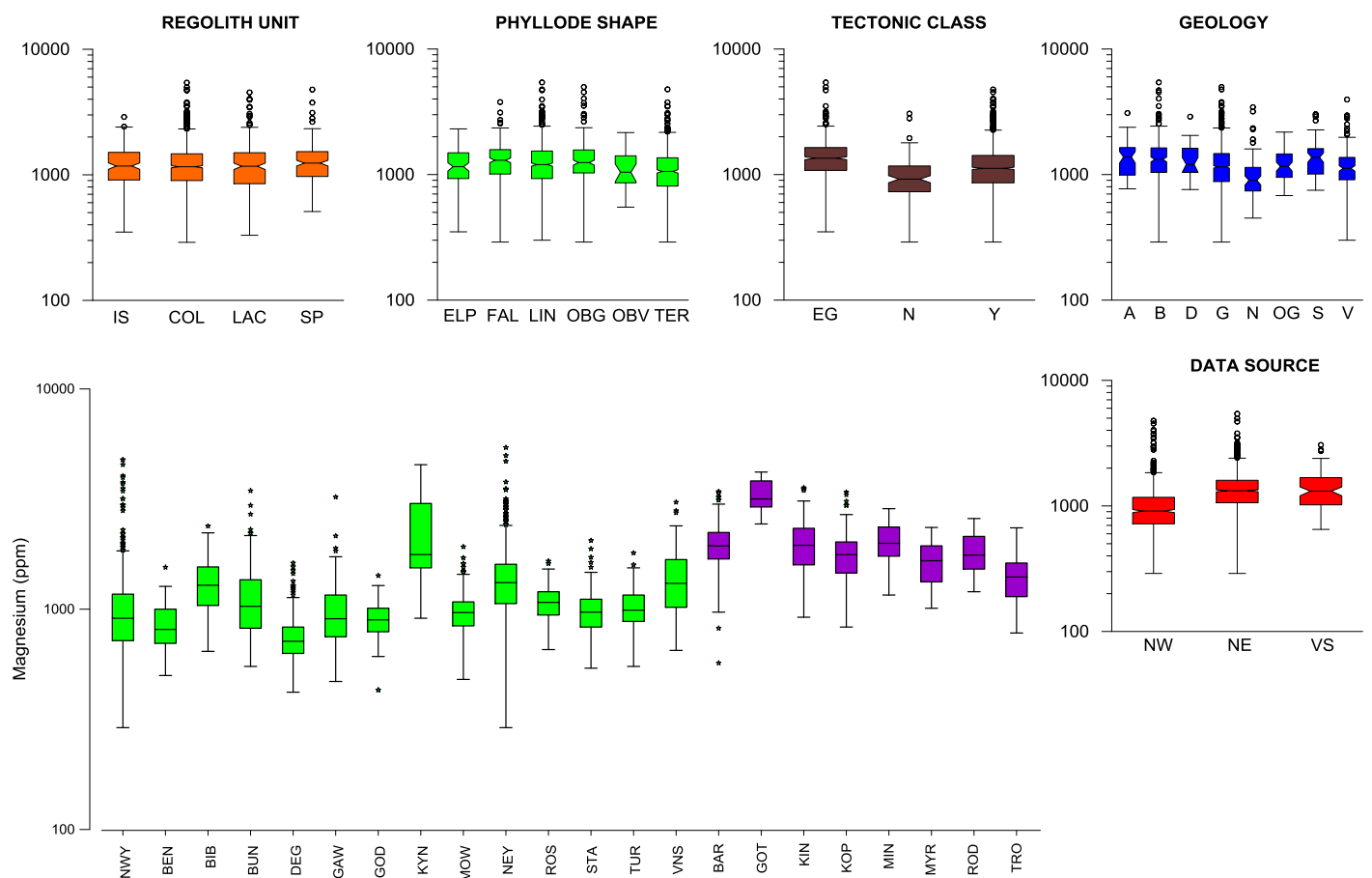
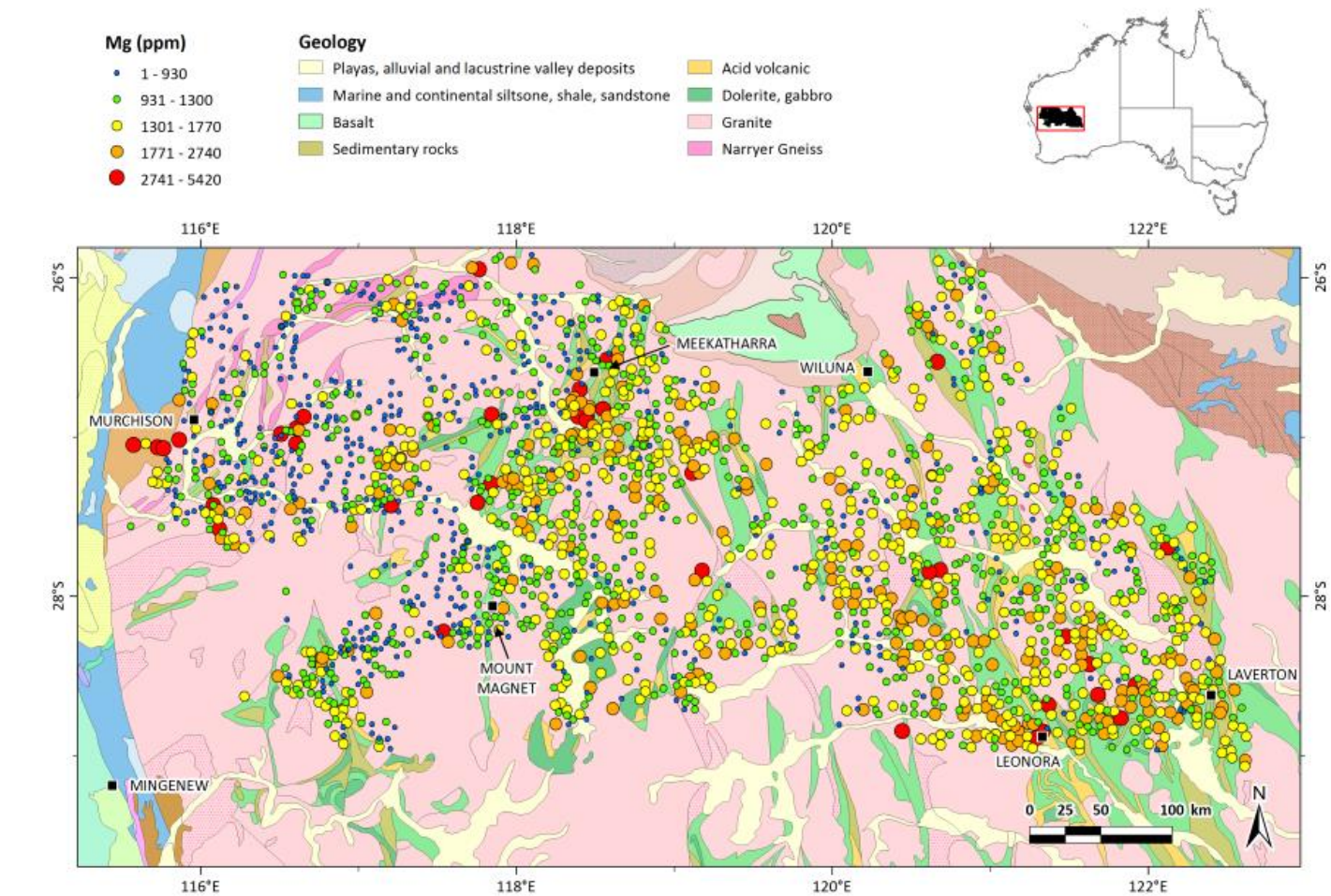
La (ppb)



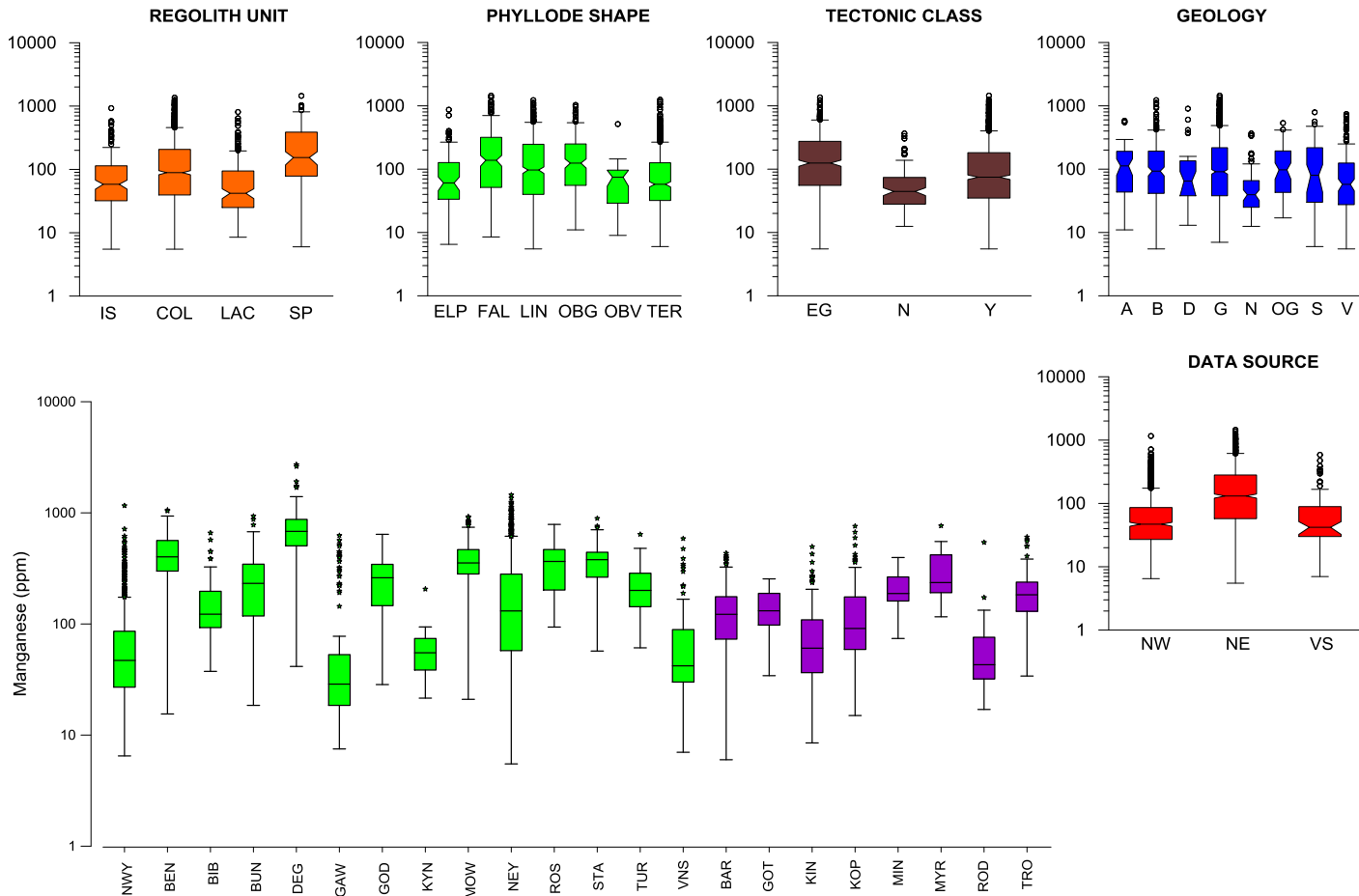
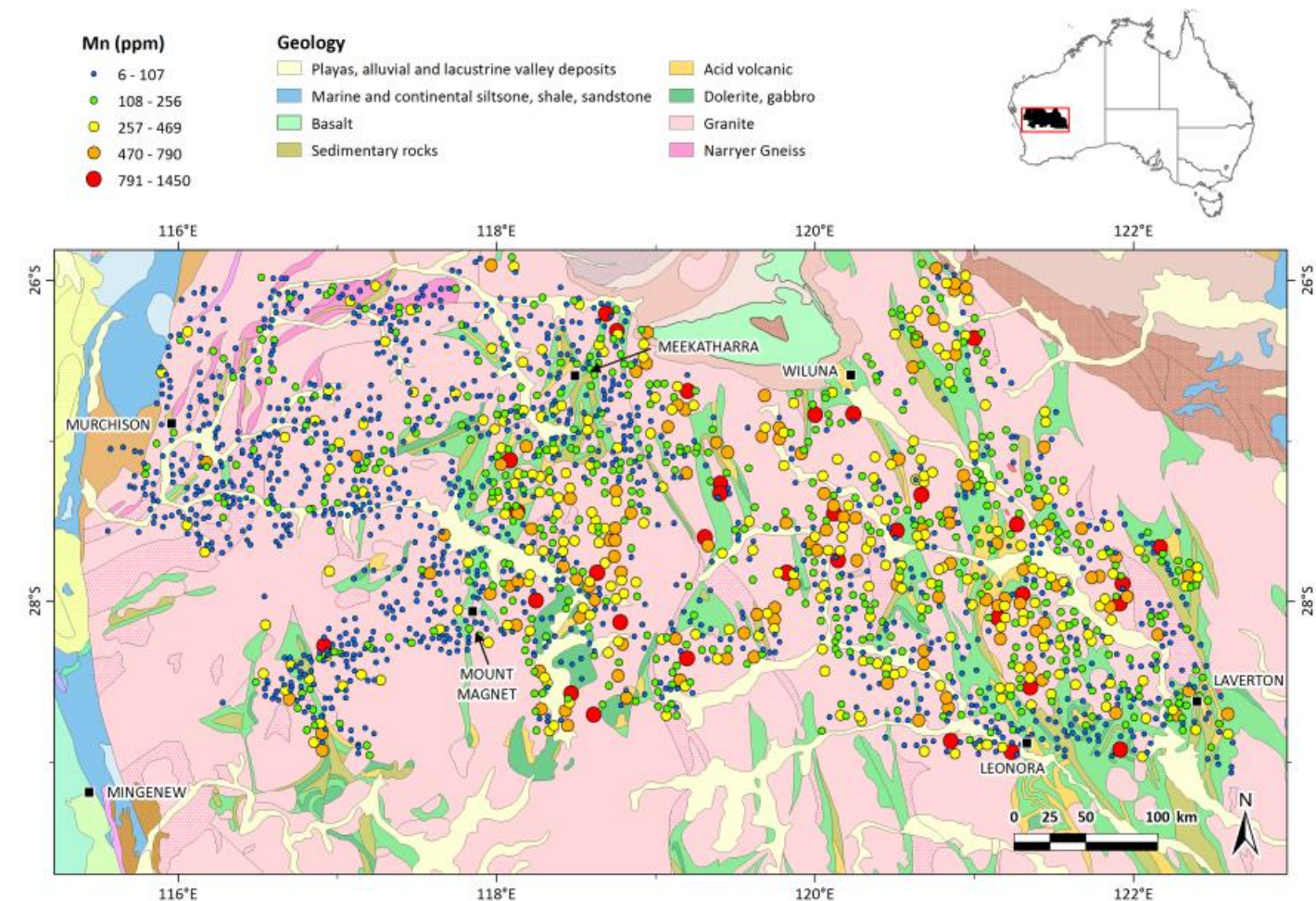
Li (ppm)



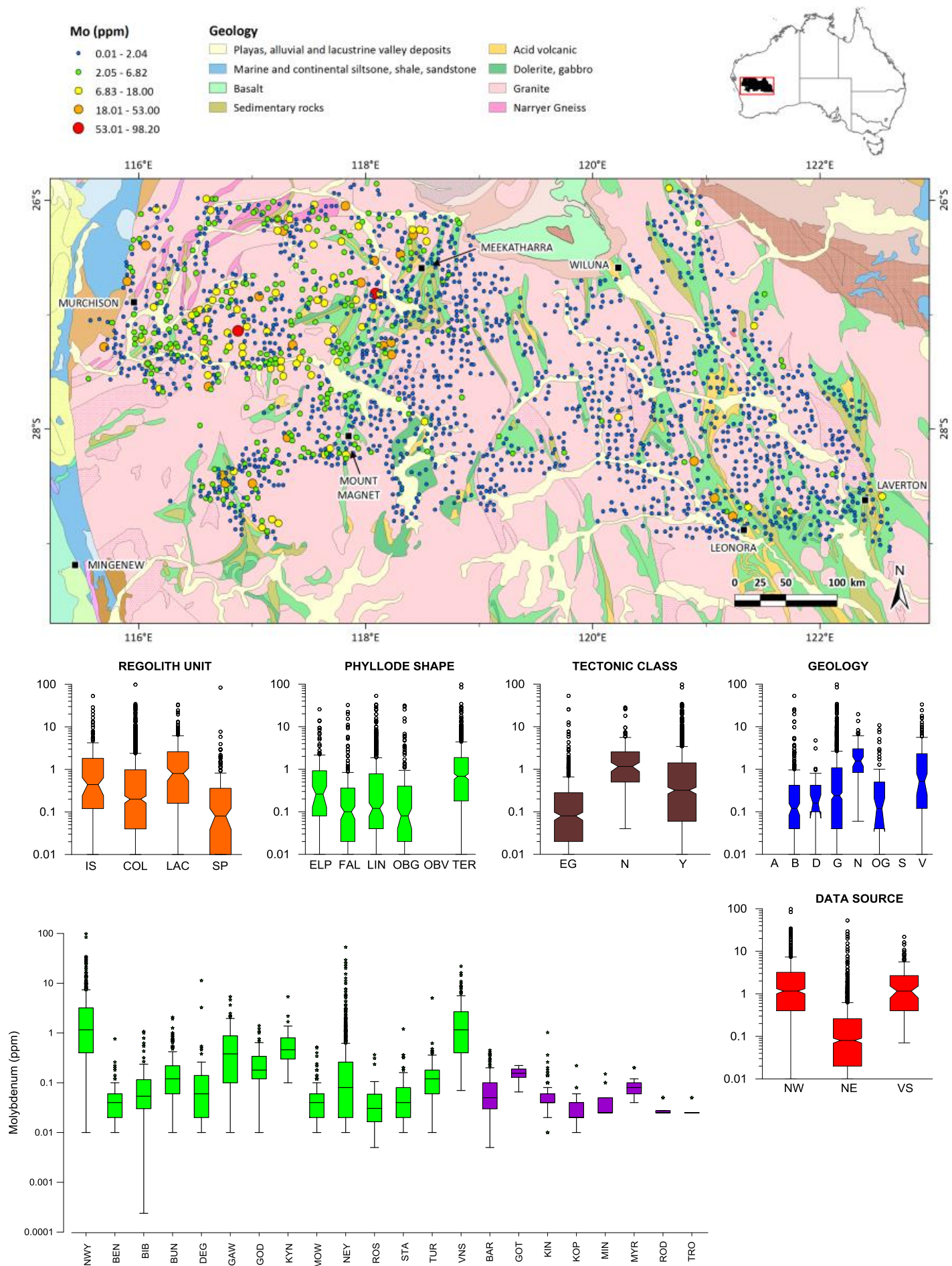
Lu (ppb)



