Article

Multi-Media Geochemical Exploration in the Critical Zone: A Case Study over the Prairie and Wolf Zn–Pb Deposits, Capricorn Orogen, Western Australia

Anicia Henne *, Nathan Reid, Robert L. Thorne, Samuel C. Spinks, Tenten Pinchand and Alistair White

CSIRO Mineral Resources, ARRC Building, Kensington 6151, Australia; nathan.reid@csiro.au (N.R.); robert.thorne@csiro.au (R.L.T.); samuelcspinks@gmail.com (S.C.S.); tenten.pinchand@csiro.au (T.P.); alistairjrwhite@gmail.com (A.W.)

* Correspondence: anicia.henne@csiro.au

Abstract: In this study, we compared traditional lithochemical sample media (soil) with hydrochemical (groundwater), biogeochemical (plant matter of mulga and spinifex), and other near-surface sample media (ferro-manganese crust), in a case study applied to mineral exploration in weathered terrain, through the critical zone at the fault-hosted Prairie and Wolf Zn–Pb (Ag) deposits in Western Australia. We used multi-element geochemistry analyses to spatially identify geochemical anomalies in samples over known mineralization, and investigated metal dispersion processes. In all near-surface sample media, high concentrations of the metals of interest (Zn, Pb, Ag) coincided with samples proximal to the mineralization at depth. However, the lateral dispersion of these elements differed from regional (several km; groundwater) to local (several 100’s of meters; solid sample media) scales. Zinc in spinifex leaves over the Prairie and Wolf deposits exceeded the total concentrations in all other sample media, while the metal concentrations in mulga phyllodes were not as pronounced, except for Ag, which exceeded the concentrations in all other sample media. These observations indicate potential preferential metal-specific uptake by different media. Pathfinder elements in vegetation and groundwater samples also indicated the Prairie Downs fault zone at the regional (groundwater) and local (vegetation) scale, and are, therefore, potentially useful tools to trace fault systems that host structurally controlled, hydrothermal Zn–Pb mineralization.

Keywords: biogeochemistry; hydrochemistry; spinifex; mulga; groundwater; mineral exploration

1. Introduction

Much of the Australian continent is deeply weathered, and this can obscure surface signatures of mineralization at depth [1,2]. This provides a fundamental challenge for mineral explorers who target concealed mineral deposits under or within the critical zone. Therefore, a combination of geochemical avenues for vectoring towards these concealed mineral occurrences in weathered terrains is needed. The critical zone encompasses the materials from vegetation (top of canopy) down to (and including) the groundwater–bedrock interface [3,4]. Pathfinder elements associated with mineralization at depth undergo complex dispersion processes within the diverse materials of the critical zone, including and combining mechanical, hydromorphic and biological mechanisms that can mobilize (dilute and/or transport) and precipitate (enrich and/or relocate) metals [1]. Due to the complex nature of dispersion processes, different near-surface geochemical exploration media may be affected by some or all of these dispersion processes to varying degrees. Hence, different sample media may need to be utilized for different targets, depending on the prevailing dispersion processes, commodities, geological context, and the scale of the survey. Here, we present an interdisciplinary approach, comparing traditional lithochemical sample media (soil) with hydrochemical (groundwater), biogeochemical (plant matter), and other non-traditional sample media (i.e., ferro-manganese crust) (Figure 1b–e), in a case study applied to mineral exploration in weathered terrain through the critical zone.
In northern Western Australia identified a multi-element (Au, As, Zn) halo in the Coyote Prospect in
a case study applied to mineral exploration in weathered terrain through the Prairie and Wolf Zn (Pb–Ag) deposits (Figure 1a).

It is common practice in mineral exploration to utilize geochemical soil surveys to
narrow down mineral targets for drill hole planning. Over the past four decades, applied
research on exploration media has aimed to improve cost efficiency and limit environmental
impacts compared to traditional exploration drilling programs. Some of these exploration
media include biogeochemical substrates, such as plants [5–13], termites [14–17] and
microorganisms [18,19], groundwater [20,21], and other non-traditional surface media (e.g.,
iron–manganese crusts; [22]). Here, we present data obtained from vegetation growing
on residual cover, and compare these data to other near-surface geochemical exploration
media (soil, groundwater, and ferro-manganese crusts) obtained in previous studies over
the same area [22–24], and evaluate their utility in exploration activities in a case study
over the Prairie and Wolf Zn (Pb–Ag) deposits (Figure 1a).

Plants, similarly to all living organisms, require nutrients for growth and cell func-
tion (e.g., the metals Co, Fe, Mn, Cu, Mo, Ni, and Zn; [25]). Plants can access these
metals from their growth medium (soil) and directly from groundwater via deep tap
root systems [1] through homeostatic transportation [26]. Depending on environ-
mental factors, metal type, metal interactions within the plant [27] and plant species [28],
metals can accumulate in plant tissues [1] or at sorption barriers [29]. For some ele-
ments, a direct relationship between metal concentrations in plant organs and their.im-
mediate environment exist, especially for those metals that are potentially toxic (e.g.,
Ag, As, Cr, Ni, Pb, Sb, U; Butt et al., 2005). The use of plant-based biogeochemical ap-
proaches (also referred to as phyto-exploration) for mineral exploration has been reported
in Canada [9,30] and Russia [27,29,31,32], and several studies in Australia also indicate
promising results [5,10,11,33–35]. In arid parts of Australia, plants such as spinifex were
shown to be an effective biogeochemical exploration sample medium compared to soils
influenced by sheet flow and aeolian dispersion, which can result in dilution at or near the
surface of anomalous geochemical signatures at depth [10,11]. A successful case study at
the Coyote Prospect in northern Western Australia identified a multi-element (Au, As, Zn,
and S) halo in Triodia pungens over Au mineralization [10]. Smaller-scale studies on mulga
highlighted the potential for prospect-scale sampling at the Jaguar VHMS and the Moolart
Well Au Prospect [34], and the Big Bell, Harris Heights, Millawarrie and Blackmans Au
Prospects [36].

In addition to biogeochemical exploration tools, efficient techniques for hydrochem-
ical exploration have also been developed and tested in Australia [37–41] and delivered
valuable exploration geochemical data [20,21,42]. Groundwater geochemistry can pro-

---

**Figure 1.** Study area and sample material overview. (a) Location of study area in Western Australia. (b) Photograph of a *Triodia basedowii* (spinifex) plant. (c) Photograph of Fe–Mn crust. (d) Photograph of *Acacia aneura* (mulga) plant. (e) Photograph of a water bore.
vide chemical information about the lithology below and/or within the critical zone. As groundwater migrates through the subsurface, it interacts with (mineralized) rocks [42] and, therefore, captures a broader signature than other near-surface sample media. Groundwater chemistry can, therefore, be a useful tool to obtain compositional, as well as structure- (faults, shear zones) and process- (e.g., weathering of sulfides, hydrothermal alteration) related information, often associated with mineralization at depth [24]. This can be especially helpful in areas where thick transported cover obscures soil sample chemistry, e.g., at the polymetallic Abra deposit, where groundwater chemistry indicated anomalous Pb and W concentrations related to the deposit at depth [24].

This study is part of a series of research studies on the (bio)geochemistry of ore and related sampling materials relevant to exploration activities over the Prairie-Wolf study area [22,23,43]. In these studies, field observations and a variety of different sample media were collected over the Prairie Downs and Wolf deposits, as well as other associated prospects concealed by residual cover. In addition, samples from a regional, broad-scale study of groundwater across the Capricorn Orogen [24] coincided with the Prairie-Wolf study area. Since the collection of these data, the definition of parameters (e.g., the contamination factor), which lead to the exclusion of several data points from the original study, have been revised [44]. Here, we present data on vegetation sample media (spinifex and mulga), provide a more detailed analysis of the groundwater samples directly over the study area, and include groundwater data that were previously excluded from the regional study. In addition, we re-analyze the soil data previously reported by Spinks et al. (2017) [23] using statistical methods to identify outliers and define the most likely anomalies for Ag, Zn, and Pb in soil samples. The aim of this study was to investigate some of the major differences in the complex geochemical dispersion processes of metals through the critical zone and into different sample media, and compare the suitability of these different media as near-surface exploration tools.