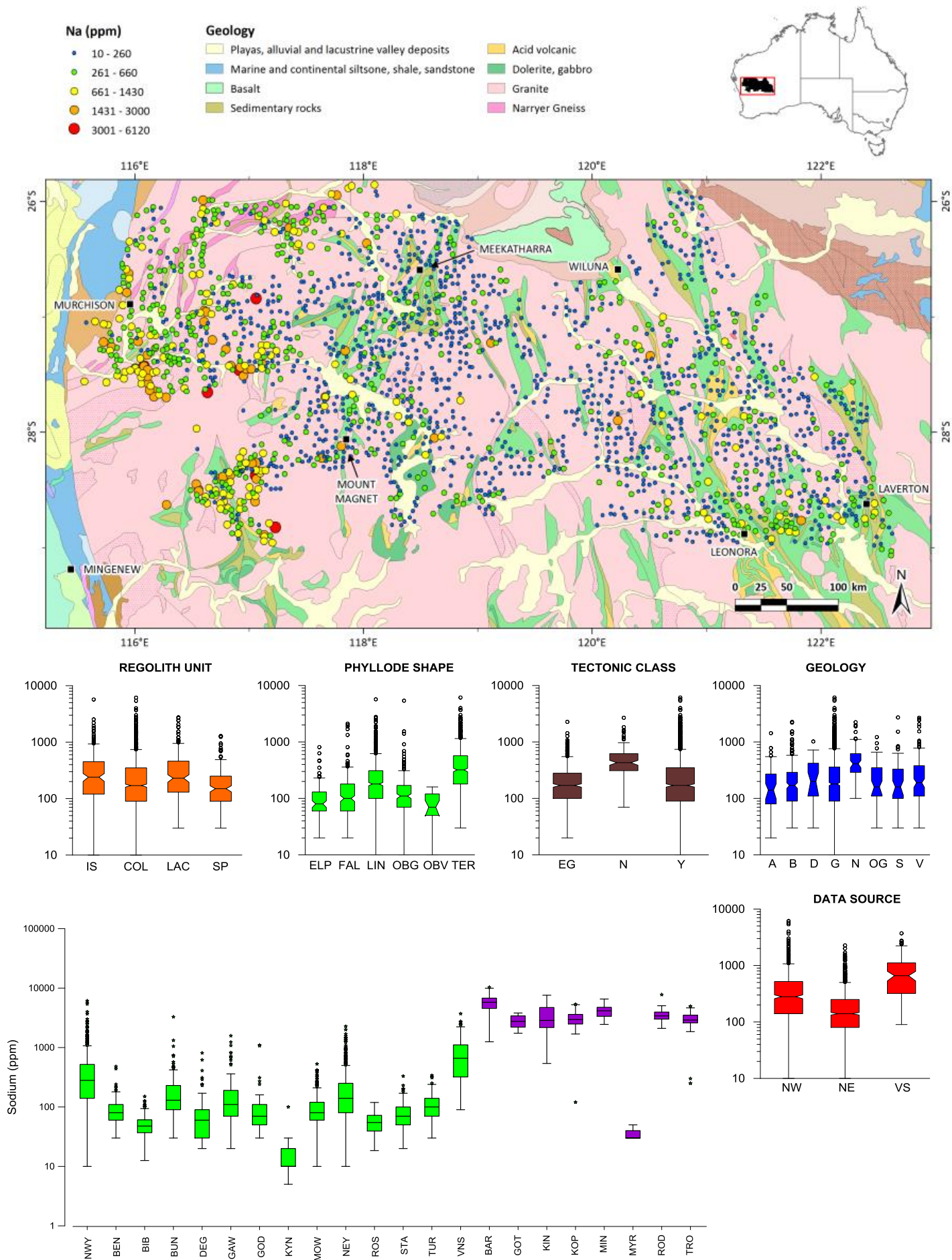
Mg (ppm)



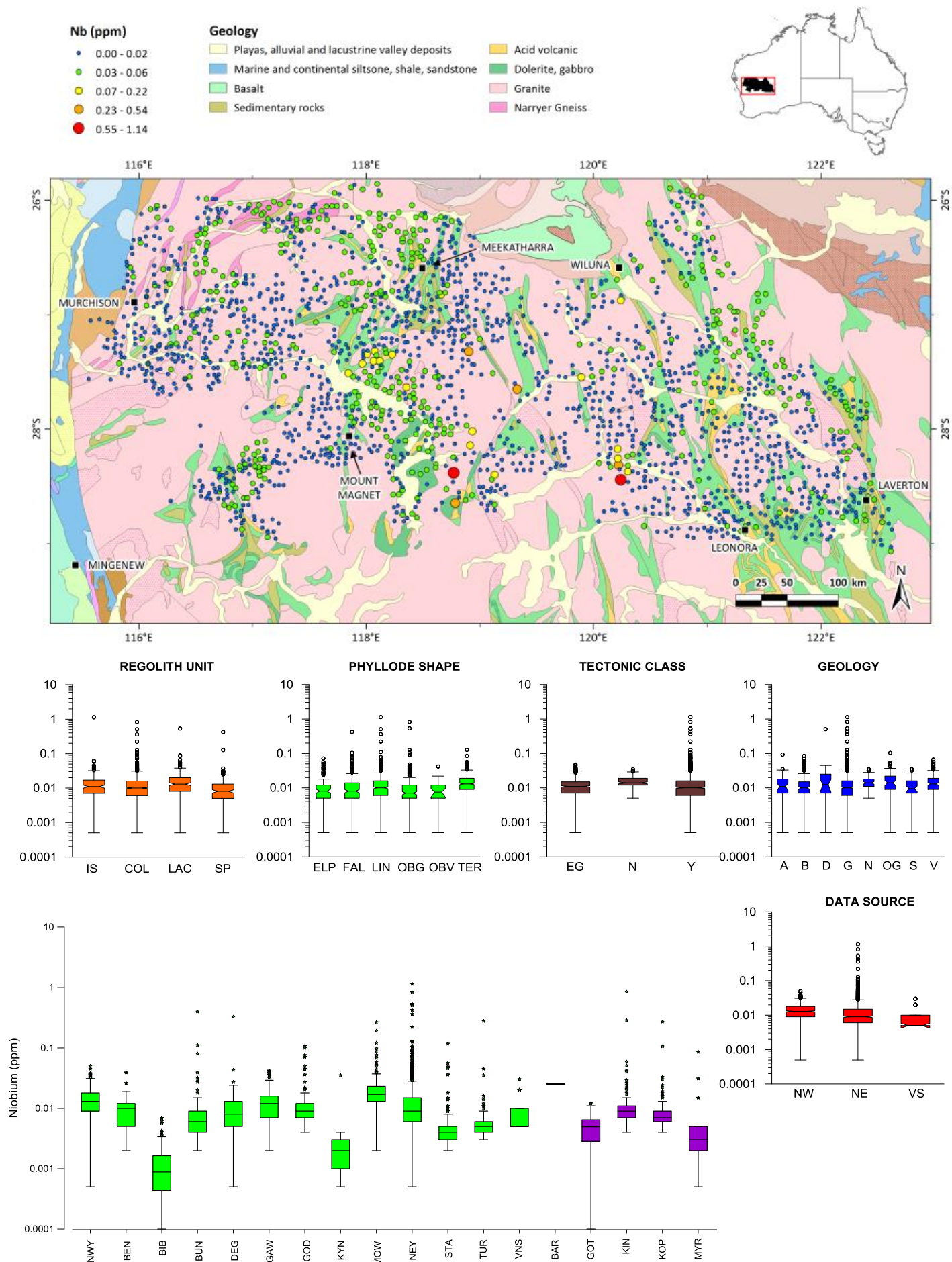
Mn (ppm)



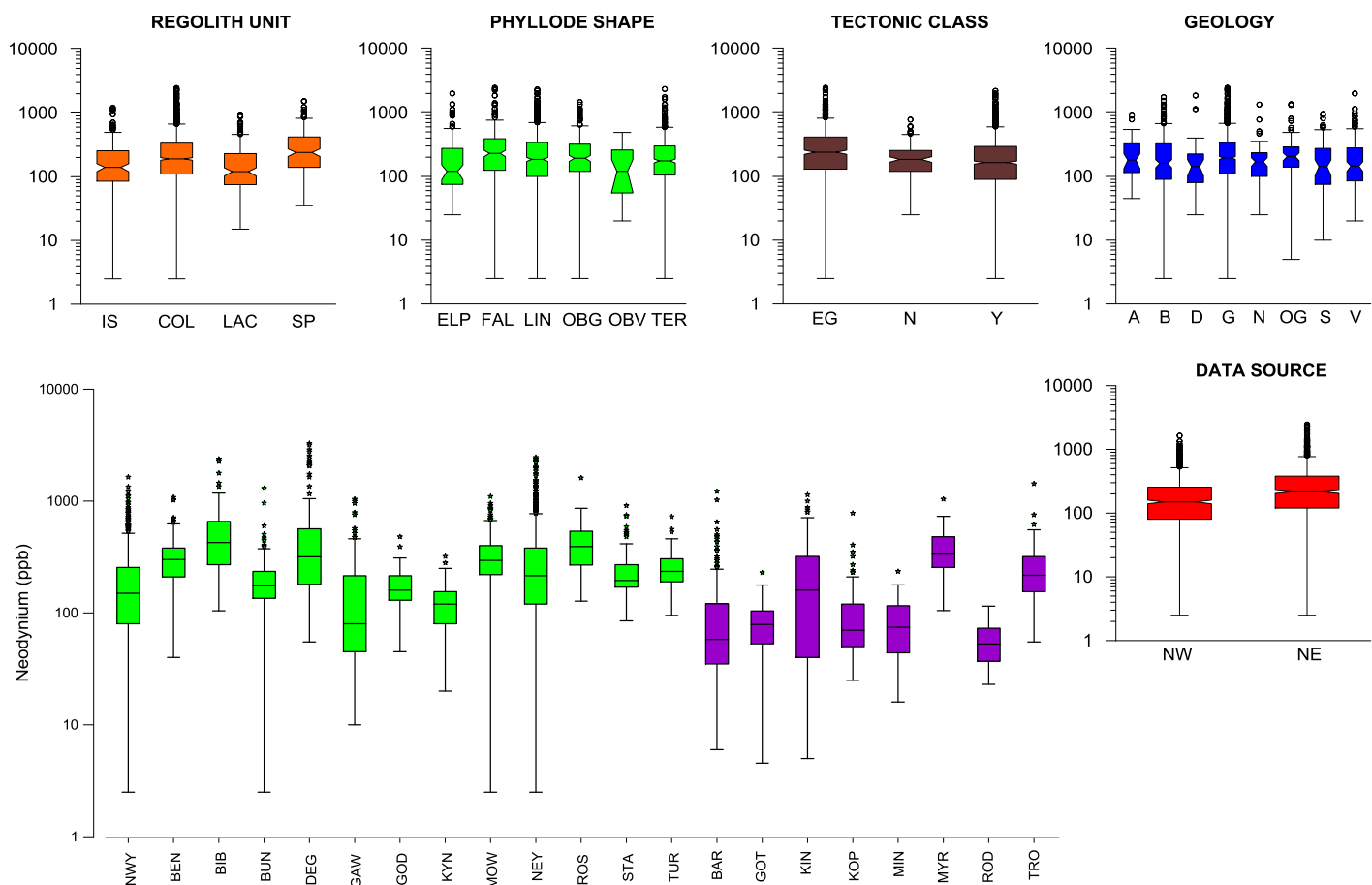
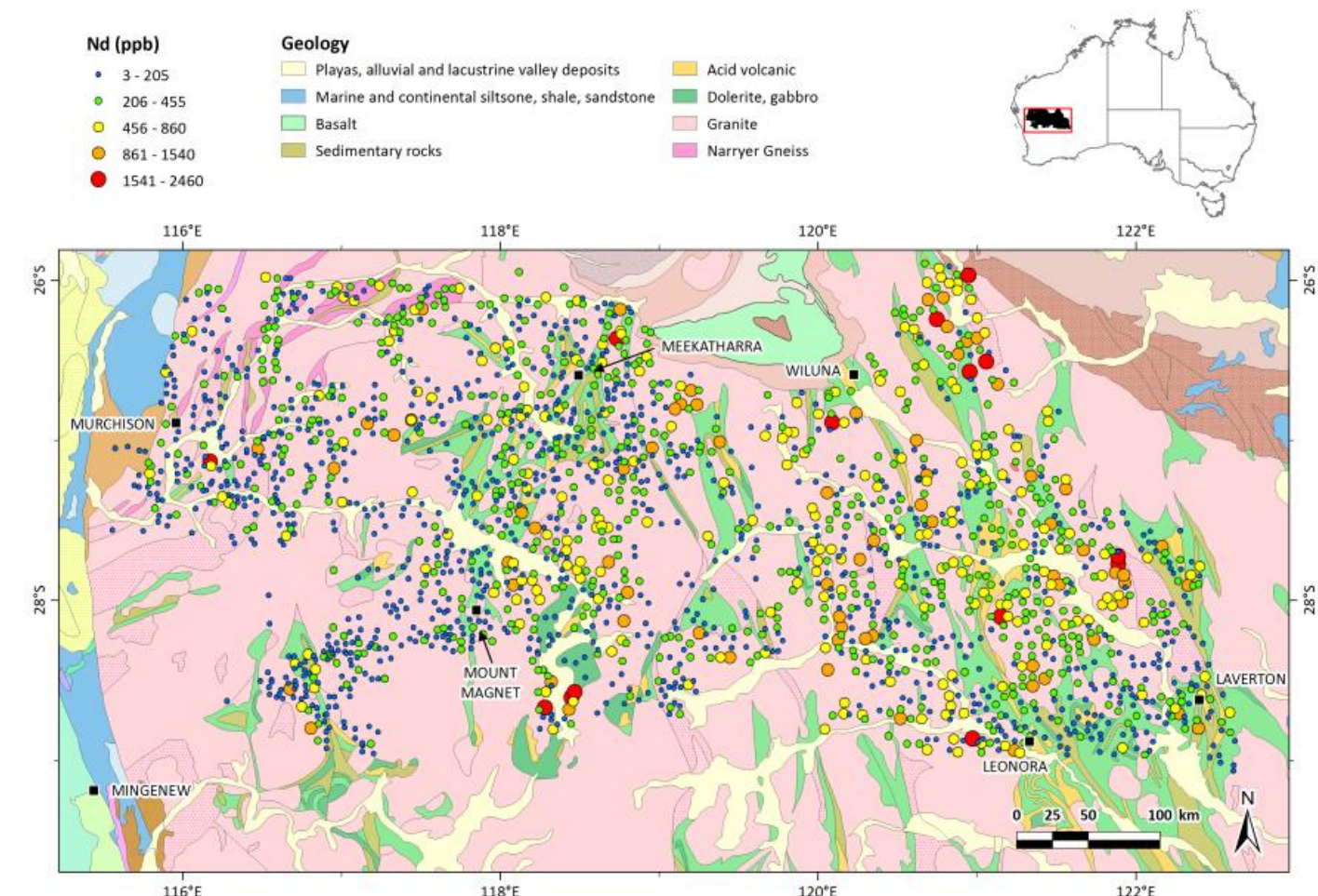
Mo (ppm)



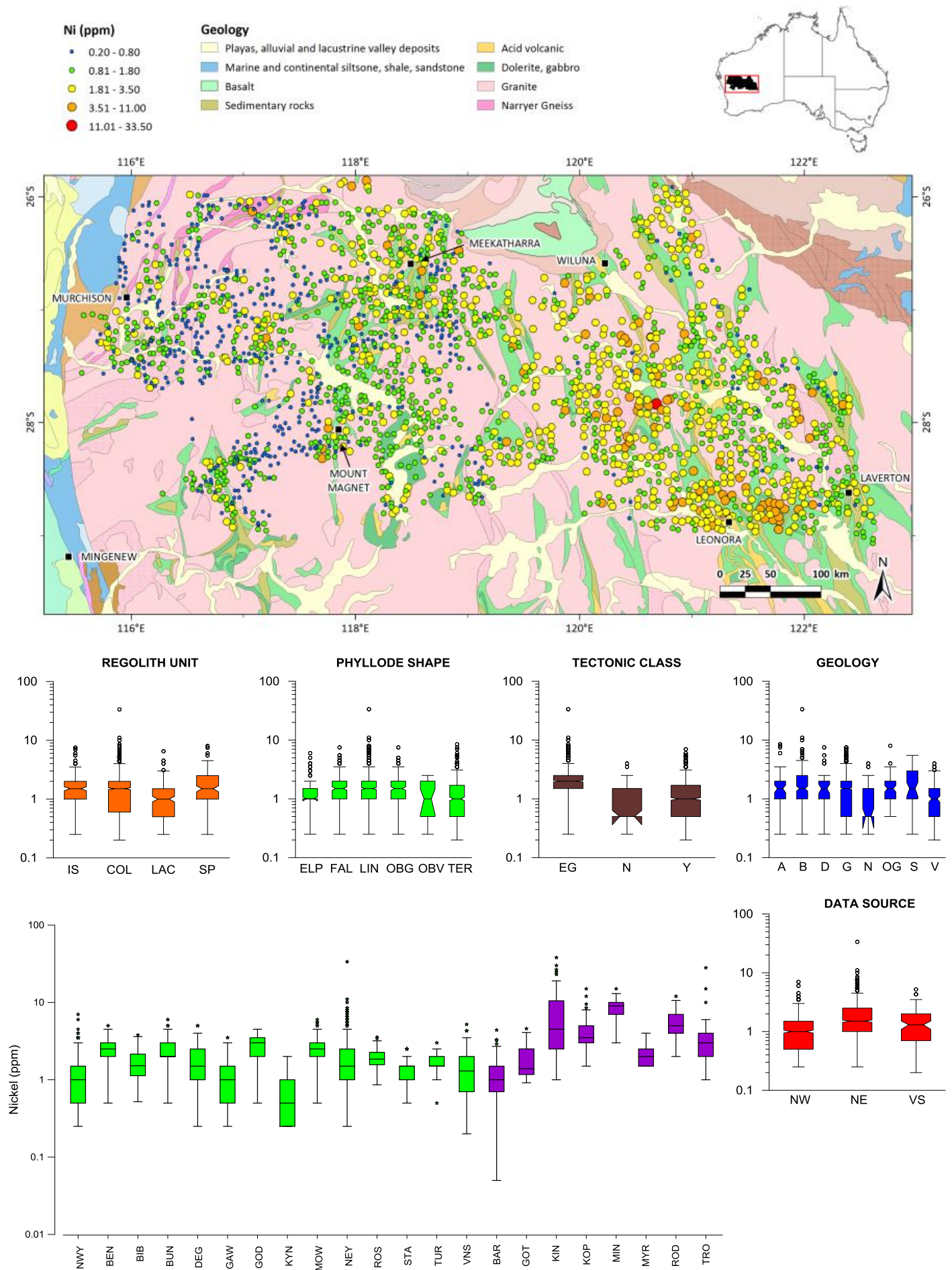
Na (ppm)



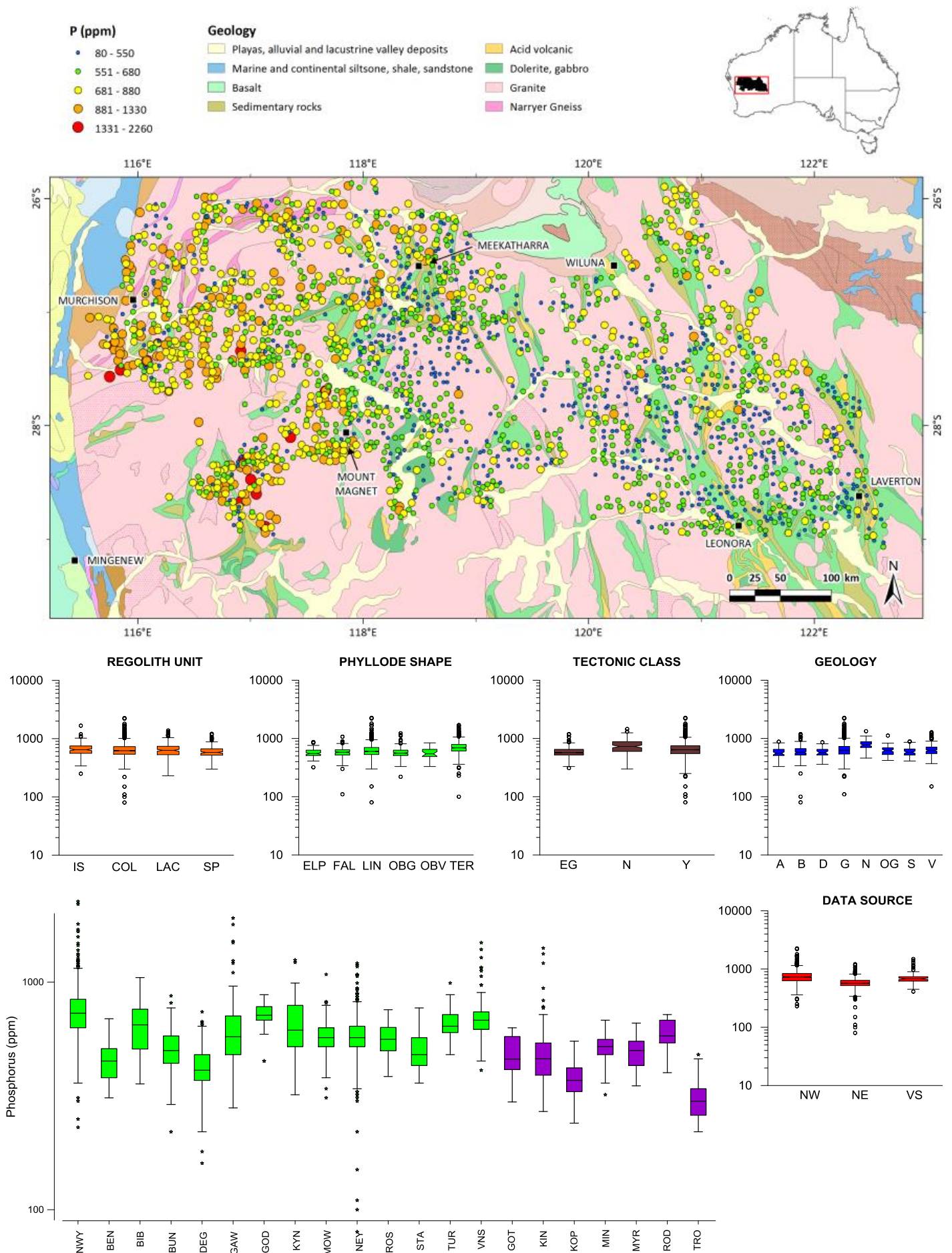
Nb (ppm)



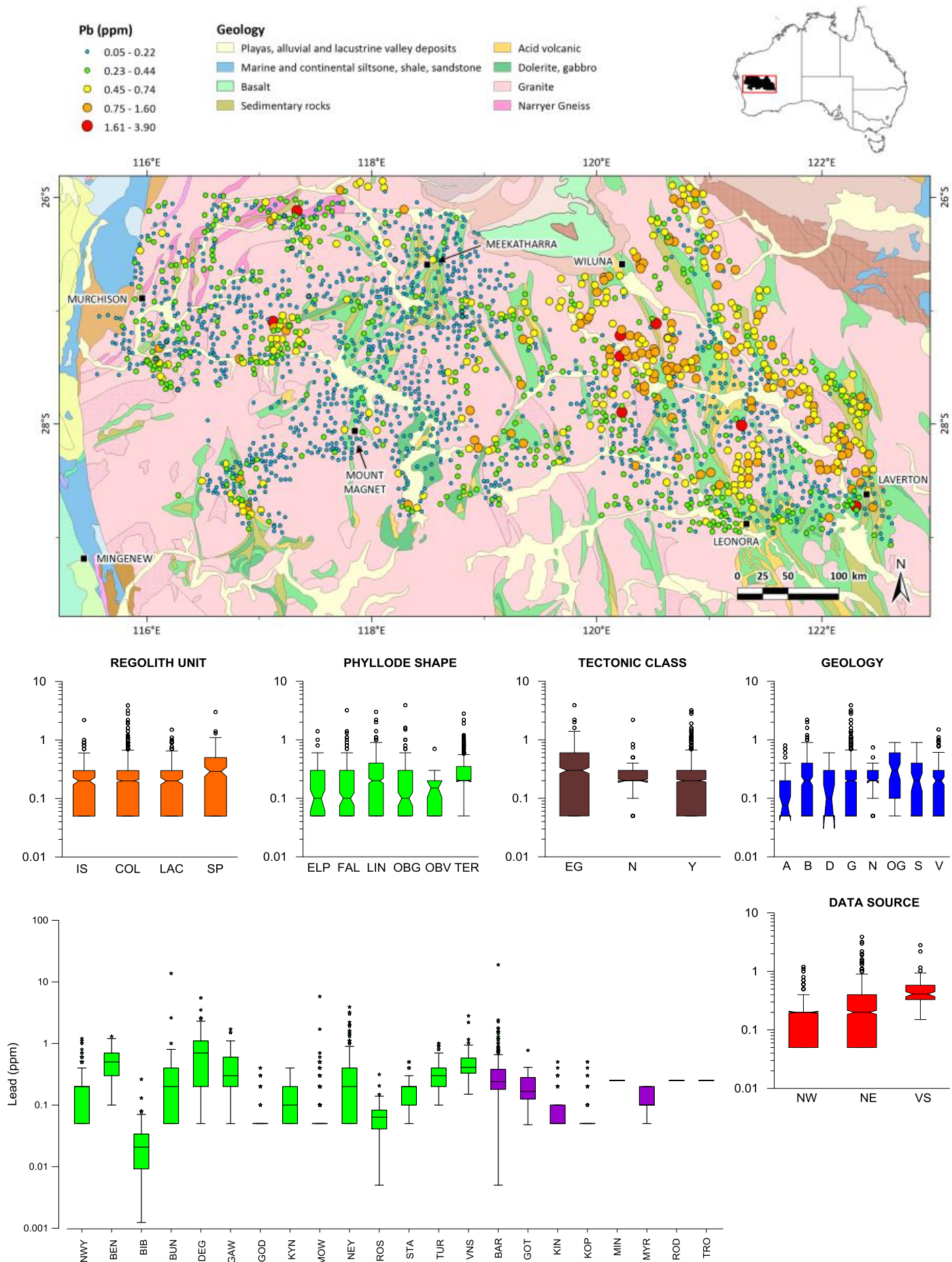
Nd (ppb)



Ni (ppm)



P (ppm)



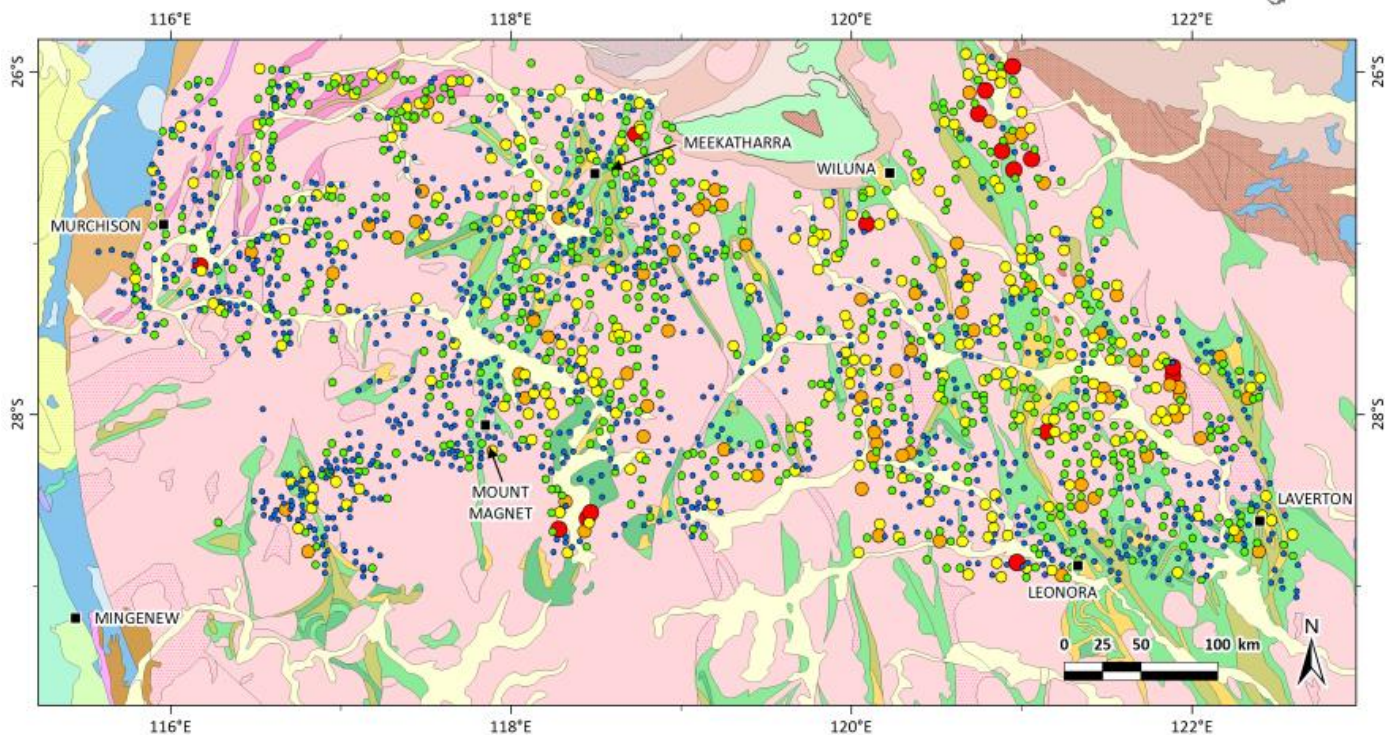
Pb (ppm)

Pr (ppb)

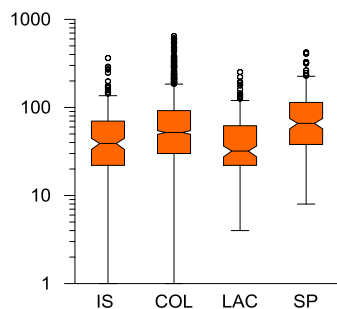
- 1 - 54
- 55 - 118
- 119 - 222
- 223 - 386
- 387 - 646

Geology

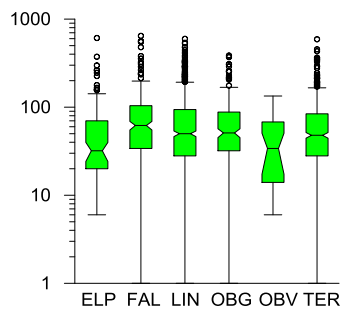
- Playas, alluvial and lacustrine valley deposits
- Marine and continental siltstone, shale, sandstone
- Basalt
- Sedimentary rocks
- Acid volcanic
- Dolerite, gabbro
- Granite
- Narryer Gneiss



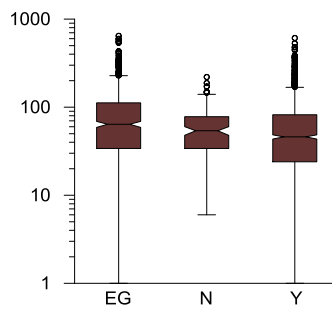
REGOLITH UNIT



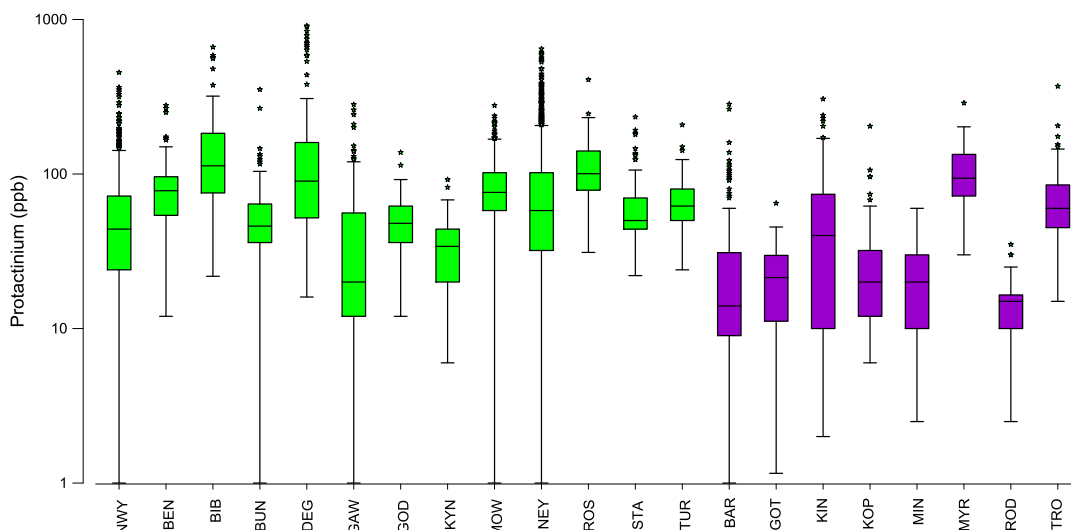
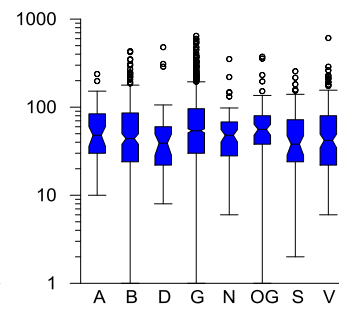
PHYLLOIDE SHAPE