**Study Area**

The Prairie Downs Zn–Pb (Ag) deposit is located in the northern margin of the Capricorn Orogen, approximately 60 km southwest of Newman, in northern Western Australia (Figure 1a), and comprises two main deposits, the Prairie Downs main zone and the Wolf Prospect, herein referred to as the Prairie-Wolf deposits (Figure 2a). These two deposits host shallow polymetallic hydrothermal Zn–Pb±Cu mineralization [22] and are located approximately 1000 m apart within the Prairie Downs Fault Zone. This complex, NW–SE trending fault system offsets clastic sediments of the Bresnahan and Edmund Groups [45,46] in the SW, against continental flood basalts of the Fortescue Group [47] in the NE (Figure 2a). The crustal scale fault zone is a long-lived system that has likely been active between 2.2 Ga [48] and 1.0 Ga [46]. The main mineralization within the Prairie-Wolf deposits is hosted by massive sulfides (galena, sphalerite, and chalcopyrite, with minor pyrite, and Zn-rich tetrahedrite; [22,43]), which occur mainly in massive quartz veins (Prairie Downs; [43]) and brecciated, hydrothermally altered mafic rocks (Wolf; [43]). The mineralized assemblage crops out at the surface of the fault zone as weathered sulfides, Cu-oxides, and fully weathered voids in quartz outcrop after sulfide [23].

The mafic rocks within the area underwent regional metasomatism, followed by a second, more localized, metasomatic event related to the fault-hosted mineralization, which subsequently led to Zn–Pb–Sn–Ag–K–Ba–Tl–Sb–Ge–U–Th–Cd–Hg–Se–REE enrichment [43,49]. Although the upper limit of the main mineralized zone is situated tens of meters below the current exposure, there are pronounced geochemical anomalies in the soils and ferro-manganese crusts across the fault zone, close to the main Prairie-Wolf deposits [22,23]. Thus, there is strong evidence for the dispersion of elements from the ore zone to the surface.
The two most prominent plant species within the Prairie-Wolf study area are hard spinifex (*Triodia basedowii*) (Figure 1b) and mulga (*Acacia aneura*) (Figure 1d). Both plants are native to arid regions of Australia. Hard spinifex (*Triodia basedowii*) is a densely tufted, perennial grass that grows up to 1.3 m tall, with woolly leaf sheaths and very hard, sharp leaves [50]. It is common on flat to gently sloping and undulating sandplains, dune fields, dune swales, and sandhills [51]. *Acacia aneura* (mulga) is a woody shrub or tree that grows up to 3.5 m or 15 m tall, respectively [50]. The species has bright yellow, oblong flowers and terete to elliptic phyllodes (=leaf stalks) [52] that are 2 to 11 cm long, and up to 1 cm wide. *Acacia aneura* is the dominant species of many shrublands and woodlands of inland Australia [53], with an irregular distribution across central and Southern Australia.

Figure 2. Sample locations (a) over the region and (b) over the Prairie Wolf deposits and associated prospects. T1 to T4 indicate sampling transects of mulga and spinifex plants. Please refer to the Supplementary Data for a lithological legend.
Groundwater across the Capricorn Orogen generally indicates fresh water (<3000 TDS) with a neutral pH and a shallow water table (<10 m) [24].

2. Methods and Materials

2.1. Plant Samples

A total of 37 spinifex (Triodia basedowii) and 32 mulga (Acacia aneura) samples were collected from four transects (T1 to T4, Figure 2b) traversing the fault zone that hosts the Prairie (T3; 12 spinifex and 8 mulga samples) and Wolf (T2; 9 spinifex and 8 mulga samples) deposits, and the Husky (T1; 11 spinifex and 10 mulga samples) and Anomaly B (T4; 5 spinifex and 6 mulga samples) prospects. In addition, 8 spinifex and 30 mulga samples were collected away from known mineralization (Figure 2a). Each spinifex sample consisted of approximately 300 g of leaf material collected from several plants of consistent age within a 2 m² area. Only plants in good health were sampled to avoid the likelihood of changes in chemical structures induced by insects, bacteria or fungi. Mulga samples consisted of terminal branchlets, which contain phyllodes (a leaf stalk with similar function to a leaf) and twigs in varying proportions. Due to heavy grazing and the varying state of the health of plants, only phyllodes were analyzed. Plants of spinifex and mulga growing in or near drill spoils and in, or close to, drainages were avoided, as plants growing in drainage channels often have higher elemental concentrations than those in adjacent settings [6,7]. To prevent sample contamination, watches, jewelry, and other metallic objects were removed during sampling and powder-free, nitrile gloves were used and changed between each sample. Samples were stored in breathable cloth bags for transport and during oven-drying at 45 °C for 48 h. Spinifex leaves and mulga phyllodes in our study were not washed prior to sample processing, as this has previously shown to dissolve metals from the plant organ (the leave/phyllode) and unwashed samples generally follow the same metal concentration trends as washed samples [34]. High concentrations of elements with relatively low uptake rates (e.g., high Fe, Zr, Th, Al, Ti, Cs and Hf; Supplementary Data, Table S1) in spinifex leaves along transects over the Prairie-Wolf study area are likely related to dust contamination caused by drilling activities and cattle movement. Contamination is a common side effect of plant sampling in exploration field settings, and anomalously high concentrations of these low-uptake elements do not correspond directly with the anomalous elements of interest (Pb, Zn and Ag). Therefore, contamination in our spinifex samples is deemed negligible. The contamination effect was not observed in mulga samples, likely due to the different phyllode morphology compared to the needle-like leaf blades of spinifex [54]. Spinifex plants have the ability to tightly roll leaves, which may trap dust particles. Dried leaves/phyllodes were powdered in a Retsch knife mill, GM300, manually homogenized and split in half. One half of the sample was sent for multi-element chemistry analyses, the other half was retained and stored as reference material.

Powdered plant samples underwent microwave-aided aqua regia digestion to extract metals and were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer Nexion 300Q at LabWest Mineral Analysis Pty Ltd. in Perth, Australia), for the following elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. Sample duplicates were analyzed every 30th sample for quality control. In addition, laboratory standards (cabbage leaf CRM, BCR61) were analyzed every 10 samples to determine analytical bias.

2.2. Groundwater

As part of a regional hydrochemistry study of the Capricorn Orogen in Western Australia, 1034 groundwater samples were collected by Thorne et al. (2018) [24]. A subset of 133 of these samples are presented here and interpreted on a deposit (Prairie-Wolf study area) rather than a regional (Capricorn Orogen) scale. In addition, here, we use the revised definition of the sample contamination factor (CF) [44], which enables the inclusion
of additional samples. The samples presented here include the immediate Prairie-Wolf sampling area (5 samples located along the fault trace above the Prairie and Wolf deposits) and a further 128 samples to define the regional context (Figure 2a,b). Groundwater samples were collected from pre-existing wells and bores ordinarily used for livestock and human consumption, as well as from exploration bore holes. Where possible, bailed samples were collected 5 m below the surface. The depth of the water table was recorded with a dip meter. Waters were analyzed for pH, temperature, conductivity (EC) and oxidation potential (Eh) at the time of sampling (see Thorne et al. (2018) [24] for details on calculations and quality assurance and quality control (QAQC)).