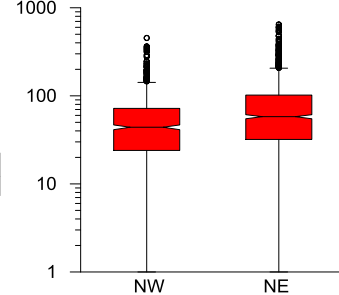
TECTONIC CLASS



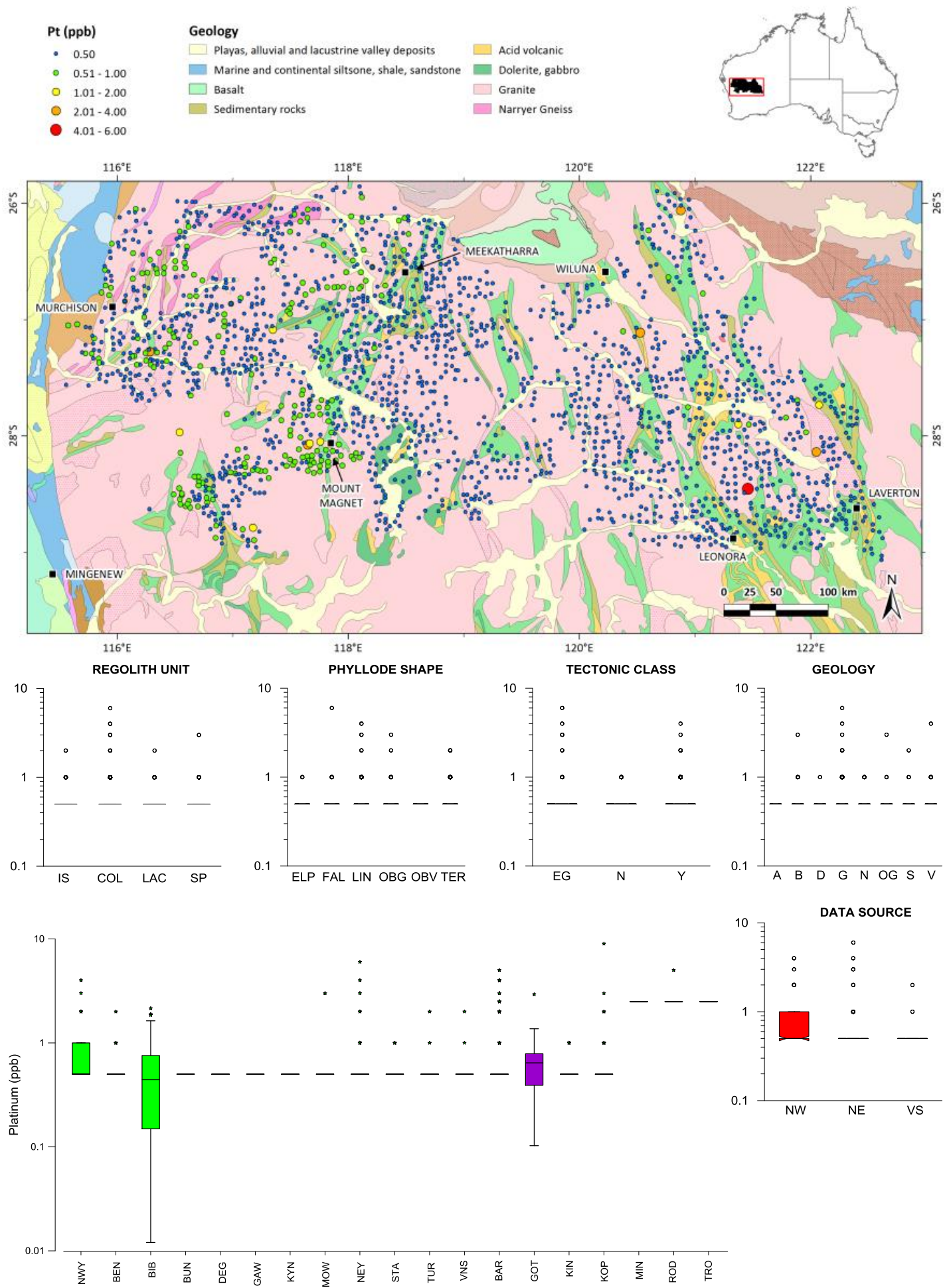
GEOLOGY



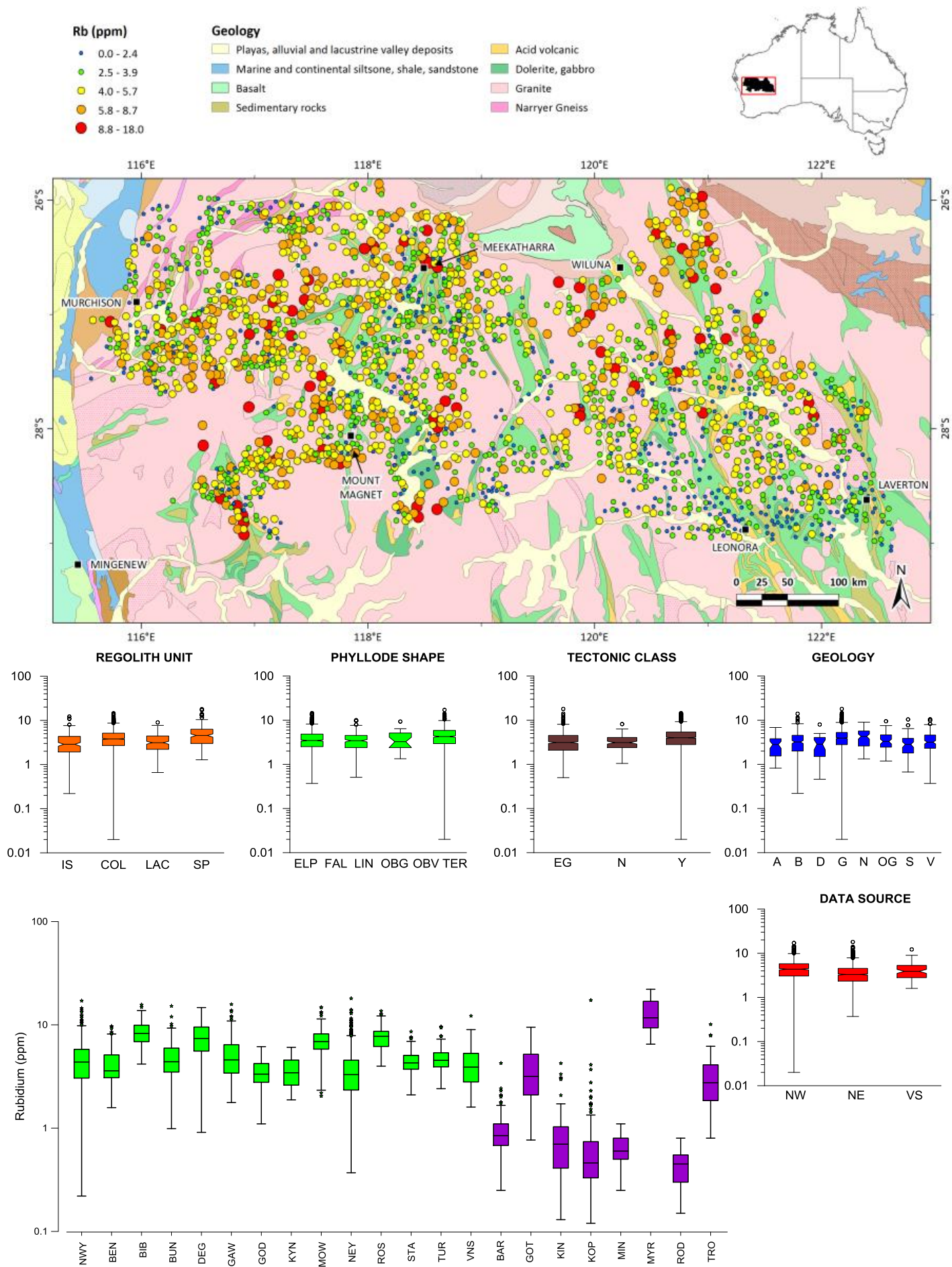
DATA SOURCE



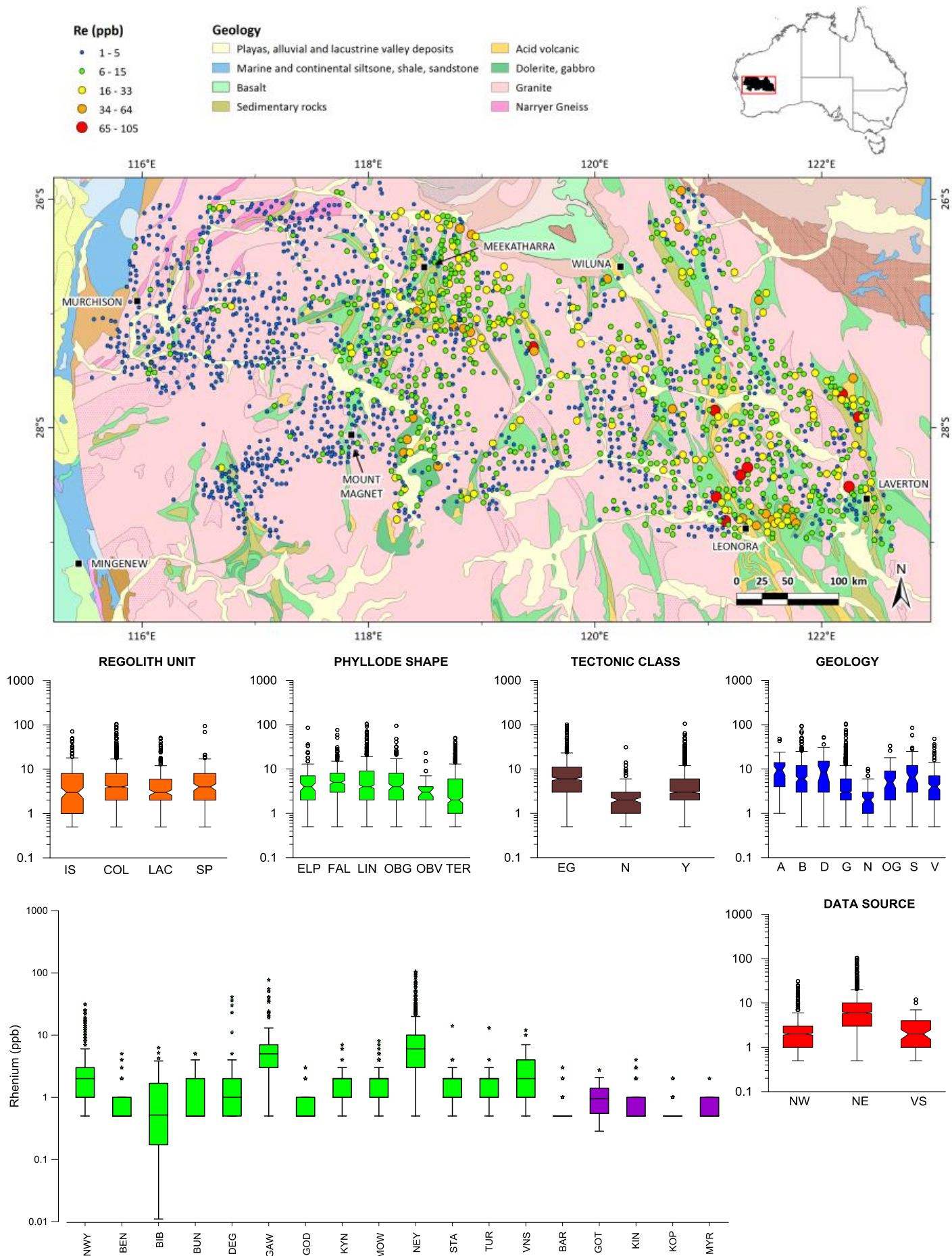
Pr (ppb)



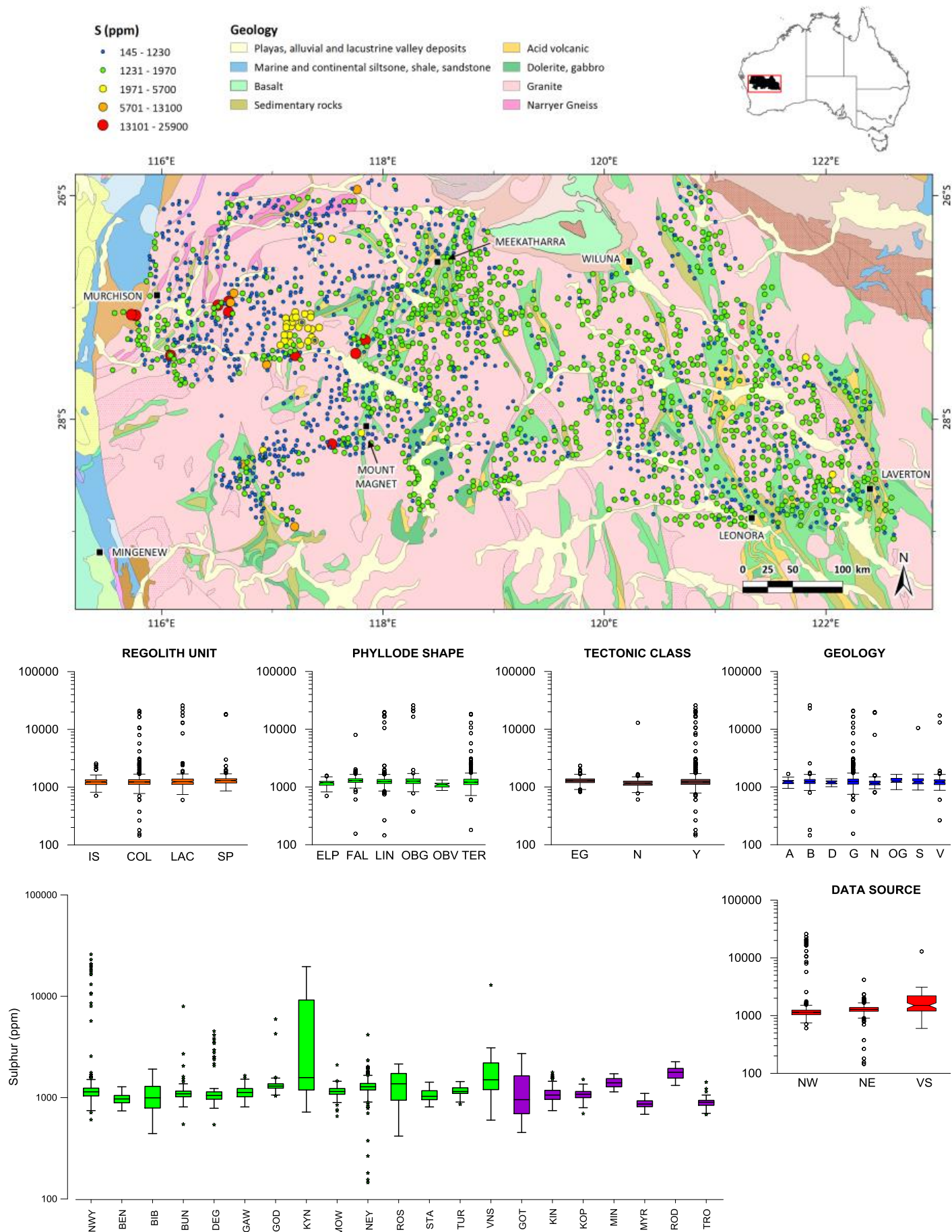
Pt (ppb)



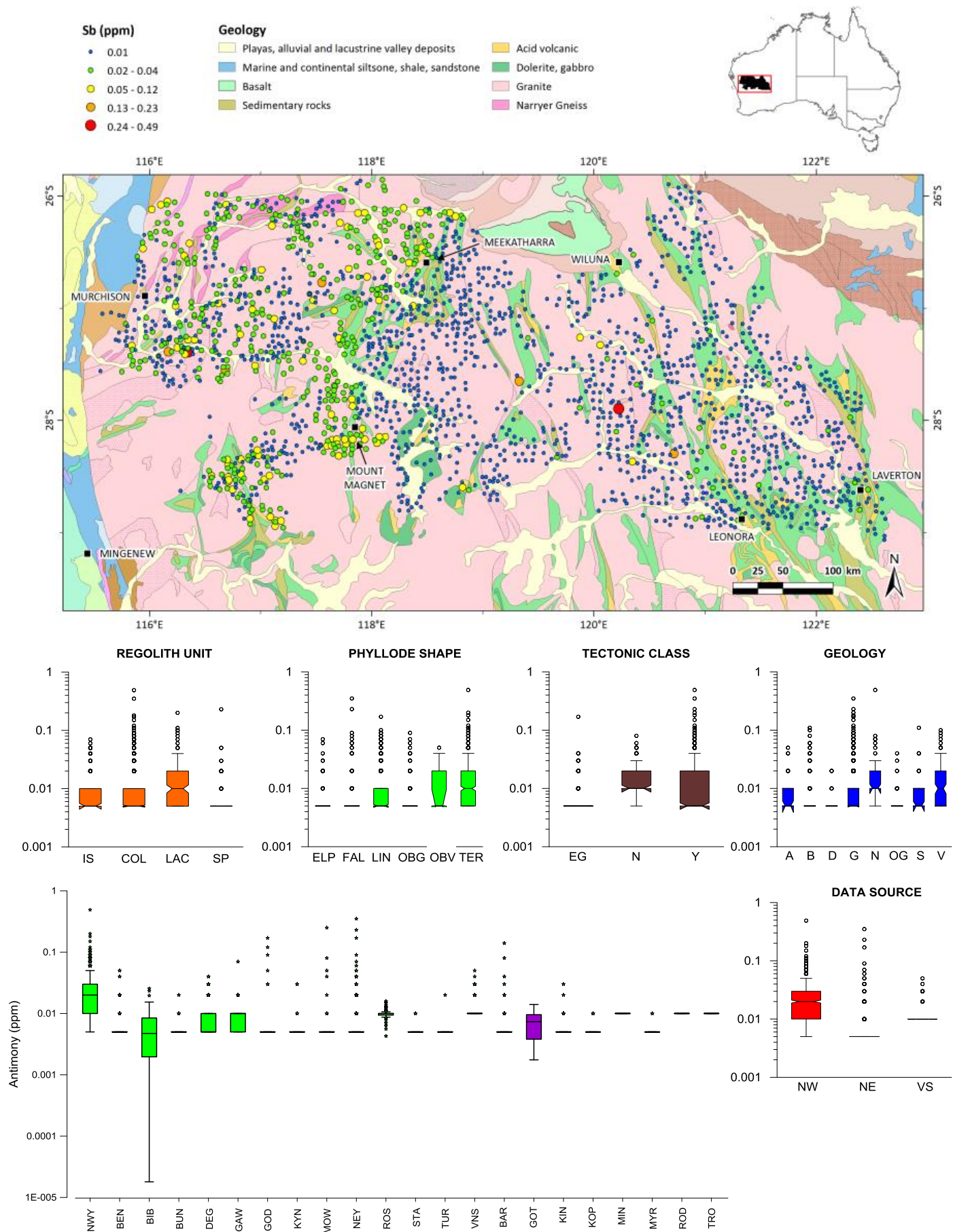
Rb (ppm)



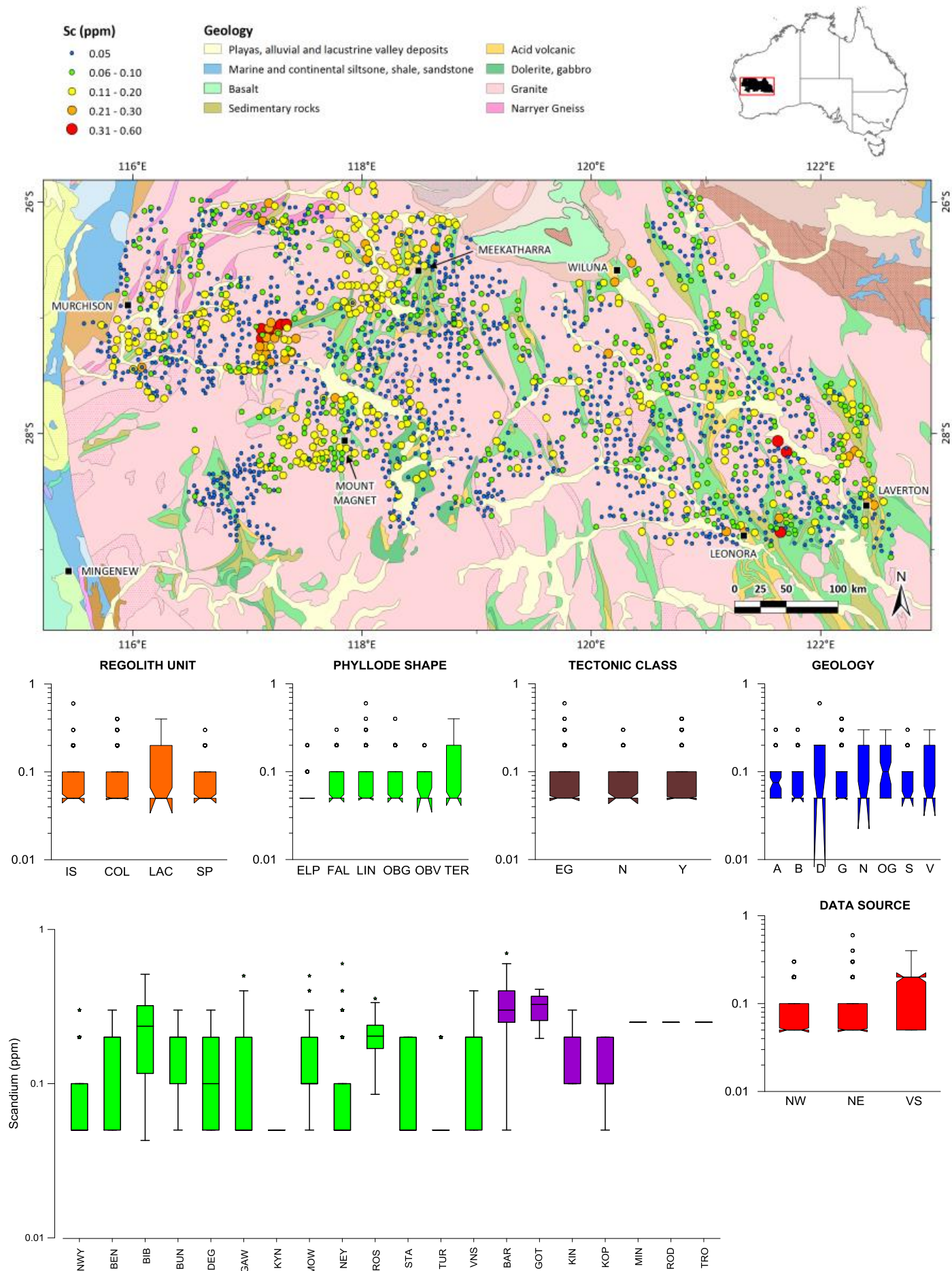
Re (ppb)