All water samples were collected in high-density polyethylene bottles. At each site, four samples were collected. Two samples were unfiltered and collected for HCO$_3^-$ titration (approximately 100 mL) and for low-level (ppt) Au, Ag, Pt and Pd analyses (approximately 1000 mL) using carbon sachets (comprised of 1 g of activated carbon in a nylon mesh) at CSIRO Laboratories in Kensington, WA, Australia. The carbon sachets were ashed, dissolved in aqua regia and analyzed via ICP-MS at Bureau Veritas Minerals in Cannington, WA, Australia (refer to Thorne et al. (2018) [24] for detailed methods).

In addition, approximately 100 mL of water was collected for anion analysis and another 100 mL was collected for ICP-OES and ICP-MS analysis. These two samples were filtered through nitrocellulose filter papers that had 0.45 µm pore sizes. Major anions (Cl, SO$_4^{2-}$, Br, F and NO$_3^-$) were analyzed by ion chromatography using a Dionex ICS-2500 at CSIRO Laboratories Waite, SA, Australia. A sample split was also analyzed for total N, dissolved organic carbon (DOC) and PO$_4^{3-}$. Major and trace elements were analyzed by ICP-OES (Al, B, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr and Zn) and ICP-MS (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Th, U, V, W, Y, Yb, Zn and Zr) at CSIRO Waite Laboratory, SA, Australia (see Thorne et al. (2018) [24] for detailed methodology, detection limits and QAQC). Data presented in this study were interrogated in ioGAS (version 7.2) and all values below detection limits were replaced with half the detection limit value. These values were used for interrogation (variability maps, probability plots, correlation matrices and statistical summaries) and are displayed in all tables, maps, box and scatter plots herein.

2.3. Soil, Ore and Ferro-Manganese Crust Samples

As part of previous studies, 6 ore [22], 878 soil [23] and 73 ferro-manganese crust [23] samples were collected across the Prairie-Wolf fault zone. We use some of this data here for context and comparison to plant and groundwater data (Figure 2a,b). The main mineral phases in ore (galena, sphalerite and chalcopyrite, with minor pyrite, and Zn-rich tetrahedrite) were determined by microprobe analyses on polished thin sections. Soil samples underwent multielement chemistry at ALS Minerals, Perth, Australia and ferro-manganese crust samples underwent selective chemical dissolution followed by ICP-MS at LabWest Mineral Analyses Pty Ltd., Perth, Australia. Please refer to [23], and [22] for detailed methods and QA/QC.

2.4. Data Processing

Soil, groundwater and vegetation data presented in this study were interrogated in ioGAS (version 7.2) and all values below detection limits were replaced with half the detection limit value. Analytes from soil surveys were then log-transformed and Z-score normalized using the z-log score transformation function in ioGAS. Variability maps and probability plots for soil data were generated on the normalized data to identify outliers and define most likely anomalies for Ag, Zn and Pb in soil samples. These transformed data are displayed in figures where indicated. Box plots, correlation matrices and statistical summaries (vegetation and groundwater data) were also generated in ioGAS. Due to the variability in Fe–Mn crust samples, a direct relative comparison of metal concentrations among each sample was not possible ([23] and metals displayed in maps in this study have been normalized to Mn (metal/Mn) and thus are expressed as ratios where indicated.
3. Results

3.1. Plant Samples

Spinifex samples along the Wolf and Prairie transects (T2 and T3, respectively) (Figure 3) were markedly enriched in a range of elements, including Zn, Pb, Ag, Au, Bi, Cs, Ga, Li, Na, Nb, Sb, Te, Th, Ti, Zn, V, and Fe, compared to those collected away from known mineralization (Supplementary Data, Table S1), and none of these elements were anomalously high in transects 1 (Husky) and 4 (Anomaly B) (Supplementary Data). However, the elements Cr (up to 7.92 ppb) and Re (up to 1.25 ppb) were elevated along transect 1 (Husky) compared to all other samples (Supplementary Data). The highest values for Zn and Pb along transects 2 and 3 correlated with the location of the Prairie and Wolf deposits at depth, as defined by drilling activities (Figure 3a,e). However, the highest Ag concentrations were measured in spinifex leaves from plants located just to the NE of the deposits (up to ~250 m; Figure 3c). The median Zn concentrations over the Prairie and Wolf transects were 44.5 ppm, with the highest Zn concentration (295.7 ppm) almost three times higher than the highest Zn concentration (106.5 ppm) in the remaining spinifex samples (median of 25.4 ppm; Supplementary Data). Lead concentrations reached up to 3777.0 ppb along the Prairie and Wolf transects, with a median concentration of 104.0 ppb. Lead concentrations within the remaining dataset had a median of 32.0 ppb, with a maximum of 136.0 ppb. The distribution of Zn positively correlates with Pb and Cd concentrations in our Prairie-Wolf dataset (R = 0.82). However, Ag did not correlate with any other element. Around the Prairie-Wolf deposits, spinifex leaf samples also showed anomalous concentrations in various ore- and fault- (fluid pathway) related elements (e.g., K, Na, Ba; Supplementary Data, Table S1).

Zinc concentrations in mulga phyllodes do not show appreciably anomalous concentrations along either the Prairie (T3) or the Wolf (T2) transects, with median concentrations of 16.8 ppm Zn compared to 12.2 ppm Zn (Supplementary Data), and no spatial distribution pattern, indicative of the mineralization at depth, was observed (Figure 4a). Indeed, the highest Zn values (up to 40.2 ppm; Supplementary Data, Table S2) in mulga phyllodes were recorded over the Husky transect (T1; Figure 5a). Along the Prairie and Wolf transects, mulga phyllodes were enriched in Ag (up to 6.2 ppb; Figure 4c), Pb (mean of 96.6 versus 54.2 ppb; Figure 4d; Supplementary Data), and, to a lesser degree, in Pt, Ba, Au, Bi, and Cs compared to the surrounding data (Supplementary Data; Table S2). The highest Pb value (456.0 ppb) along the Prairie and Wolf transects was almost three times that of the highest background value (158.0 ppb). No correlation was observed between Zn or Pb and other elements within the dataset. Silver showed a weak correlation with Cu (R = 0.5).

3.2. Groundwater Samples

Water table measurements along the fault line ranged from 14.4 m to 32.2 m compared to a regional average of 10.6 m, while pH measurements did not record an appreciable difference (median pH of 7.2 along the fault line versus pH 7.4 in the region; Supplementary Data). Relative to the regional data (Figure 5a), the groundwater sampled along the fault line over the Prairie-Wolf deposits is markedly enriched in a range of relevant elements, including Pb, Ag, Sn, K, Ba, Sb, Ge, Cd, Se, Ca, Mg, Li, Co, Cr, Ni, the platinum group metals Pt and Pd, and the REE Y, La, Ce, Pr, and Nd (Supplementary Data). Indeed, the Pb concentration in sample GW129 (82.2 ppb) is more than 16 times higher than the highest value within the region (3.5 ppb; Figure 5a,b). The same groundwater sample also shows some of the highest values within the region of Co, Ni, As, Cr, some REE, and the only detectable Th within the region (Supplementary Data). Silver concentrations along the Prairie Downs fault zone range from 6 to 4946 ppt, compared to a regional median of 16.0 ppt, and a highest background concentration of 571 ppt (Supplementary Data). While Pb and Ag are markedly enriched within the fault line samples, Zn concentrations over the Prairie-Wolf deposits range from 16.3 ppb to 89.0 ppb, compared to a regional median value of 22.9 ppb and maximum of 553 ppb Zn. Similarly, other elements, known to be enriched in locally metasomatized rocks [43,49], are not reflected in groundwater. This includes U,
which shows a distinct elevation in groundwater samples in granitic lithologies, rather than along the fault zone (map not shown). Silver in groundwater samples is strongly correlated with W (R = 0.94) and, to a lesser extent, with Sb (R = 0.83). Zinc is weakly correlated with the REEs Ce (R = 0.55) and La (R = 0.56).

Figure 3. Metal concentrations in spinifex leaves along transects T2 (Wolf deposit) and T3 (Prairie deposit) and box plots of metal concentrations in spinifex leaves within the study area (grey boxes, n = 24) versus those along transects T2 and T3 (orange boxes, n = 21). (a) Spatial distribution of Zn concentrations in spinifex leaves along the Wolf and Prairie transects. (b) Box plot of Zn (ppm) in spinifex leaves. (c) Spatial distribution of Ag (ppb) concentrations in spinifex leaves along the Wolf and Prairie transects. (d) Box plot of Ag in spinifex leaves. (e) Spatial distribution of Pb (ppb) concentrations in spinifex leaves along the Wolf and Prairie transects. (f) Box plot of Pb in spinifex leaves. Triangles in box plots indicate far outliers.
3.2. Groundwater Samples

Water table measurements along the fault line ranged from 14.4 m to 32.2 m compared to a regional average of 10.6 m, while pH measurements did not record an appreciable difference (median pH of 7.2 along the fault line versus pH 7.4 in the region; Supplementary Data). Relative to the regional data (Figure 5a), the groundwater sampled along the fault line over the Prairie-Wolf deposits is markedly enriched in a range of relevant elements, including Pb, Ag, Sn, K, Ba, Sb, Ge, Cd, Se, Ca, Mg, Li, Co, Cr, Ni, the platinum group metals Pt and Pd, and the REE Y, La, Ce, Pr, and Nd (Supplementary Data). Indeed, the Pb concentration in sample GW129 (82.2 ppb) is more than 16 times higher than the highest value within the region (3.5 ppb; Figure 5a,b). The same groundwater sample also shows some of the highest values within the region of Co, Ni, As, Cr, some REE, and the only detectable Th within the region (Supplementary Data). Silver concentrations along the Prairie Downs fault zone range from 6 to 4946 ppt, compared to a regional median of 16.0 ppt, and a highest background concentration of 571 ppt (Supplementary Data). While Pb and Ag are markedly enriched within the fault line samples, Zn concentrations over the Prairie-Wolf deposits range from 16.3 ppb to 89.0 ppb, compared to a regional median value of 22.9 ppb and maximum of 553 ppb Zn. Similarly, other elements, known to be enriched in locally metasomatized rocks [43,49], are not reflected in

3.3. Soil and Ferro-Manganese Crust Samples

While the highest measured concentrations of Zn (7900 ppb) and Pb (5400 ppb) in soil samples were not recorded over the Prairie and Wolf deposits, the median concentrations for Zn, Pb, and Ag did show distinct elevation above the deposits, with more than three times the amount of Zn (620 ppb versus 170 ppb) and more than double the amount of Pb (69 ppb versus 25 ppb) and Ag (7.8 versus 2.9 ppb) (Supplementary Data). Herein, this soil data were log-transformed and z-score normalized to minimize false positive values and identify high anomalous outliers within the datasets, based on probability plots (Figure 6a−c). Very strongly anomalous Zn values coincide with both the Prairie and Wolf deposits at depth (Figure 6a). However, other isolated anomalous Zn values were also observed. Several outliers of Pb coincide with the Prairie and Wolf deposit locations, and further isolated outliers were observed along the fault line, as well as an anomalous cluster located over and near the Husky Prospect (Figure 6b). Anomalous Ag values cluster over the Prairie and Wolf deposits at depth, with only three other isolated anomalous values in the surrounding area (Figure 6c).
groundwater. This includes U, which shows a distinct elevation in groundwater samples in granitic lithologies, rather than along the fault zone (map not shown). Silver in groundwater samples is strongly correlated with W ($R^2 = 0.94$) and, to a lesser extent, with Sb ($R^2 = 0.83$). Zinc is weakly correlated with the REE Ce ($R^2 = 0.55$) and La ($R^2 = 0.56$).

Figure 5. Groundwater samples within the study area. (a) Lead concentrations in groundwater samples. (b) Logarithmic scale box plot (ioGAS version 7.2) of Pb in regional groundwater samples ($n = 132$). Triangles in box plots indicate far outliers. Outlier indicated in red represents the extremely high Pb concentrations in a sample along the Prairie Downs fault zone (arrow in (a)). Data below detection limit were replaced with half the detection limit. (c) Silver concentrations over the study area, indicating elevated values along the Prairie-Downs fault line. (d) Box plot (ioGAS version 7.2) of Ag (in ppt) in regional groundwater samples ($n = 132$). Triangles in box plots indicate far outliers. Outliers indicated in red represent the high Ag concentrations in three samples along the Prairie-Downs fault line (arrow in (a)). Please refer to the Supplementary Data for a lithological legend.
The compositions of ferro-manganese crust samples were presented in Spinks et al. (2017) as metal/Mn ratios, and showed distinctly elevated ratios clustering over the Prairie and Wolf deposits at depth for a range of metals, including Zn (Figure 6d) and Ag, as well as Pb, with median concentrations over the Prairie-Wolf deposits of more than eight times (80.4 ppb) that of the background median concentrations (9.0 ppb; Supplementary Data).

4. Discussion

4.1. Controls on Geochemical Dispersion of Elements from Mineralization to Different Near-Surface Sample Media at Surface

One of the major controls over the concentration of metals and other elements within the critical zone is their abundance in the parent material, with their initial concentrations generally inherited from the geochemistry of the bedrock [1,55]. However, whether metal signatures are preserved in weathered rock and soil is dependent on the time and rate of exposure, and the solubility of the minerals hosting the metals of interest, as well as the interaction with organisms and groundwater [1]. As groundwater travels through the critical zone, it can interact with mineralization at the bedrock interface, facilitating the dissolution of metal-bearing sulfides ([42]; Figure 10). The dissolution of sulfide phases leads to the liberation of associated metals, e.g., Zn and Pb from galena and sphalerite from the Prairie and Wolf deposits (Figure 10). Groundwater is an important agent for...
element transport and dispersion in the critical zone, and these pathfinder elements can be transported over large distances [42], and can be incorporated into other sample media, such as soil and vegetation (Figure 10). During transport in aqueous solutions, metals exist as free ions (e.g., Zn$^{2+}$) and/or metal complexes with several organic and inorganic ligands [56,57], and their mobility (solubility and precipitation as secondary minerals) is further dependent on water pH and the availability of “scavenging” clays and/or Fe and Mn oxides [58]. Unsurprisingly, groundwaters sample a large volume of material, and are, therefore, affected by a range of parent materials and can form large dispersion haloes (km; [21]). The mineral–groundwater interface is also the loci of current alteration and weathering processes, and may reflect non-equilibrium conditions.

The extensive fault system over the Prairie-Wolf study area was a likely conduit for hydrothermal fluids that caused mineralization and metasomatism [43] and is also a likely conduit for enriched groundwaters, as faults and fractures represent zones of higher porosity through which fluids can move more easily [59]. These zones, along with the high chemical reactivity of sulfides in areas of mineralization, facilitate deeper weathering [60] than in the surrounding rock. Therefore, the tectonic framework of the region likely plays a key role in increased metal concentrations in groundwaters by increasing surface area and volume exposure, and, therefore, accelerating weathering and mineral alteration compared to intact lithologies (e.g., Pb; Figure 5). However, they also serve as transport conduits to displace soluble products of weathering [1].