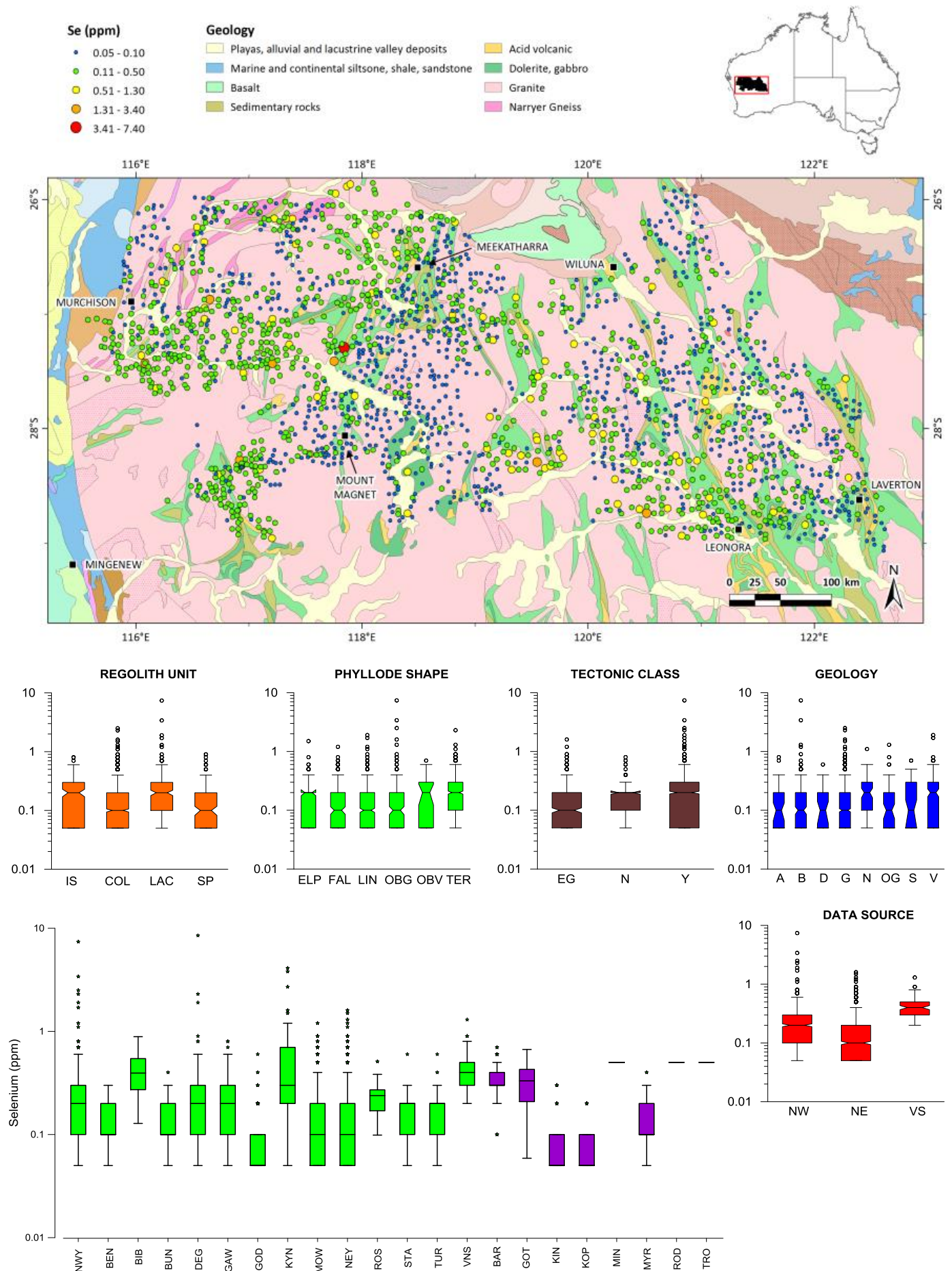
S (ppm)



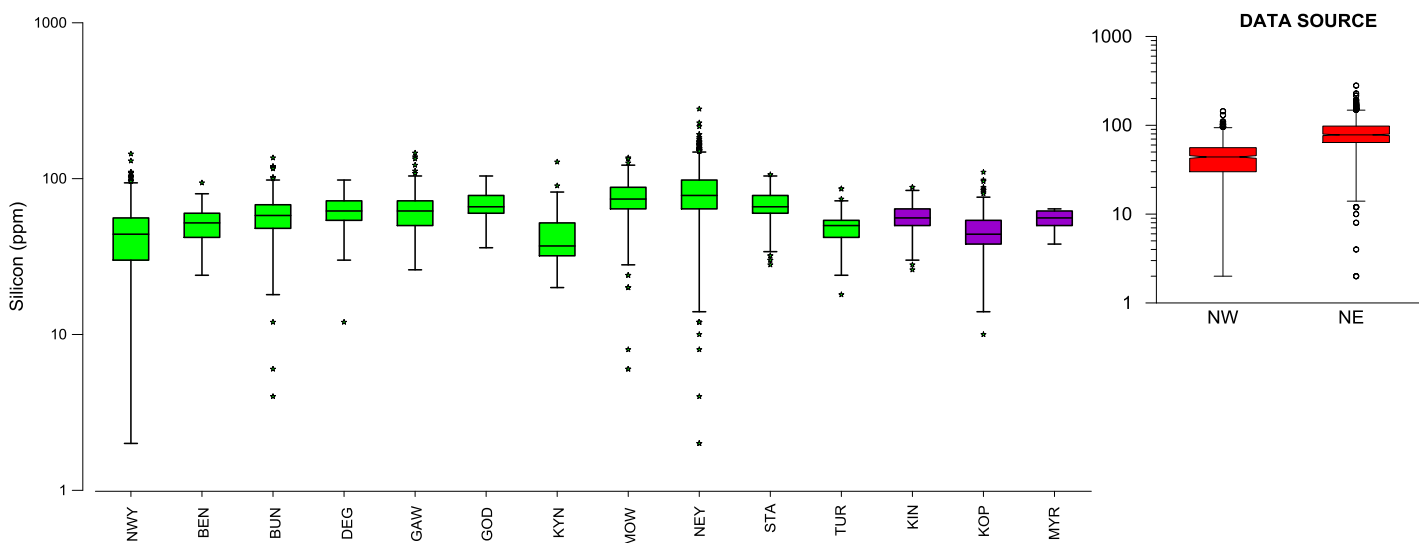
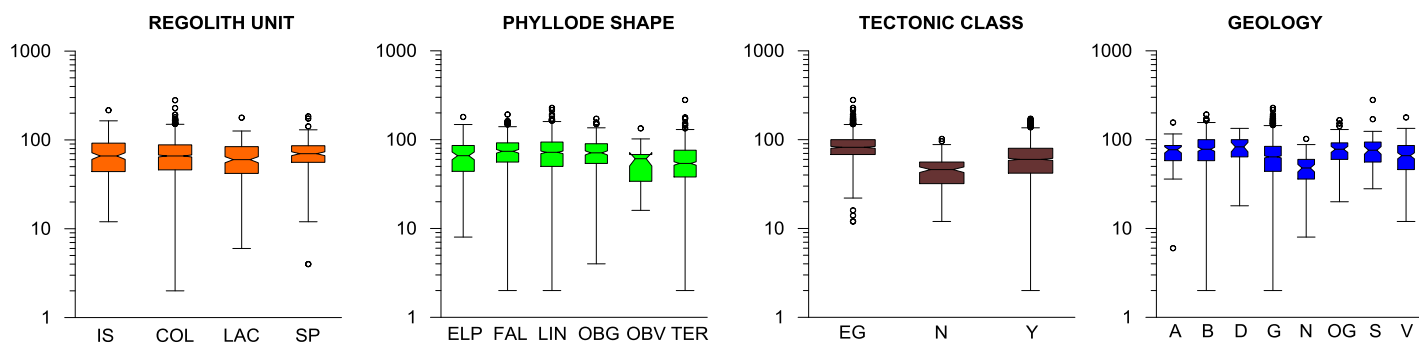
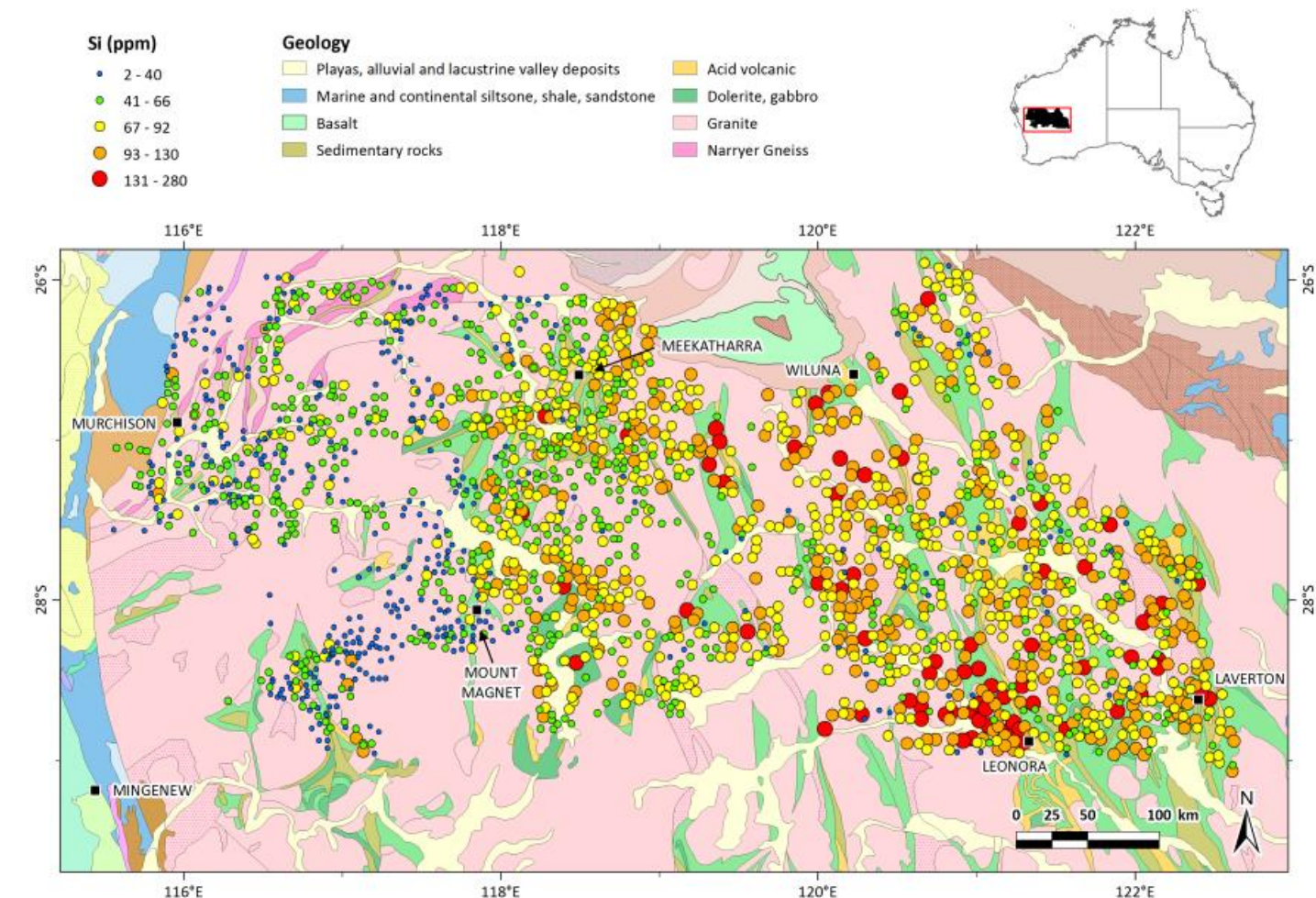
Sb (ppm)



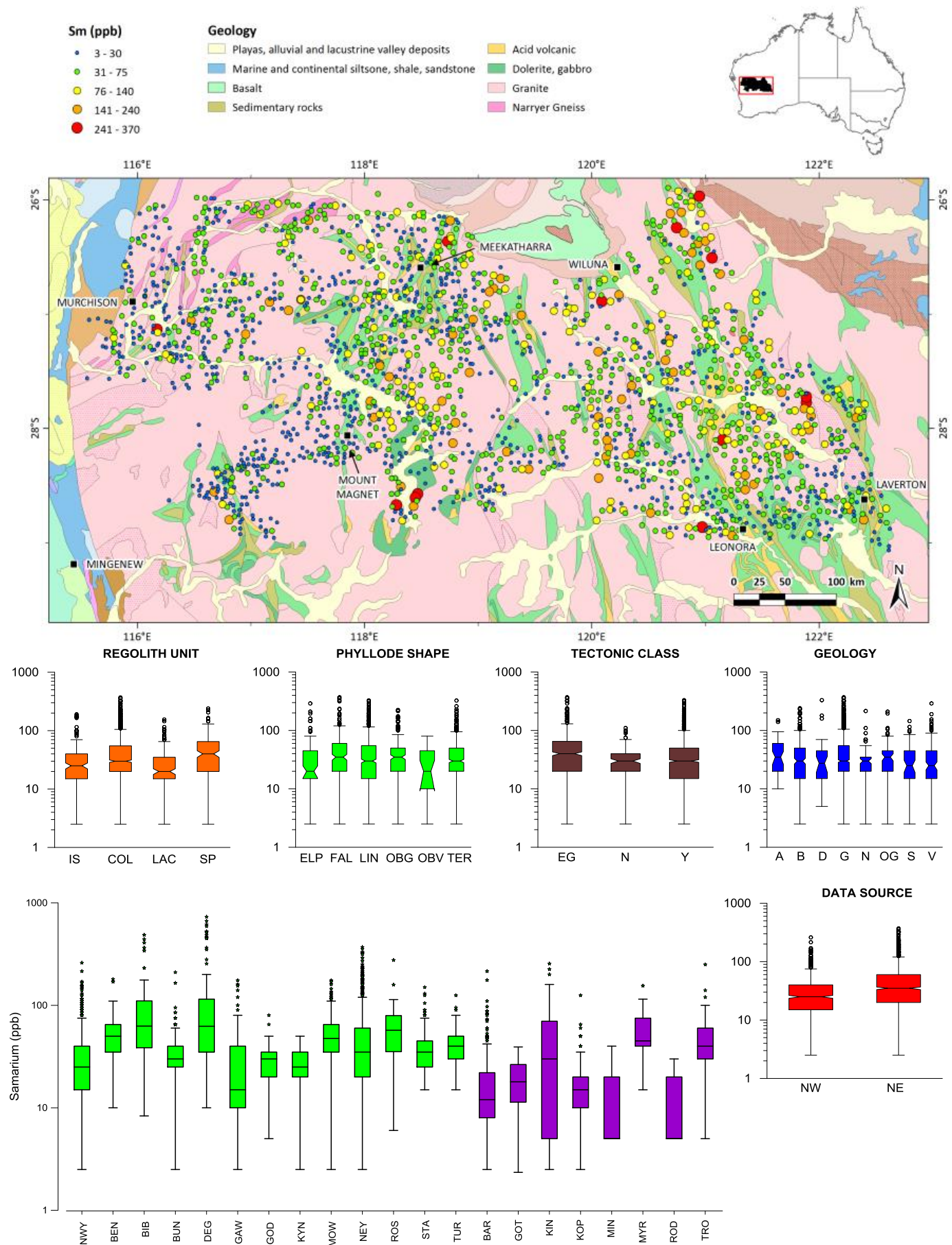
Sc (ppm)



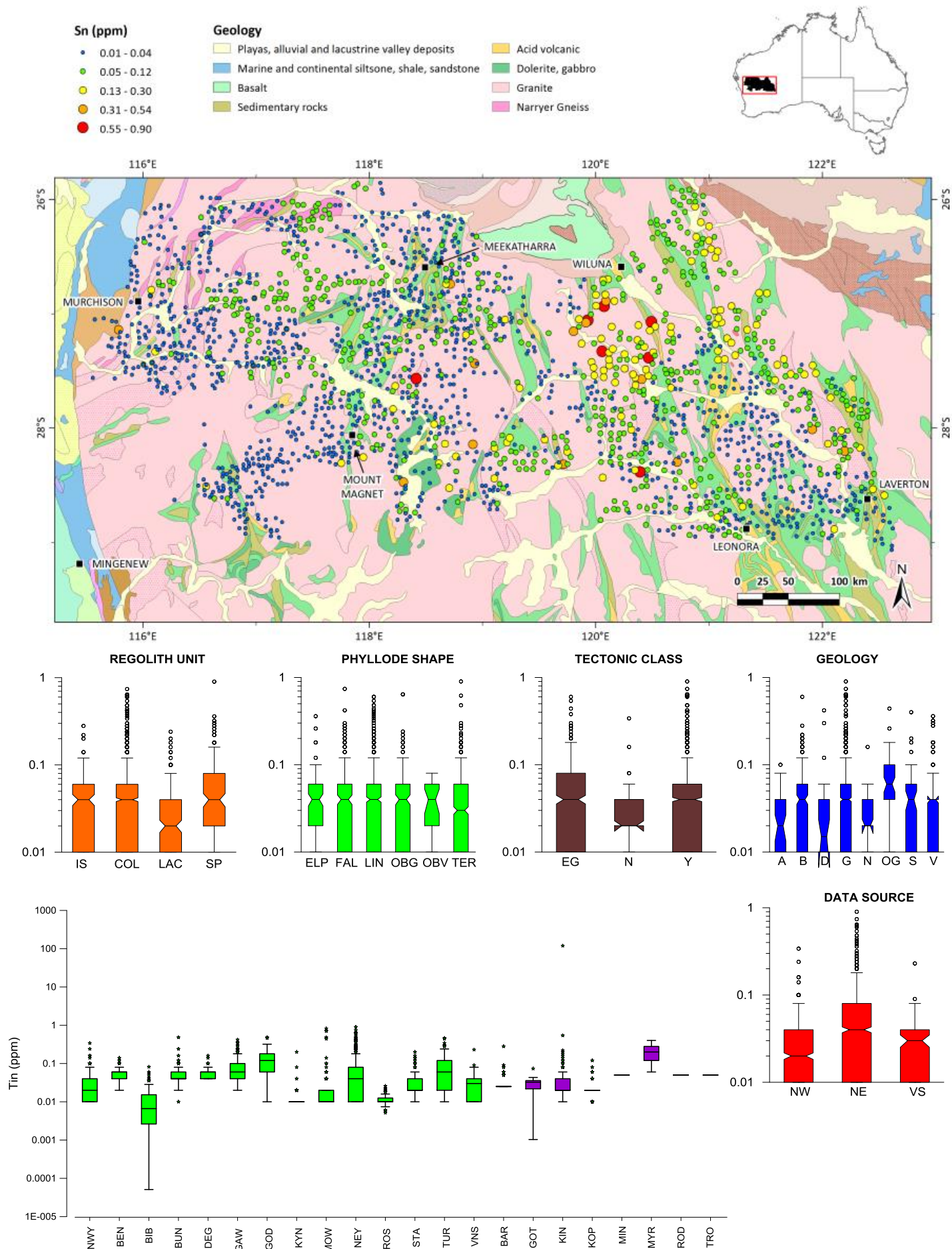
Se (ppm)



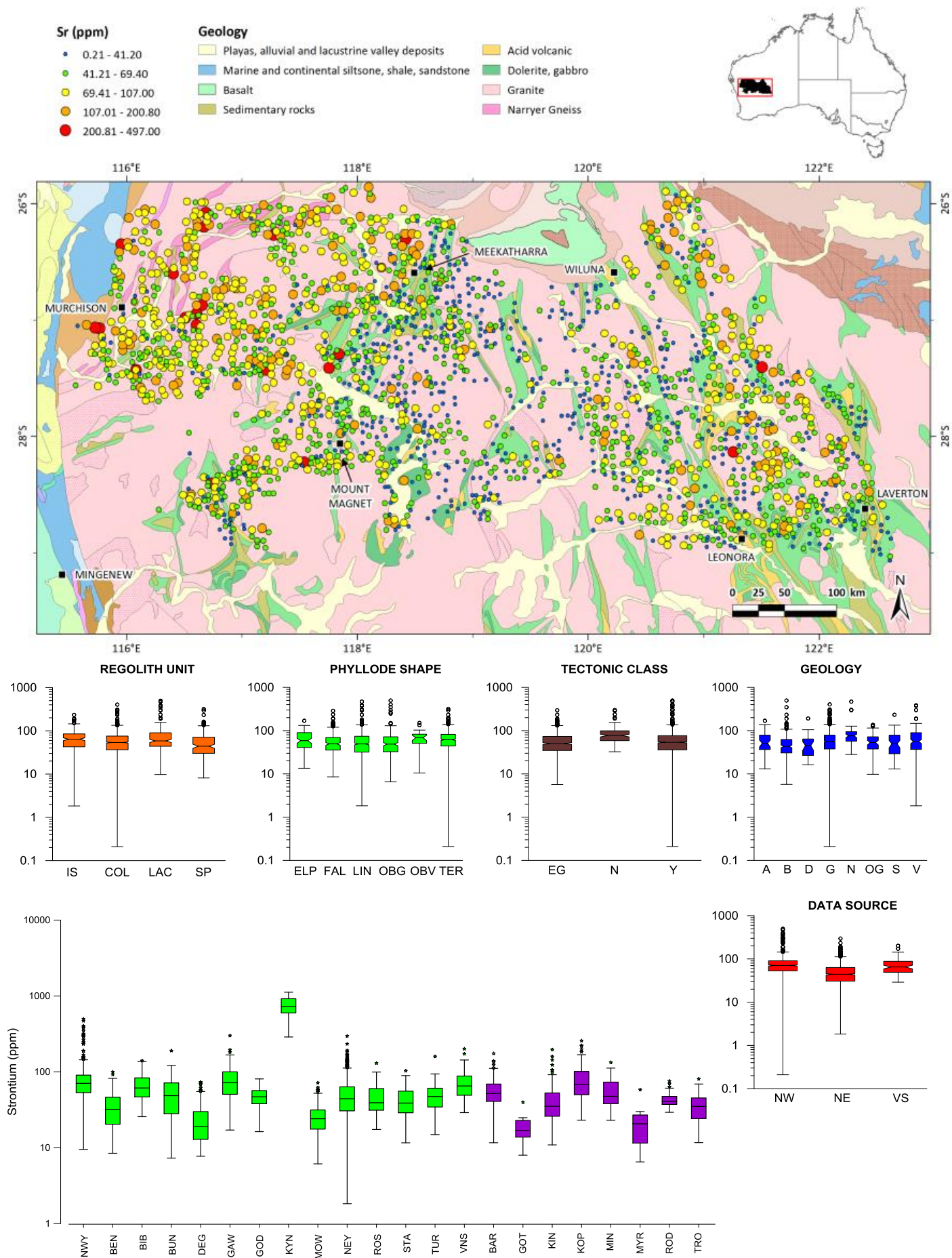
Si (ppm)



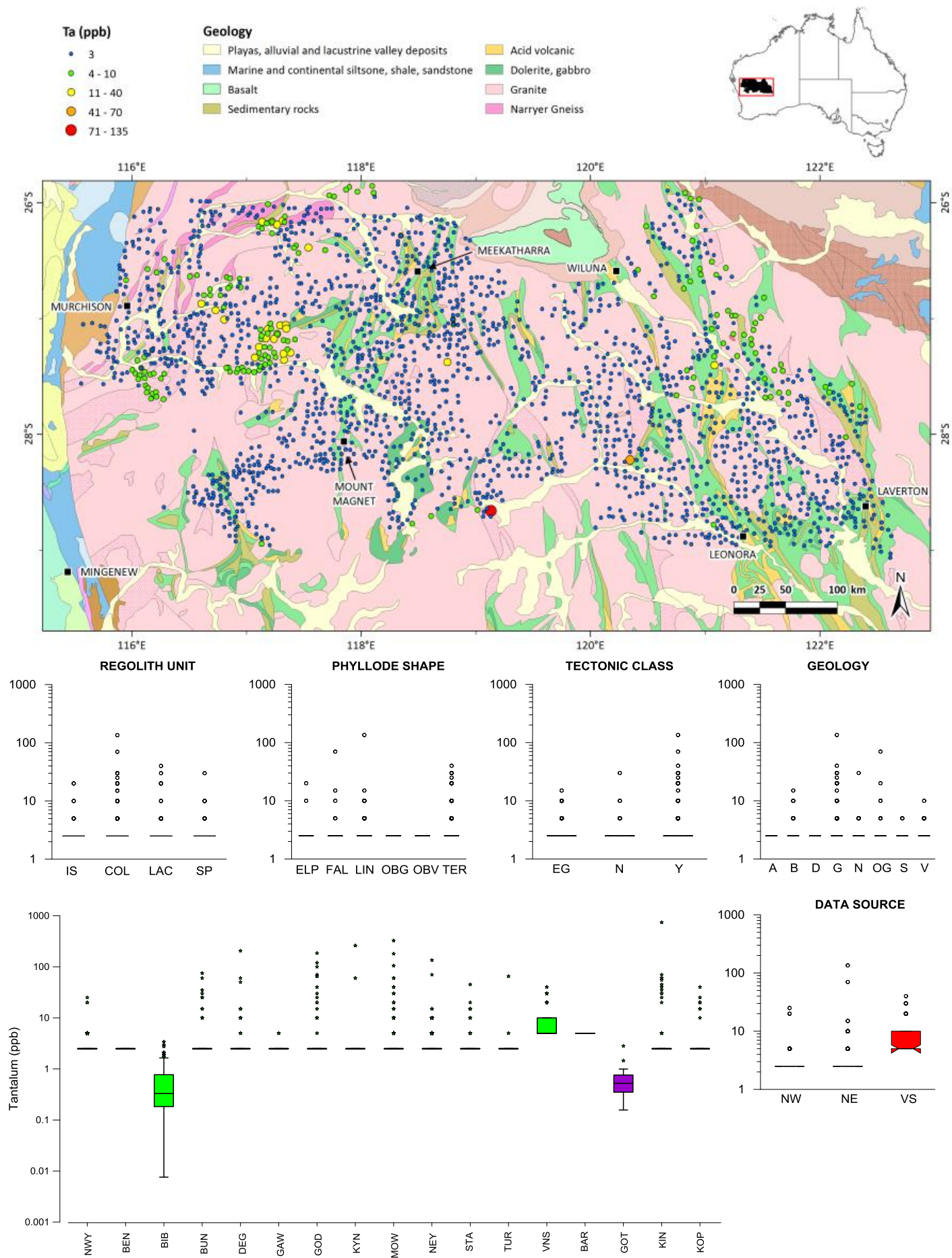
Sm (ppb)



Sn (ppm)

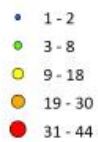


Sr (ppm)

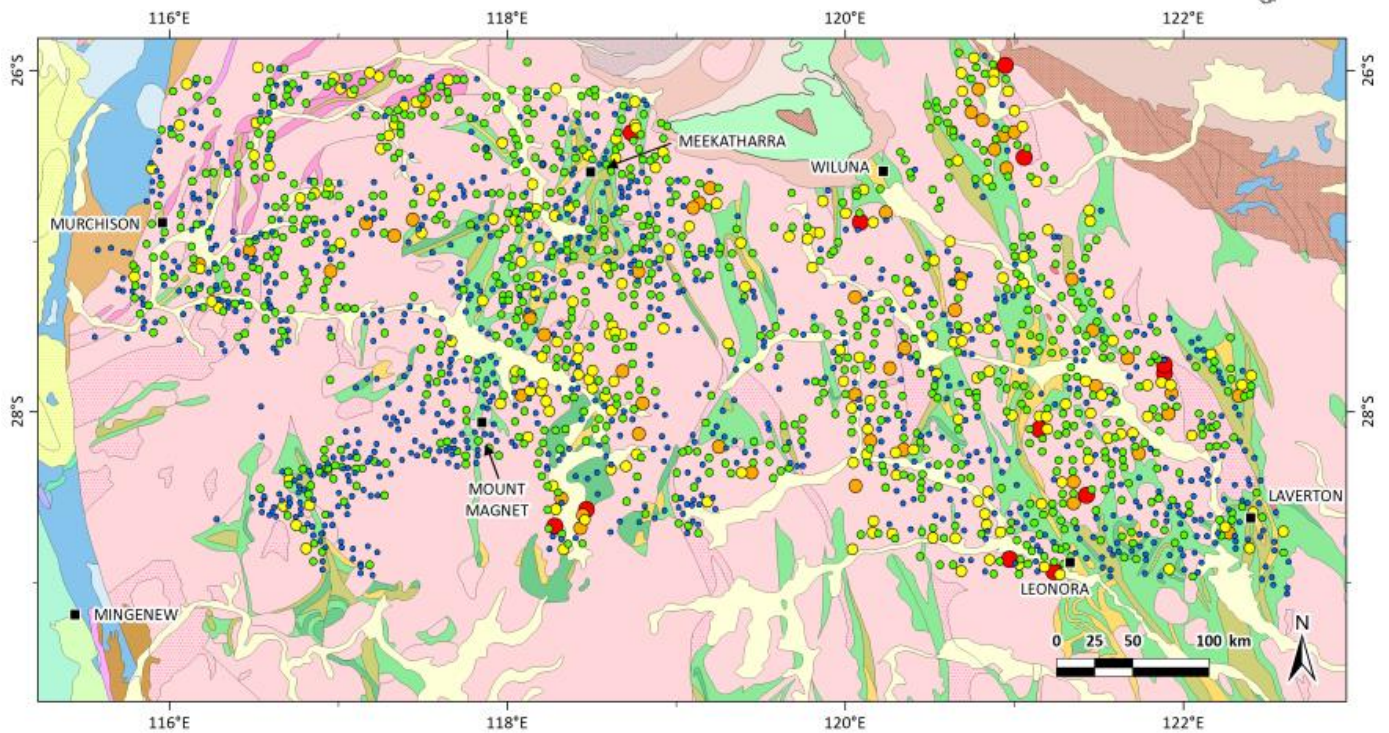
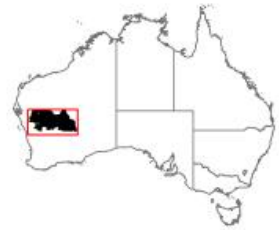
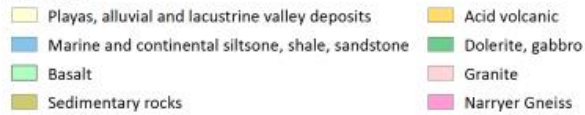


Ta (ppb)

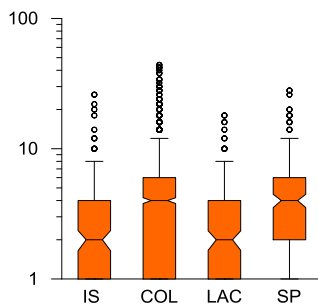
Tb (ppb)



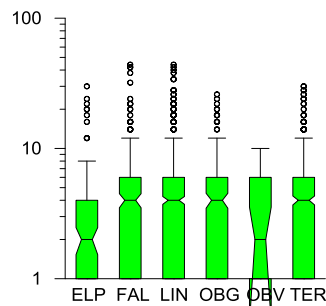
Geology



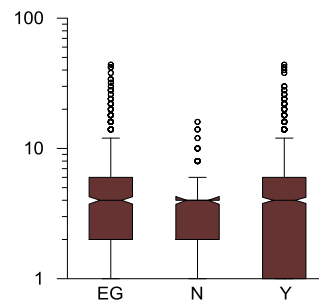
REGOLITH UNIT



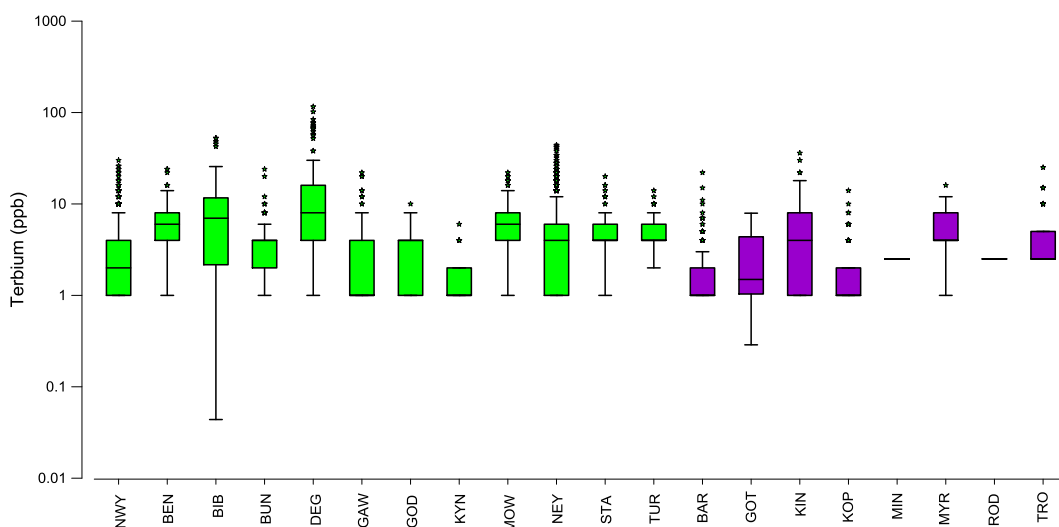
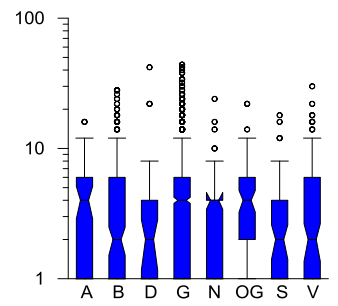
PHYLLITE SHAPE