The root systems of many vegetation types (e.g., trees, shrubs, grasses) in water-limited environments can access these groundwater sources (e.g., vegetation in Western Australia; [61], with root depths measured that exceed 30 m [62]. Thus, these plants can incorporate pathfinder elements from groundwater (Figure 10) into their organic structure as nutrients [5,9] or accumulate metals in or around their plant organs (e.g., roots) to combat toxicity [1]. Both groundwater and plants with tap roots can, therefore, carry elemental signatures from large volumes of the critical zone. Plants with dimorphic root systems (exhibiting both shallow lateral roots and deep tap roots that can access groundwater; Figure 10) can also access metals from their local growth media (water within the upper soil layers; Dawson and Pate, 1996). The metal concentration in vegetation can, therefore, be dependent on hydromorphic dispersion [7], e.g., in the direction of drainage, as is likely the case for Ag in our vegetation samples (Figure 3, Figure 4, and Figures 8–10). In addition, plants can exudate organic and amino acids to enhance metal dissolution from soil components, which are then bound in, and transported as, complexes (e.g., Zn; [63]). It is, therefore, not surprising that the enriched metal concentrations observed in soils (e.g., up to 7900 ppb Zn; [23]), Fe–Mn crusts (up to 6960 ppb Zn; [22], and mafic rocks (up to 9690 ppm Zn; [43]) over the fault zone within the Prairie-Wolf study area are also reflected in our spinifex samples (up to 296 ppm Zn; Figure 3a).

While the geochemical properties of soil reflect the immediate parent material to some degree, this is dependent on the solubility of minerals and the mobility of mineral constituents. In addition, some metals may be recycled through the decay of vegetation and re-enter organic-rich soil horizons ([1]; Figure 10), locally increasing metal concentrations. Furthermore, within the Prairie-Wolf study area, and the Capricorn Orogen in general, ferro-manganese crusts are a frequent feature [23]. Both manganese and iron oxides have very high adsorption capacities for heavy metals and trace elements [58,64–67], and can “scavenge” metals from their environment. The high metal concentrations in soil (Figure 6a–c) and ferro-manganese crusts (Figure 6d), with well-defined spatial distributions, are further evidence for the local dispersion of metals through the critical zone. However, the formation of ferro-manganese crusts is limited by the availability of Mn within the soil, which is a function of the composition of the underlying lithology [23]. Within our study area, ferro-manganese crust distributions were, therefore, limited to areas with Mn-bearing lithologies (Figure 6d and Figure 10), and clustered near the fault zone.
4.2. Comparison of Metal Signatures in Near-Surface Sample Media

In all five of the different near-surface sample media presented here, high concentrations of the metals of interest (Zn, Pb, Ag) coincided with samples proximal to the mineralization at depth (Figure 7a,b). Groundwater samples a much greater volume than any of the other sample media discussed here, which affects the necessary sample spacing. However, sample spacing was also dependent on the number of available bores. Therefore, groundwater samples cannot be compared at the same scale as the other sample media. While metal concentrations of Pb, Zn, and Ag in groundwater samples were generally significantly lower than in solid media (e.g., ppt Ag in groundwater versus ppb Ag in soil samples; Figure 7a,b), high-contrast, well-defined anomalies were identified for both Pb and Ag along the Prairie-Downs fault zone (Figure 5a,b), with one instance of anomalously high Pb (82.1 ppb) in similar ranges to solid sample media (e.g., median Pb concentration of 69 ppb in soil samples over the Prairie and Wolf deposits; Figure 6b; Supplementary Data). While the soil data show a very well-defined, high-contrast anomaly, with little apparent dispersion (100′s of m) for Zn (Figure 6a), Pb and Ag concentrations are less consistent, and isolated false positives do exist (Figure 6b,d). However, a comparison of soil and plant data along the Prairie transect (T3) shows a very strong signal of Ag and Pb in soils (Figure 8b,d). Interestingly, high Pb concentrations were also observed in spinifex samples (Figures 3e, 7b and 8b). Compared to soil and mulga samples along transect T3, both Pb and Zn appear to be better captured within spinifex leaves (Figure 8b,c), while Ag is best retained in soil samples (Figure 8d). Lead concentrations in ferro-manganese crusts along the Wolf transect (T2) are distinctly elevated compared to plant samples (Figure 9b). However, Ag appears to be preferentially captured by mulga phyllodes (Figure 9d), while Zn in spinifex leaves is three orders of magnitude higher (ppm vs. ppb; Figure 9c) than in ferro-manganese crusts and mulga phyllodes. These observations indicate potential preferential, metal-specific uptake by different media. Zinc is easily adsorbed to organic matter in soil [68] and Mn oxides, and is an essential nutrient for plants [56]. As such, it is not surprising that the highest Zn concentrations were observed in these media.

Over the Prairie-Wolf deposits, high concentrations of the main metals of interest in mulga and spinifex samples were measured immediately over the surface projection of the deposit at depth, identifying high-contrast, well-defined anomalous targets in both datasets (Figures 3 and 4). Anomalous concentrations of Pb in mulga phyllodes along the Prairie and Wolf transects were less pronounced than those in spinifex samples (Figures 8b and 9b). Silver concentrations, on the other hand, were distinctly higher in mulga samples than in spinifex samples, while Zn did not show any appreciable spatial correlation in mulga phyllodes (Figure 4a). Zinc is an essential micronutrient for all living organisms [56] and, as such, it is not surprising that Zn is contained in all plant samples, with little appreciable differentiation in mulga phyllodes. However, a very strong correlation with much higher concentrations (median concentrations of 44.5 ppm versus 18.3 ppm; Supplementary Data) was observed in spinifex leaves. Therefore, mulga appears to be a better indicator plant for Ag, while spinifex accumulates higher concentrations of Pb and Zn. Silver anomalies in the vegetation samples were offset from the mineralization, with dispersion over several hundred meters in the direction of the local drainage system in both vegetation types (Figures 3, 4 and 8–10), but only limited dispersion within the sampled soils (Figures 6 and 10). The dependency of some metals on hydromorphic dispersion has previously been demonstrated ([7]; Figure 10). However, the dissociation between Ag concentrations in soil and vegetation samples may also indicate localized mechanical dispersion processes (e.g., downslope displacement of Ag-bearing materials; Figure 10).
Silver anomalies in the vegetation samples were offset from the mineralization, with dispersion over several hundred meters in the direction of the local drainage system in both vegetation types (Figures 3, 4 and 8–10), but only limited dispersion within the sampled soils (Figures 6 and 10). The dependency of some metals on hydromorphic dispersion has previously been demonstrated [7]; Figure 10). However, the dissociation between Ag concentrations in soil and vegetation samples may also indicate localized mechanical dispersion processes (e.g., downslope displacement of Ag-bearing materials; Figure 10).

Figure 7. Logarithmic scatter plots of metal concentrations (ppb) in samples by media. Values below detection limits have been replaced by half detection limit values. (a) Silver over Zn. (b) Silver over Pb. * Samples proximal to deposits were defined as follows: groundwater—5 samples along fault line over Prairie Wolf deposits; mulga and spinifex—samples from transects T2 and T3 (including those not directly above the deposit); soil and Mn–Fe crust—samples directly above the Prairie and Wolf deposits as defined in Figure 2b.
Figure 8. Metal concentrations in mulga, spinifex and soil samples along transect T3 (Prairie deposit). (a) Location of samples along transect T3 over the Prairie deposit. (b) Lead concentrations in mulga, spinifex and Fe–Mn crust samples along transect T3. (c) Zinc concentrations in mulga, spinifex and Fe–Mn crust samples along transect T3. (d) Silver concentrations in mulga, spinifex and Fe–Mn crust samples along transect T3.

4.3. Implications for Exploration

All near-surface sample media presented in this study have been indicative of the Prairie and Wolf mineralization at depth. However, differences in the total metal concentrations, as well as relative trends, are apparent (Figures 7–9). These are likely due to complex dispersion processes within the critical zone that mobilize and precipitate these metals, such as the preferential uptake of essential nutrient elements by plants, the relative mobilities of the elements of interest into soil pore waters and groundwaters, and the preferential adsorption of some elements onto clays and Fe/Mn crusts (Figure 10). These processes lead to differences in total metal concentrations (e.g., groundwater versus solid sample media; Figure 7), preferential metal-specific uptake (e.g., Ag in mulga, Pb in spinifex leaves, and Zn in ferro-manganese crusts and soils; Figures 8 and 9), and differences in dispersion scales (i.e., extent of dispersion haloes in groundwater versus soil samples, Figures 5, 6 and 10; vegetation versus soil samples, Figure 8). Hence, different sample media may be useful exploration tools, depending on the type of mineralization, the depth of cover, the cover type, the structural context, and the scale of the target area, and anomalies may be intercepted offset from mineralization at depth (e.g., Figures 4d, 6a, 8d and 9d).
Figure 9. Metal concentrations in mulga, spinifex and Fe–Mn crust samples along transects T2 (Wolf deposit). (a) Location of samples along transect T2 over the Wolf deposit. (b) Lead concentrations in mulga, spinifex and Fe–Mn crust samples along transect T2. (c) Zinc concentrations in mulga, spinifex and Fe–Mn crust samples along transect T2. (d) Silver concentrations in mulga, spinifex and Fe–Mn crust samples along transect T2.
Figure 10. Summary sketch of the main metal dispersion processes related to sample media collected over the Prairie-Wolf study area. Sketch is not to scale.

Groundwater can differentiate fault systems at regional scales (10’s of km) and potential fluid pathways (km scale), which may host mineralization and, thereby, guide where to perform closer spaced sampling, as shown by the example of Pb at a geological terraine scale (the Capricorn Orogen; [24]), and Pb and Ag at a regional scale (Figure 5a,b). Exploration programs can, therefore, greatly benefit from this exploration tool to define larger-scale mineral targets for tenement selection and subsequent in-depth follow-up exploration. Furthermore, our data indicate that groundwater could be a potentially useful tool to trace fault systems that host hydrothermal Zn mineralization. The link of groundwater composition to the regional tectonic framework could, therefore, indicate currently unmapped faults (Figure 5a,c).

Soil data over the Prairie-Wolf study area show a very well-defined, high-contrast anomaly for Zn (Figure 6a), although Pb and Ag concentrations are less consistent, and isolated false positives do exist (Figure 6b–d). While this is not the case in our study area, the signal from depth to soil can be masked by thick and/or transported cover. Since vegetation “samples” nutrients dissolved from mineralization laterally from their growth media
(e.g., soil), as well as at depth (groundwater) below the critical zone (Figure 10), vegetation samples may be utilized in such environments. Despite their capacity to sample larger volumes via groundwater, our mulga and spinifex samples show a high-contrast, well-defined biochemical anomaly over the Prairie-Wolf deposits, with only limited dispersion halos (100’s of meters; Figures 3, 4 and 8–10), necessitating closer spaced sampling. While some metals (e.g., Zn) have stronger signals within vegetation samples than soil, sample spacing requirements are similar and results must be interpreted within the landscape context (e.g., hydromorphic dispersion in the direction of drainage and erosional and depositional processes; Figure 10). The ferro-manganese crusts are an excellent “scavenger” for metals over the Prairie-Wolf study area. However, as shown above, the spatial distribution of ferro-manganese crusts is dependent on Mn-bearing lithologies (Figures 6d and 10) and, therefore, may not be a useful tool over a large regional area.

5. Conclusions

In this study, we explored the role of vegetation, groundwater, soil, and ferro-manganese crusts in metal dispersion processes across the Prairie-Downs fault zone, and their likely use of these near-surface media as a tool for tracing geochemical anomalies. While groundwater can sample large volumes of materials and transport metals over great distances (km), neither the metals of interest nor other pathfinder elements showed appreciable lateral dispersion within soil, vegetation, or ferro-manganese crust samples (~100’s meters), and they are, therefore, not recommended as a preferred regional targeting tool. However, spinifex leaves over the Prairie and Wolf study area were markedly enriched in metals of interest, and exceeded the total concentrations in other sample media, particularly for Zn (compared to groundwater, soil, ferro-manganese crusts, and mulga samples) and Pb (compared to groundwater, soil, and mulga samples). Overall, the metal concentrations in mulga phyllodes were not as pronounced as the concentrations in spinifex leaves, with the exception of Ag, which exceeded the total concentrations in all other sample media. These observations indicate potential preferential metal-specific uptake by different media.

Pathfinder elements in vegetation and groundwater samples appear to be related to the Prairie Downs fault zone, which likely facilitated the anomalously deep water table. This, in turn, enabled groundwaters to sample mineralization at a greater depth than elsewhere in the region. As indicated by our data, groundwater sampling can, therefore, be a potentially useful tool to trace fault systems that host structurally controlled, hydrothermal Zn–Pb mineralization. Around the Prairie-Wolf deposits, spinifex leaf samples also showed anomalous concentrations in various ore- and fault- (fluid pathway) related elements (K, Na, Ba). Therefore, both sample media were able to identify the fault system at different scales; regional (groundwater) and local (vegetation). Given the finite amount of metals in a mineral system, a thorough understanding of metal dispersion processes across multiple media will aid future geochemical exploration approaches.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11111174/s1, Figure S1: Spatial distribution of Zn, Pb, Cr and Re concentrations in Spinifex; Figure S2: Lithological legend for Figures 2, 5 and 6; Table S1: Multi-element chemistry analysis of spinifex leaves and mulga phyllodes; Table S2: Statistical summary of multi-element chemistry analysis of spinifex leaves; Table S3: Statistical summary of multi-element chemistry analysis of mulga leaves; Table S4: Statistical summary of multi-element chemistry analysis of groundwater samples; Table S5: Statistical summary of multi-element chemistry analysis of soil samples; Table S6: Statistical summary of multi-element chemistry analysis of Fe–Mn crusts; Table S7: Geochemical analyses of spinifex leaf samples; Table S8: Geochemical analyses of mulga phylloide samples.

Author Contributions: Conceptualization, A.H., N.R., R.L.T.; methodology, N.R., R.L.T., S.C.S., A.W.; formal analysis, A.H.; investigation, A.H., N.R., R.L.T., S.C.S.; data curation, N.R., T.P.; writing—original draft preparation, A.H.; writing—review and editing, N.R., R.L.T.; visualization, A.H.; All authors have read and agreed to the published version of the manuscript.
**Funding:** This research was funded by the Science and Industry Endowment Fund as part of The Distal Footprints of Giant Ore Systems: UNCOVER Australia Project grant number RP04-063—Capricorn Distal Footprints). And The APC was funded by CSIRO Mineral Resources.

**Data Availability Statement:** The data presented in this study are contained within this article or supplementary material.