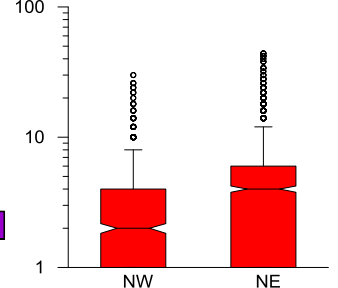
TECTONIC CLASS



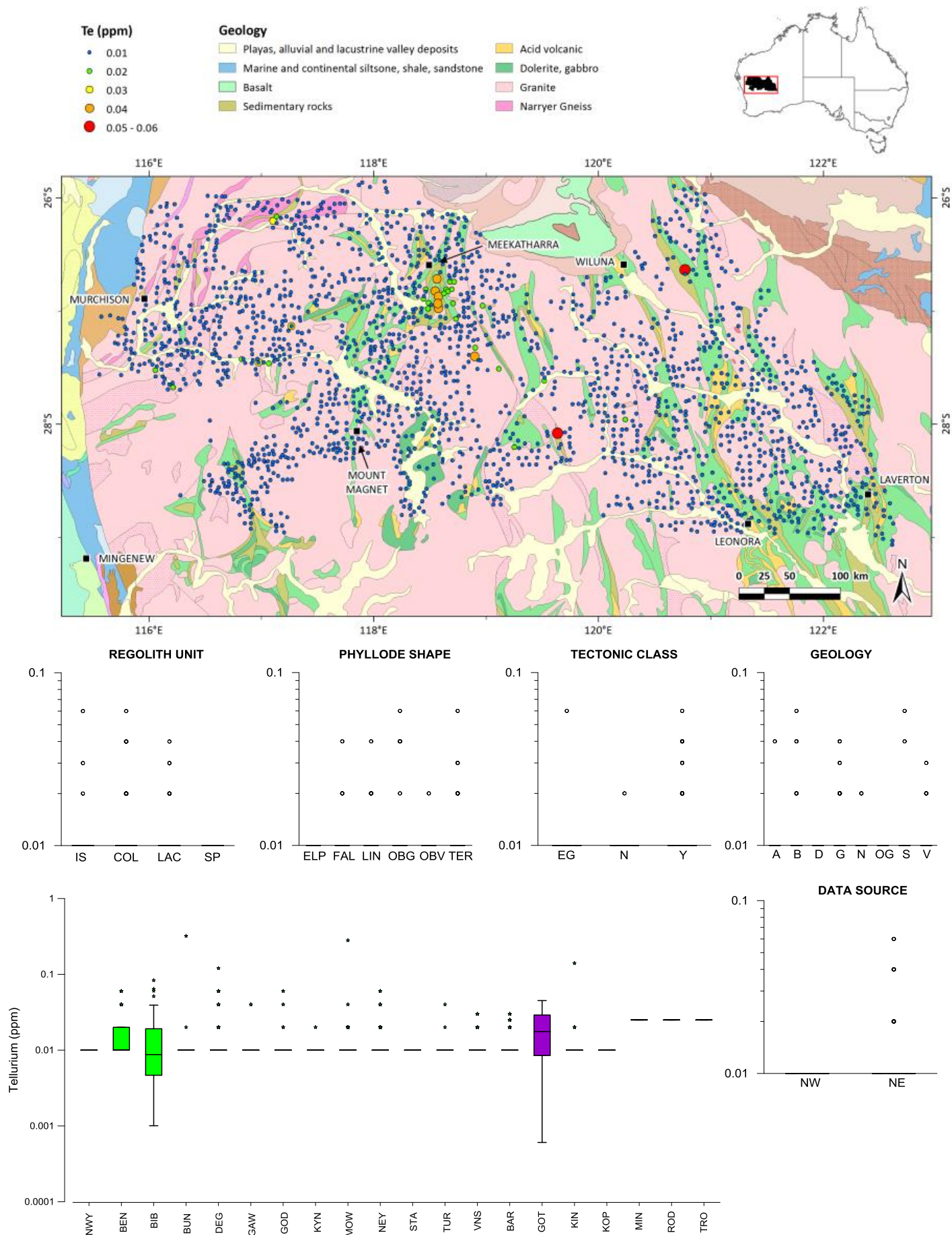
GEOLOGY



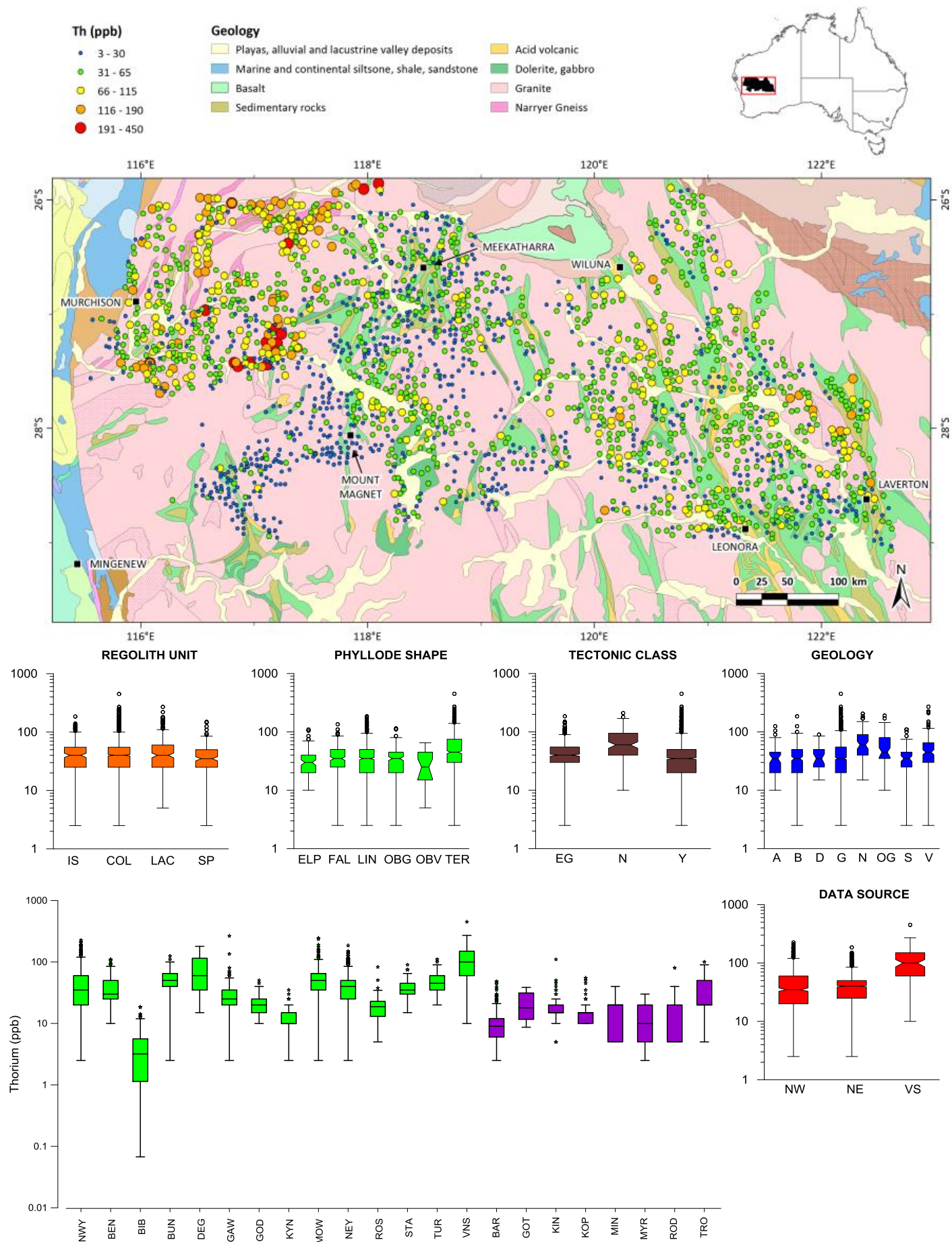
DATA SOURCE



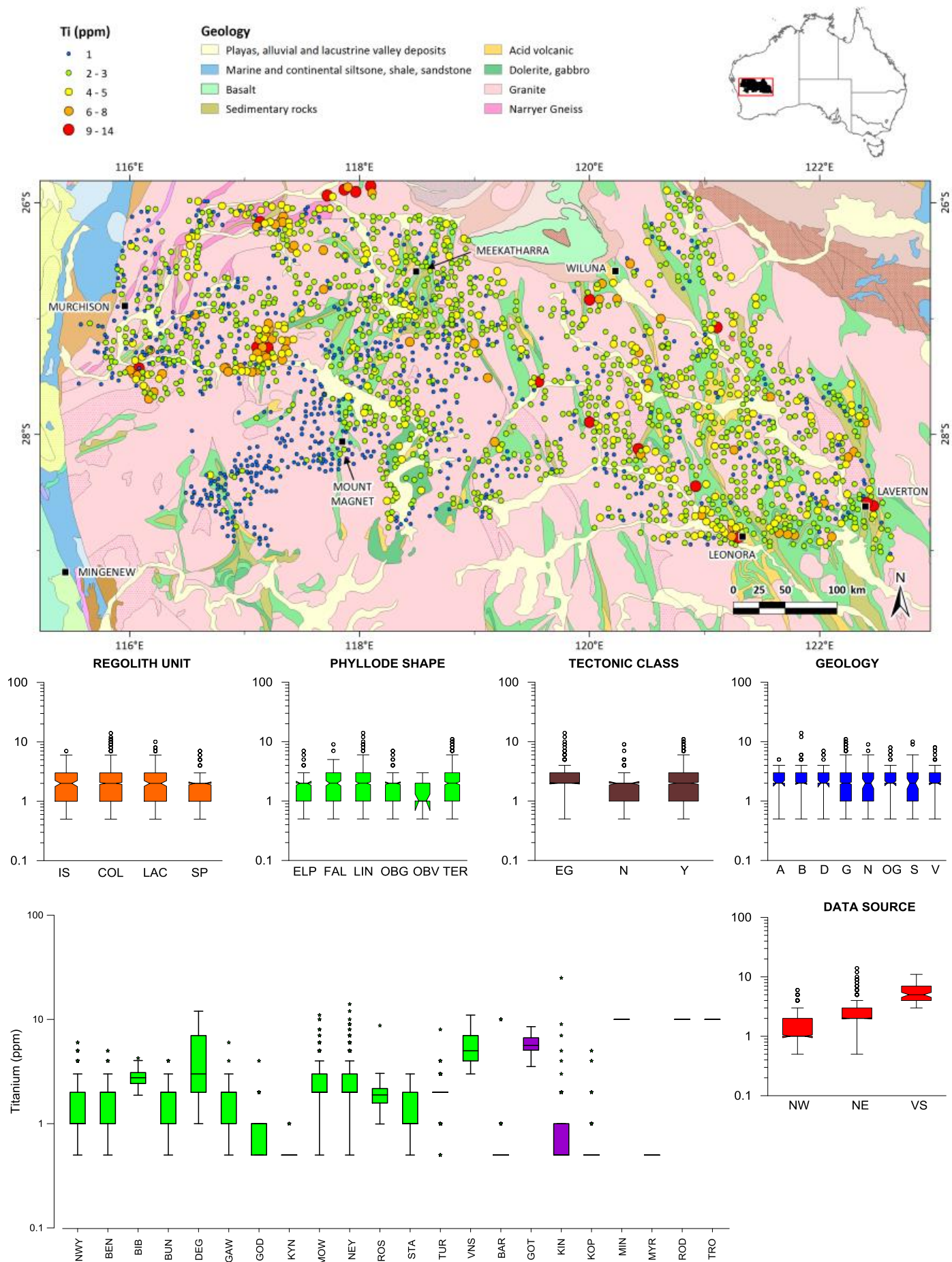
Tb (ppb)



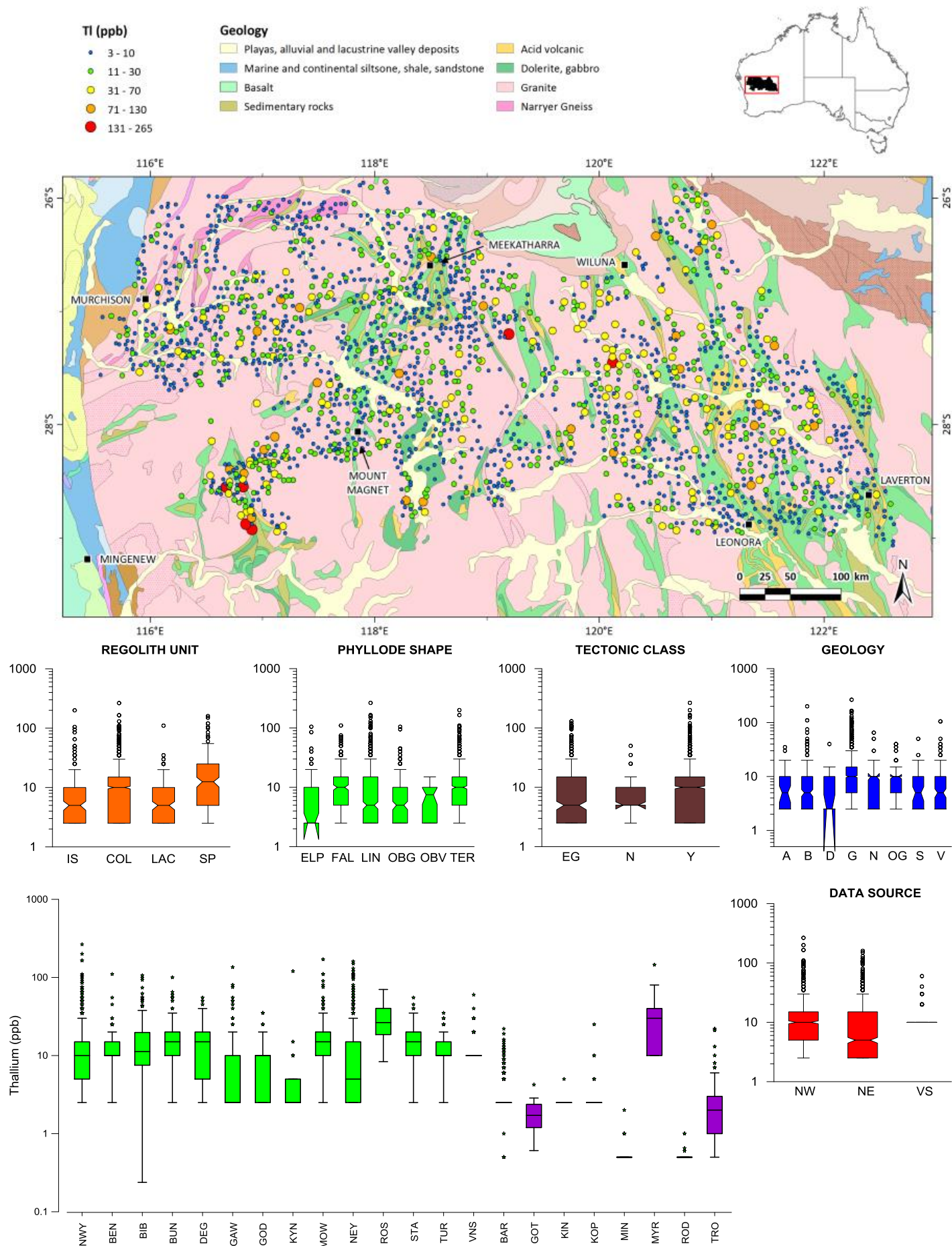
Te (ppm)



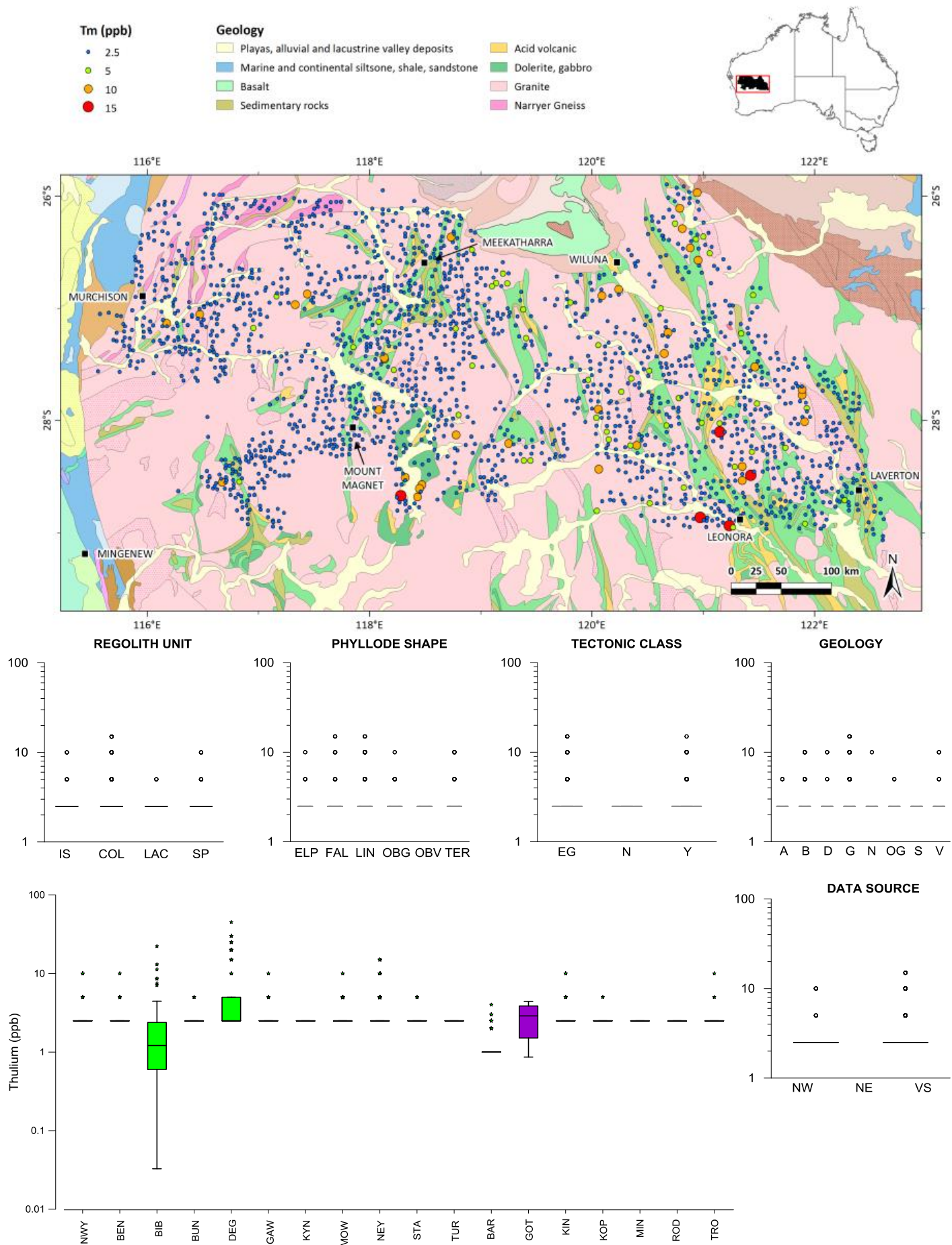
Th (ppb)



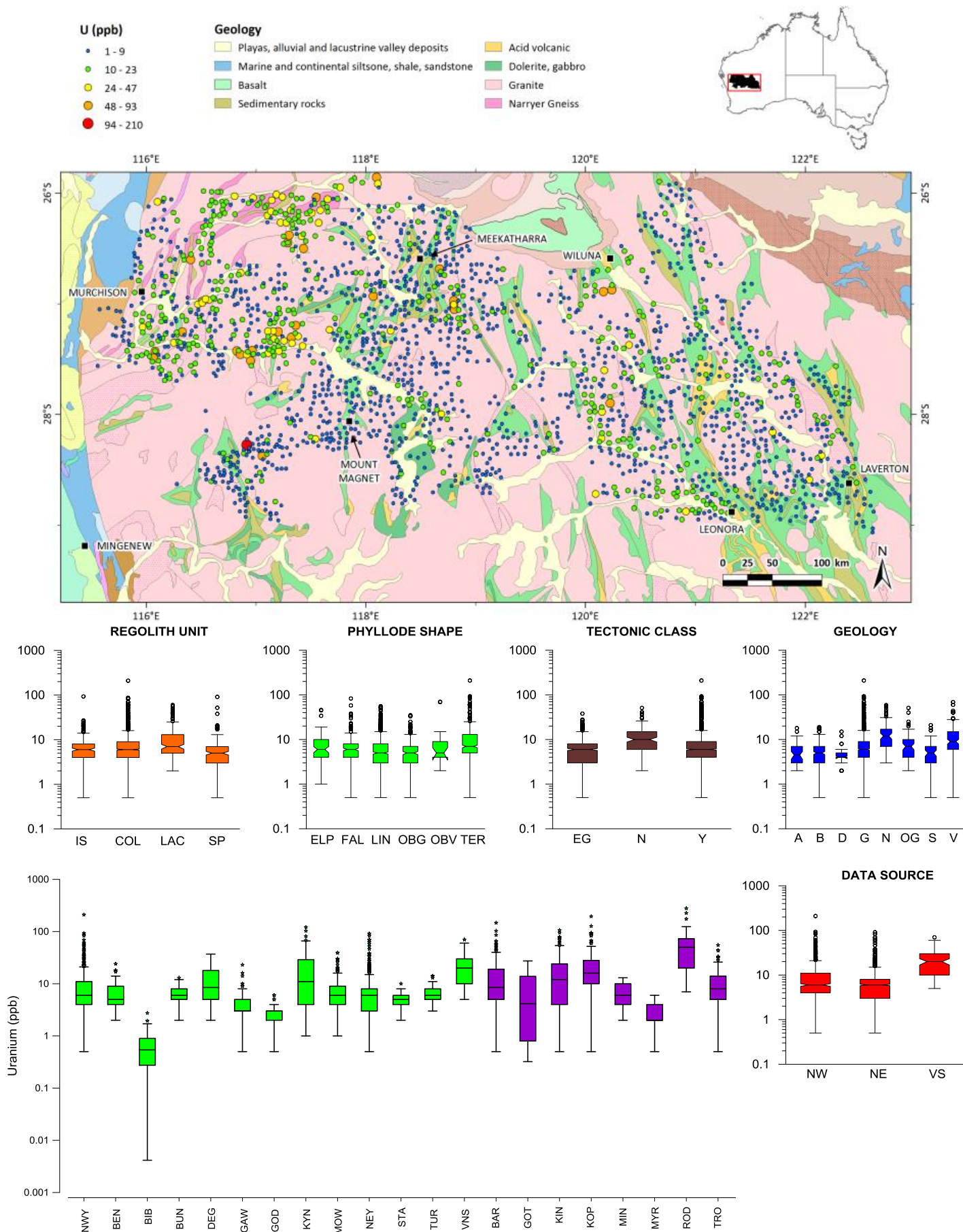
Ti (ppm)



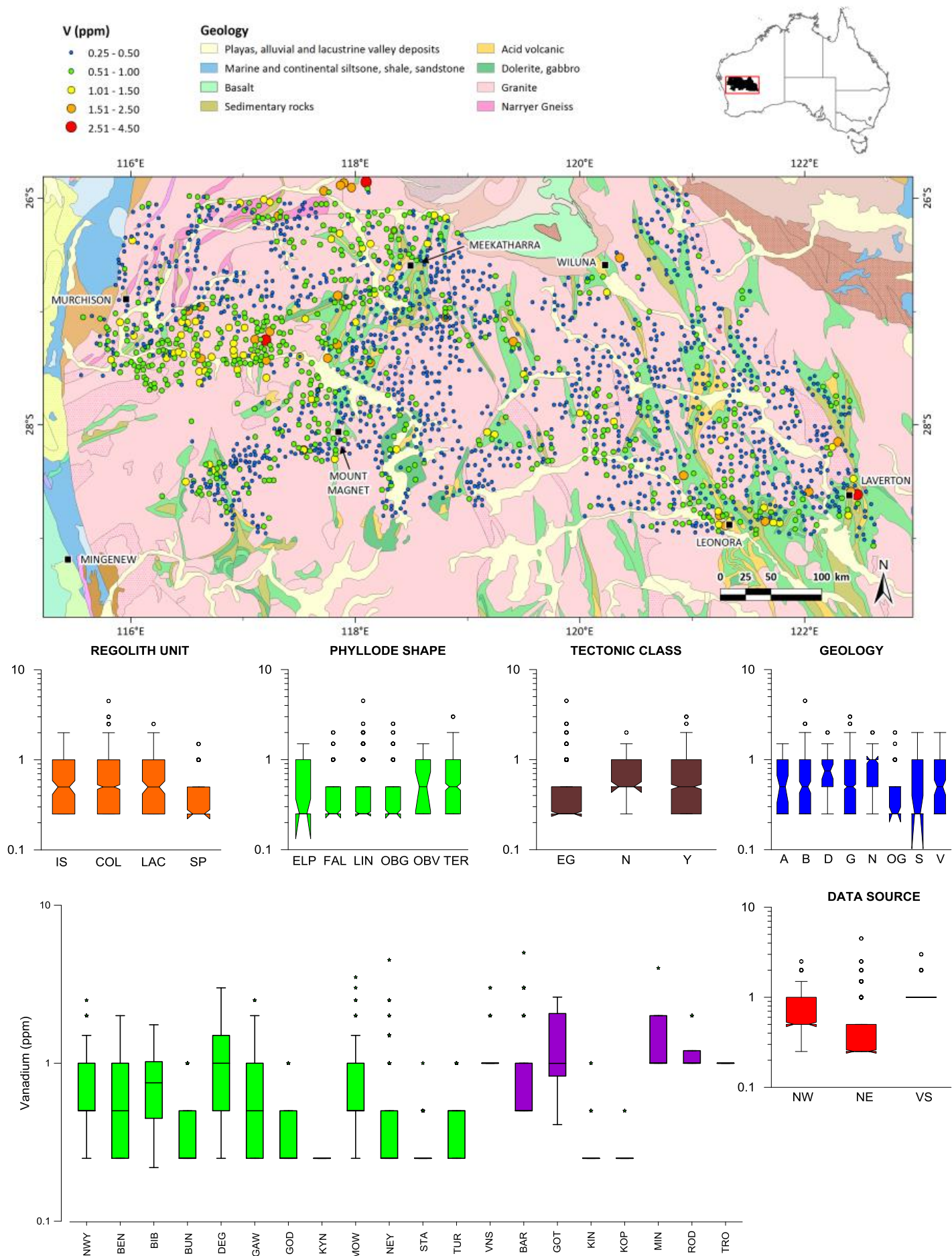
TI (ppb)