**Acknowledgments:** We thank Marindi Metals Plc. for assistance and accommodation on site and in the field. We also thank the three anonymous reviewers for their comments, which assisted in improving this manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Butt, C.R.M.; Robertson, I.D.M.; Scott, K.M.; Cornelius, M. *Regolith Expression of Australian Ore Systems*; CRC LEME: Perth, Australia, 2005; 431p.
2. Anand, R.R.; Butt, C. A guide for mineral exploration through the regolith in the Yilgarn Craton, Western Australia. *Aust. J. Earth Sci.* 2010, 57, 1015–1114. [CrossRef]
3. Brantley, S.L.; White, T.S.; White, A.F.; Sparks, D.; Richter, D.; Pregitzer, K.; Derry, L.; Chorover, J.; Chadwick, O.; April, R.; et al. *Frontiers in Exploration of the Critical Zone*; National Science Foundation (NSF): Newark, DE, USA, 2006; 30p.
4. Guo, L.; Lin, H. Critical Zone Research and Observatories: Current Status and Future Perspectives. * Vadose Zone J.* 2016, 15, 1–14. [CrossRef]
5. Brooks, R.R.; Dunn, C.E.; Hall, G.E.M. *Biological Systems in Mineral Exploration and Processing*; Ellis Horwood Limited: Hertfordshire, UK, 1995.
6. Lintern, M.; Butt, C.; Scott, K. Gold in vegetation and soil—Three case studies from the goldfields of southern Western Australia. *J. Geochem. Explor.* 1997, 58, 1–14. [CrossRef]
7. Cohen, D.R.; Silva-Santisteban, C.M.; Rutherford Garnett, D.L.; Waldron, H.M. Comparison of Vegetation and Stream Sediment Geochemical Patterns in Northeastern New South Wales. *J. Geochem. Explor.* 1999, 66, 469–489. [CrossRef]
8. Hulme, K.A.; Hill, S.M. River red Gums as a Biogeochemical Sampling Medium in Mineral Exploration and Environmental Chemistry Programs in the Curnamona Craton and Adjacent Regions in NSW and SA. *Adv. Regolith* 2003, 2003, 205–210.
9. Dunn, C.E. *Biogeochemistry in Mineral Exploration*; Elsevier: Amsterdam, The Netherlands, 2007.
10. Reid, N.; Hill, S.M.; Lewis, D.M. Spinifex biogeochemical expressions of buried gold mineralisation: The great mineral exploration penetrator of transported regolith. *Appl. Geochem.* 2008, 123, 76–84. [CrossRef]
11. Reid, N.; Hill, S.M.; Lewis, D.M. Biogeochemical expression of buried Au-mineralisation in semi-arid northern Australia: Penetration of transported cover at the Titania Gold Prospect, Tanami Desert Australia. *Geochem. Explor. Environ. Anal.* 2009, 9, 1–8. [CrossRef]
12. Lintern, M.; Anand, R. Using gum trees for Au exploration in the Eastern Goldfields (Western Australia). In Proceedings of the 25th International Applied Geochemistry Symposium 2011, Rovaniemi, Finland, 22–26 August 2011; p. 83.
13. Collerson, K.D. Application of spinifex biogeochemistry to identify mineralisation targets in obscured basement terranes beneath the Simpson Desert in southwestern Queensland. In *Queensland Minerals and Energy Review Series*; Natural Resources and Mines: Queensland, Australia, 2014.
14. Arhin, E.; Boadi, S.; Esoah, M.C. Identifying pathfinder elements from termite mound samples for gold exploration in regolith complex terrain of the Lawra belt, NW Ghana. *J. Afr. Earth Sci.* 2015, 109, 143–153. [CrossRef]
15. Gonzalez-Alvarez, I.; Stewart, A.; Anand, R.; Sinclair, P.; Salama, W.; Laird, J.; Ibrahim, T.; Pinchard, T. Termitaria Geochemistry for Uranium Exploration in Arnhem Land, Northern Territory, Australia. In Proceedings of the SEG 2015: World-Class Ore Deposits: Discovery to Recovery, Hobart, Australia, 27–30 September 2015.
16. Sinclair, P. Termitaria sampling in uranium exploration: Refining an old technique. In Proceedings of the AGES 2017, NT Geological Survey, Alice Springs, Australia, 28–29 March 2017; pp. 74–75.
17. Arhin, E.; Captain-Esoah, M.; Berdie, B.S. *Economic Importance of Termites and Termitaria in Mineral Exploration*. In *Regolith Expression of Australian Ore Systems*; CRC LEME: Perth, Australia, 2005.
18. Leslie, K.; Van Geffen, P.W.; Macfarlane, B.; Oates, C.J.; Kyser, T.K.; Fowle, D.A. Biogeochemical indicators of buried mineralization under cover, Talbot VMS Cu–Zn prospect, Manitoba. *Appl. Geochem.* 2013, 37, 190–202. [CrossRef]
19. Bohu, T.; Anand, R.; Noble, R.; Lintern, M.; Kaksonen, A.H.; Mei, Y.; Cheng, K.Y.; Deng, X.; Veder, J.-P.; Bunce, M.; et al. Evidence for fungi and gold redox interaction under Earth surface conditions. *Nat. Commun.* 2019, 10, 1–13. [CrossRef]
20. Gray, D.J.; Noble, R.R.P.; Reid, N. Hydrogeochemical Mapping of the Northeast Yilgarn Craton. CSIRO Exploration and Mining Report No. P2009/1612 // MERIWA project M402. Minerals and Energy Research Institute of Western Australia Report No. 280. 2009, 73p. Available online: http://hdl.handle.net/102.100.100/115382?index=1 (accessed on 22 October 2021).
21. Gray, D.J.; Reid, N.; Noble, R.R.P. Improved Hydrogeochemical Exploration in the northwest Yilgarn—Adding Value to Underexplored Areas. CSIRO Report EP 143875. 2014, 86p. Available online: https://publications.csiro.au/rpr/pub?pid=csiro:EP143875 (accessed on 8 August 2014).
22. Spinks, S.C.; Uvarova, U. Fractionation of Zn isotopes in terrestrial ferromanganese crusts and implications for tracing isotopically-heterogeneous metal sources. *Chem. Geol.* 2019, 529, 119314. [CrossRef]

23. Spinks, S.C.; Uvarova, Y.; Thorne, R.; Anand, R.; Reid, N.; White, A.; Ley-Cooper, Y.; Bardwell, N.; Gray, D.; Meadows, H.; et al. Detection of zinc deposits using terrestrial ferromanganese crusts. *Ore Geol. Rev.* 2017, 80, 484–503. [CrossRef]

24. Thorne, R.L.; Reid, N.; Gray, D.J.; Balissun-Stanton, B.; Bardwell, N.; Klump, J.; Davis, A.; Ross, S.; Sobotkova, A. Hydrogeochemistry of the Capricorn Orogen. EP 182906 CSIRO, 2018, p. 106. Available online: https://publications.csiro.au/rpr/pub?list=ASE&id=csiro:EP161243&expert=false&b=RECENT&n=3&rrp=25&page=54&tr=2079&dr=all&csiro.affiliation=%7Csiro.projectBusinessUnit=50013148 (accessed on 26 June 2016).

25. Loffeld, H. Essential Trace Elements for Plants, Animals and Humans; Agricultural University of Iceland: Reykjavik, Iceland, 2005.

26. Kremer, U.; Talke, I.N.; Hanikenne, M. Transition metal transport. *FEBS Lett.* 2007, 581, 2263–2272. [CrossRef]

27. Alekseenko, V.A. *Geochemical Methods for Mineral Deposits Prospecting*; Logos: Moscow, Russia, 2005. (In Russian)

28. Bech, J.; Duran, P.; Roca, N.; Poma, W.; Sánchez, I.; Roca-Pérez, L.; Boluda, R.; Barceló, J.; Poschenrieder, C. Accumulation of Pb and Zn in Bidens triplinervia and Senecio sp. spontaneous species from mine spoils in Peru and their potential use in phytoremediation. *J. Geochem. Explor.* 2012, 123, 109–113. [CrossRef]

29. Alekseenko, V.A.; Shvydkaya, N.V.; Alekseenko, A.V.; Machevariani, M.M.; Bech, J.; Pashkevich, M.A.; Puzanov, A.V.; Nastavkin, A.V.; Roca, N. Element Accumulation Patterns of Native Plant Species under the Natural Geochemical Stress. *Plants* 2020, 10, 33. [CrossRef] [PubMed]

30. Dunn, C.E. The biogeochemical expression of deeply buried uranium mineralisation in Saskatchewan, Canada. *J. Geochem. Explor.* 1981, 15, 437–452. [CrossRef]

31. Makviyska, D.P. *Biogeochemical Methods of Prospecting*; VI.Vernadskii Institute of Geochemistry and Analytical Chemistry: Moscow, Russia, 1963.