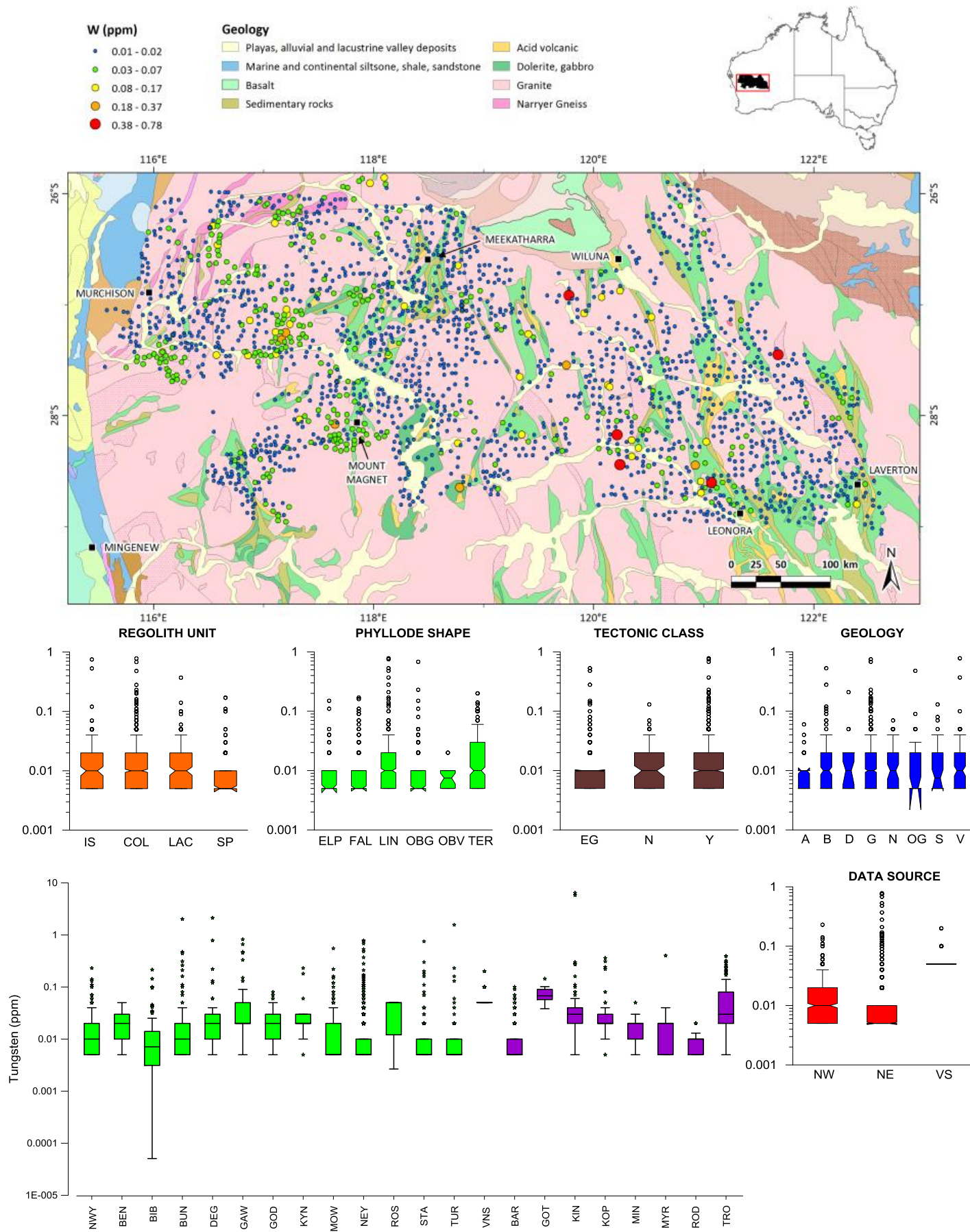
Tm (ppb)



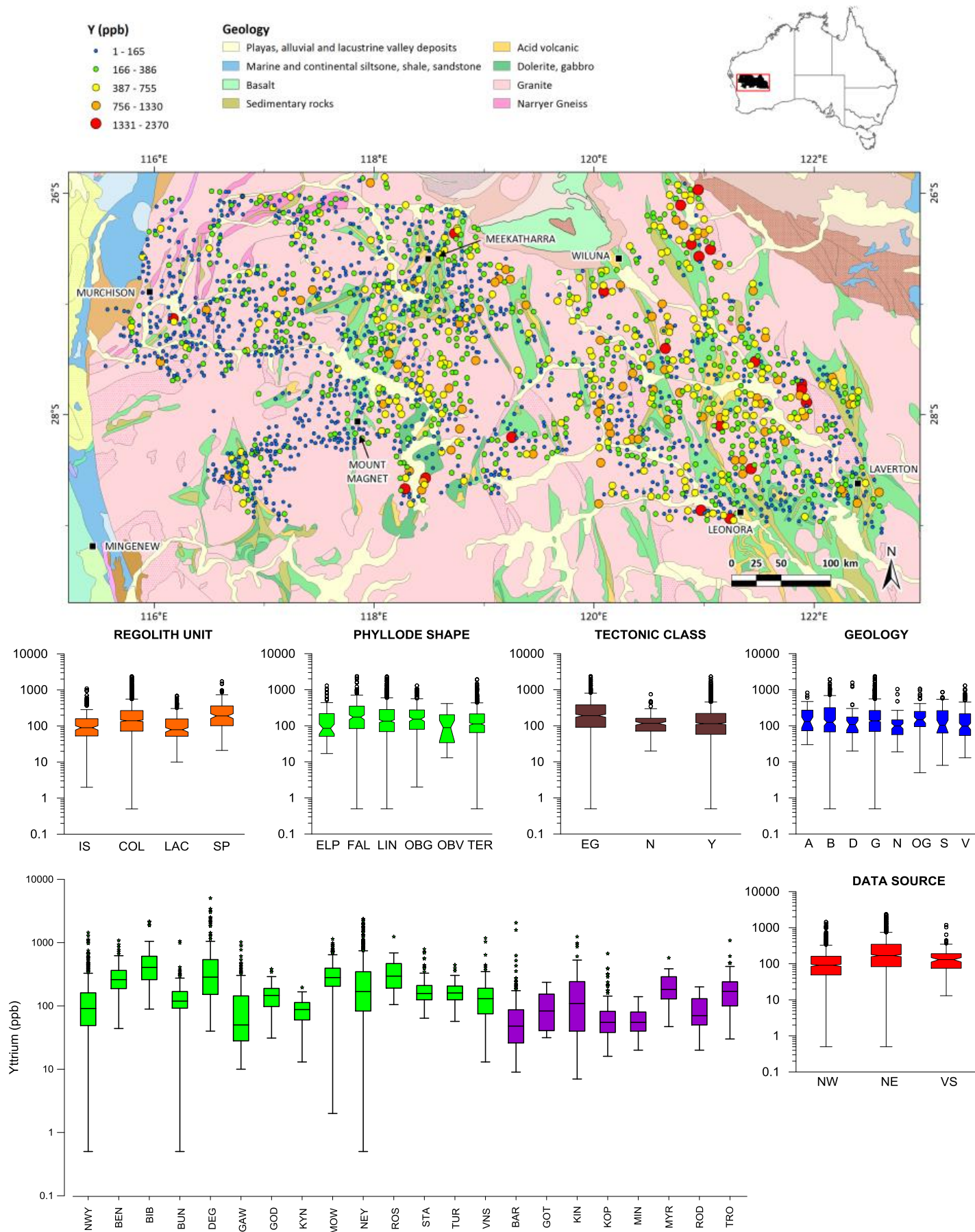
U (ppb)



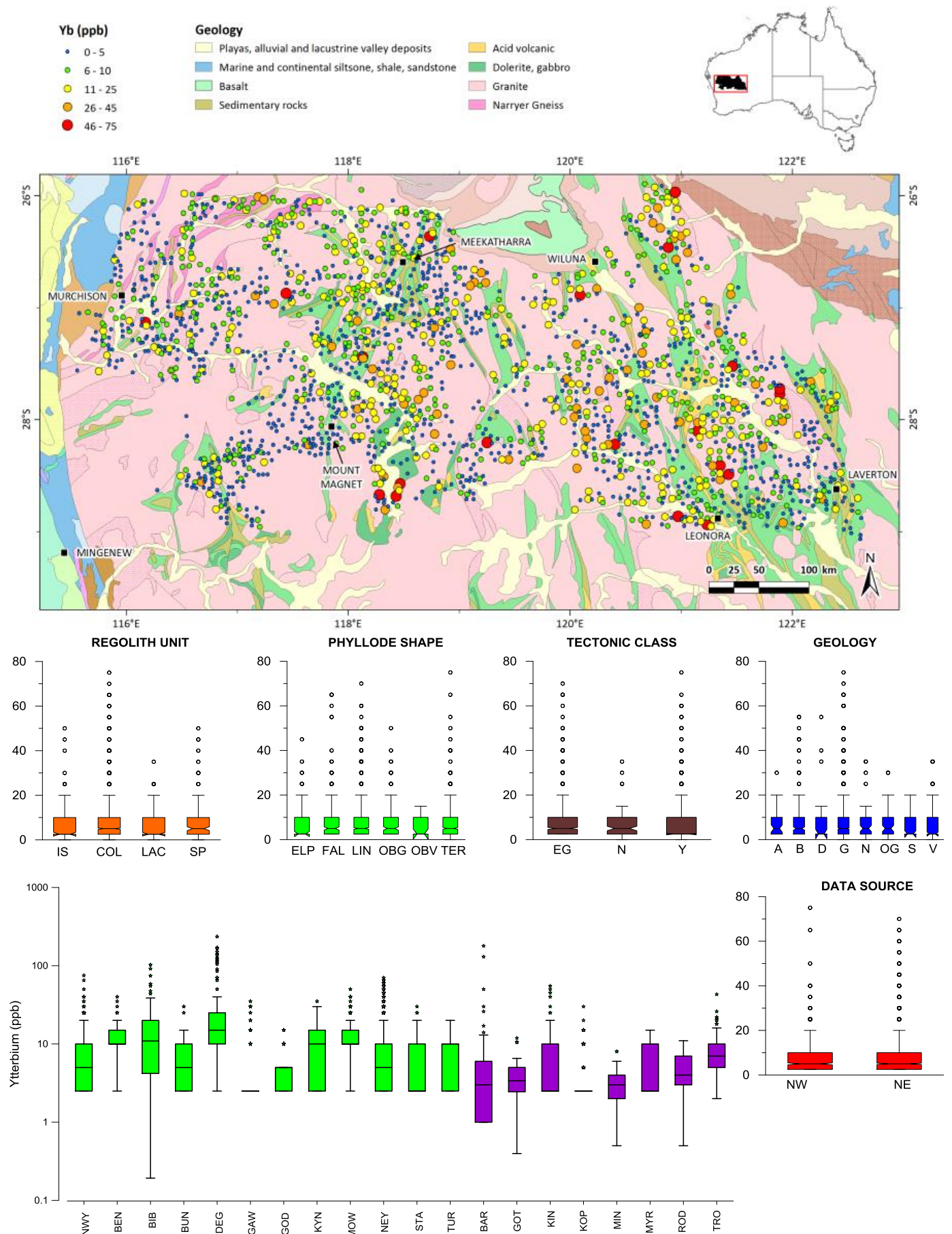
V (ppm)



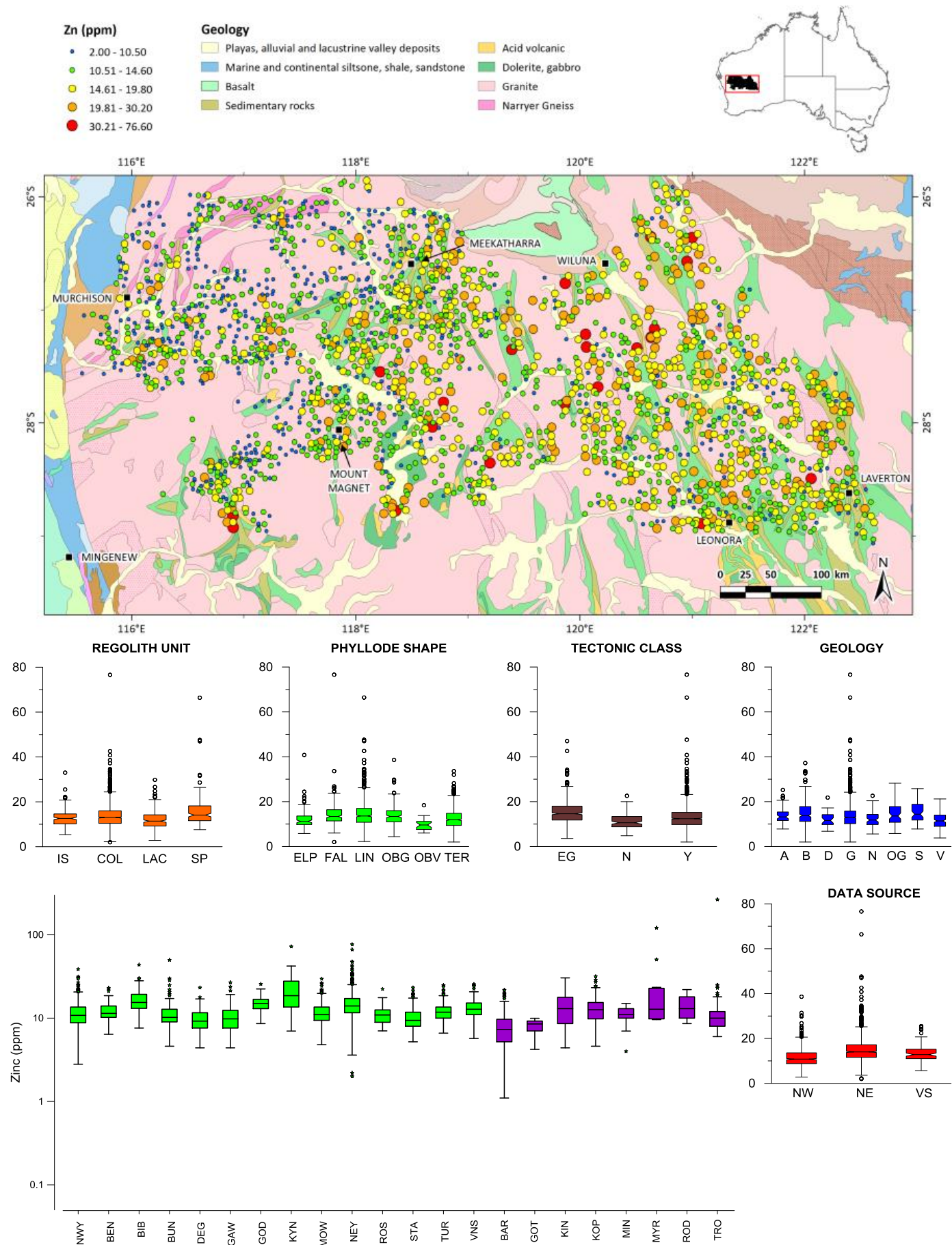
W (ppm)



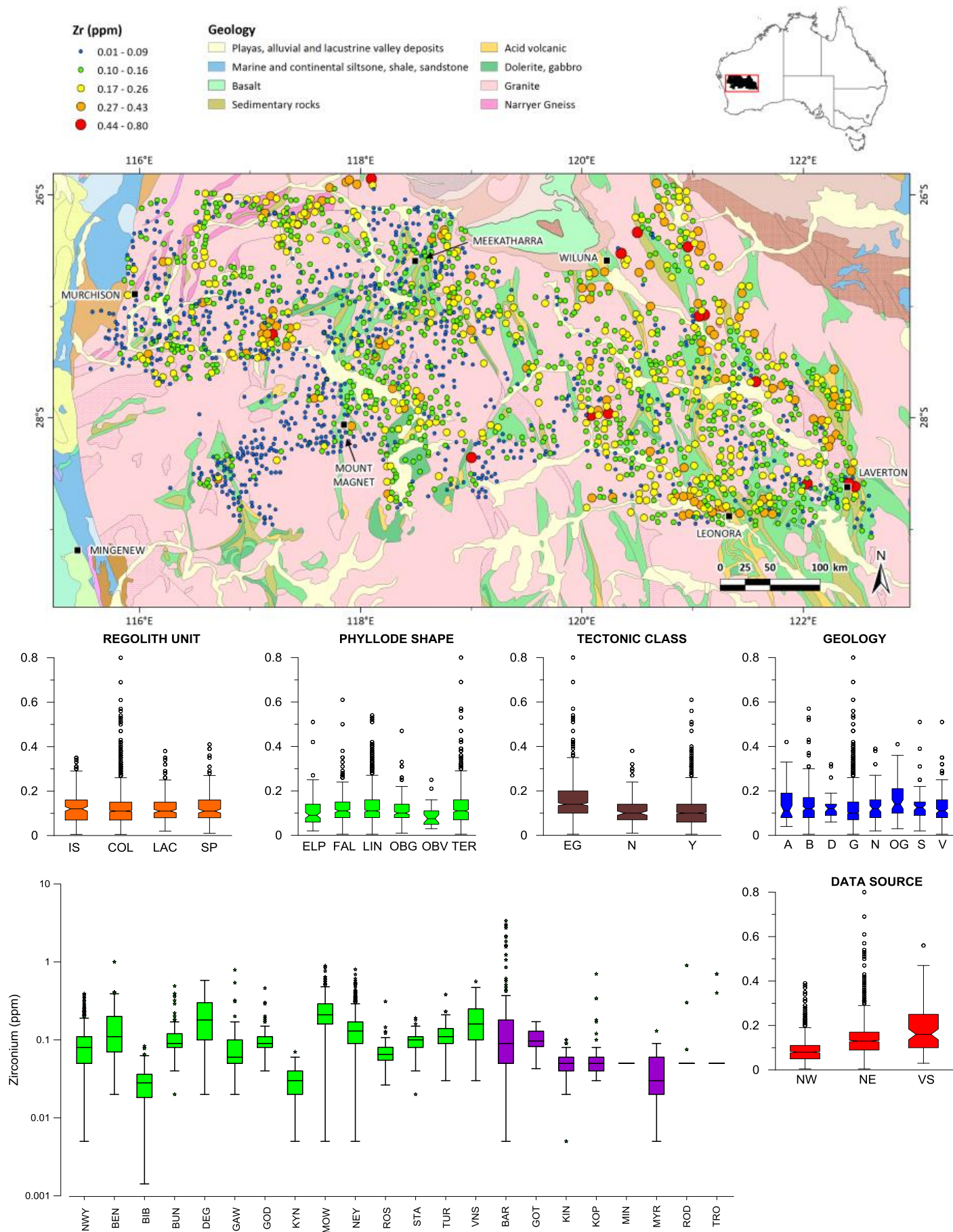
Y (ppb)



Yb (ppb)



Zn (ppm)



Zr (ppm)

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