32. Kovalevsky, A.L. *Biogeochemical Exploration for Mineral Deposits*; VNU Science Press: Utrecht, The Netherlands, 1987.

33. Cole, M.M.; Provan, D.M.J.; Tooms, J.S. Geobotany, biogeochemistry and geochemistry in mineral exploration in the Bulman-Waimuna Springs area, Northern Territory, Australia. *Trans. Inst. Min. Metall. Sect.* 1968, 77, 81–104.

34. Anand, R.; Cornelius, M.; Phang, C. Use of vegetation and soil in mineral exploration in areas of transported overburden, Yilgarn Craton, Western Australia: A contribution towards understanding metal transportation processes. *Geochem. Explor. Environ. Anal.* 2007, 7, 267–288. [CrossRef]

35. Collerson, K.D.; Hutton, L.; Wason, R. Grassroots Exploration under Cover: Spinitex Geochemistry Leads to Discovery of a New Australian Metallogenic Province. 2015. Available online: https://www.ausimmbulletin.com/feature/grassroots-exploration-under-cover/ (accessed on 1 August 2021).

36. Marshall, A.E.; Lintern, M.J. Biogeochemical investigation in the Murchison and Telfer regions of arid Western Australia. In Proceedings of the 17th International Geochemical Exploration Symposium, Applied Biogeochemistry in Mineral Exploration and Environmental Studies, Townsville, Australia, 13–14 May 1995.

37. Gray, D.J.; Noble, R.R.P. Nickel hydrogeochemistry of the northeastern Yilgarn Craton, Western Australia. In *CRC LEME Open File Report*; CRC LEME: Perth, Australia, 2006; 133p.

38. Kirste, D.; de Caritat, P.; Dann, R. The application of the stable isotopes of sulfur and oxygen in groundwater sulfate to mineral exploration in the Broken Hill region of Australia. *J. Geochem. Explor.* 2003, 78, 81–84. [CrossRef]

39. Kirste, D.M.; de Caritat, P.; McPhail, D.C. Hydrogeochemistry and transport of weathering/oxidation products of buried mineralisation. *Geochim. Cosmochim. Acta* 2004, 68, A180.

40. Pirlo, M.C.; Giblin, A.M. Application of groundwater–mineral equilibrium calculations to geochemical exploration for sediment-hosted uranium observations from the Frome Embayment, South Australia. *Geochem. Explor. Environ. Anal.* 2004, 4, 113–127. [CrossRef]

41. De Caritat, P.; Kirste, D.; Carr, G.; McCulloch, M. Ground water in the Broken Hill region, Australia; recognising interaction with bedrock and mineralisation using S, Sr and Pb isotopes. *Appl. Geochem.* 2005, 20, 767–787. [CrossRef]

42. Gray, D.J.; Noble, R.R.; Reid, N.; Sutton, G.J.; Pirlo, M.C. Regional scale hydrogeochemical mapping of the northern Yilgarn Craton, Western Australia: A new technology for exploration in arid Australia. *Geochem. Explor. Environ. Anal.* 2016, 16, 100–115. [CrossRef]

43. White, A.J.R.; Pearce, M.A.; Meadows, H.R. Distinguishing regional and local-scale metasomatic systems at the Prairie Downs Zn-Pb deposit. *Litos* 2016, 262, 247–265. [CrossRef]

44. Reid, N.; Thorne, R.; Folkes, C.; Gilmore, P.J.; Pinchard, T. *Hydrogeochemistry of the Cobar Region*. CSIRO, Australia. CSIRO EP: 207556, 2020, p. 112, Geological Survey of New South Wales Record GS2021/0054. MinEx Record 2020/21. Available online: https://www.researchgate.net/publication/350295603_Hydrogeochemistry_of_the_Cobar_region_Geological_Survey_of_New_South_Wales_Record_GS20210054_MinEx_record_202021 (accessed on 31 March 2021).

45. Thorne, A.M.; Seymour, D.B. *Geology of the Ashburton Basin, Western Australia*; Geological Survey of Western Australia: Bulletin, CT, USA, 1991; Volume 139, 162p.

46. Nelson, D.R. *Compilation of SHRIMP U-Pb Zircon Geochronology Data*, 1994; Western Australia Geological Survey: Perth, Australia, 1995; p. 244.

47. Thorne, A.M.; Trendall, A.F. *Geology of the Fortescue Group, Pilbara Craton, Western Australia*; Geological Survey of Western Australia: Bulletin, CT, USA, 2001; Volume 144, 249p.
48. White, A.J.R.; Legras, M.; Smith, R.E.; Nadoll, P. Deformation-driven, regional-scale metasomatism in the Hamersley Basin, Western Australia. *J. Metamorph. Geol.* **2014**, *32*, 417–433. [CrossRef]
49. White, A.J.R.; Smith, R.E.; Nadoll, P.; Legras, M. Regional-scale Metasomatism in the Fortescue Group Volcanics, Hamersley Basin, Western Australia: Implications for Hydrothermal Ore Systems. *J. Pet.* **2014**, *55*, 977–1009. [CrossRef]
50. Atlas of Living Australia Databases. Available online: [http://www.ala.org.au/](http://www.ala.org.au/) (accessed on 4 January 2013).
51. AusGrass2. 2021. Available online: [http://ausgrass2.myspecies.info/content/triodia-basedowii](http://ausgrass2.myspecies.info/content/triodia-basedowii) (accessed on 22 October 2021).
52. Miller, J.T.; Andrew, R.A.; Maslin, B.R. Towards an understanding of variation in the Mulga complex (Acacia aneura and relatives). *Conser. Sci. West. Aust.* **2002**, *4*, 19–35.
53. Moore, P. *A Guide to Plants of Inland Australia*; Reed New Holland: Sydney, Australia, 2005.
54. McWilliam, J.; Mison, K. Significance of the C4 Pathway in Triodia irritans (Spinifex), a Grass Adapted to Arid Environments. *Funct. Plant Biol.* **1974**, *1*, 171–175. [CrossRef]
55. Mondillo, N.; Wilkinson, J.J.; Boni, M.; Weiss, D.J.; Mathur, R. A global assessment of Zn isotope fractionation in secondary Zn minerals from sulfide and non-sulfide ore deposits and model for fractionation control. *Chem. Geol.* **2018**, *500*, 182–193. [CrossRef]
56. Orellana, F.; Verma, P.; Loheide, S.; Daly, E. Monitoring and modeling water-vegetation interactions in groundwater-dependent ecosystems. *Rev. Geophys.* **2012**, *50*, RG3003. [CrossRef]
57. Rasouli-Sadaghiani, M.H.; Sadeghzadeh, B.; Sepehr, E.; Rengel, Z. Root exudation and zinc uptake by barley genotypes differing in Zn efficiency. *J. Plant Nutr.* **2011**, *34*, 1120–1132. [CrossRef] [PubMed]
58. Manceau, A.; Lanson, M.; Geoffroy, N. Natural speciation of Ni, Zn, Ba, and as in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochim. Cosmochim. Acta* **2007**, *71*, 95–128. [CrossRef]
59. Fan, T.; Wang, Y.; Li, C.; He, J.; Gao, J.; Zhou, D.; Friedman, S.; Sparks, D. Effect of Organic Matter on Sorption of Zn on Soil: Elucidation by Wien Effect Measurements and EXAFS Spectroscopy. *Environ. Sci. Technol.* **2016**, *50*, 2931–2937. [CrossRef] [PubMed]