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Test of vegetation-based surface exploration for detection of Arctic mineralizations: The deep buried Kangerluarsuk Zn-Pb-Ag anomaly

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**Abstract**

The aim of our study was to test whether surficial geochemical techniques are applicable under arctic conditions where pedogenesis is slow or absent, and where the vegetation is arctic dwarf shrub tundra. To this end, we sampled vegetation and topsoil at a known Zn-Pb-Ag anomaly at Kangerluarsuk, northwest Greenland. This Zn-Pb-Ag mineralization surfaces in part of the test area and is deeply buried in other parts. The surface mineralization could readily be identified by element analysis of the omnipresent plant Salix glauca. The strongest signal came from the pathfinder element Tl. The target elements Pb and Ag gave only weak signals and Zn gave no signal, probably because the cellular concentration of these elements is actively regulated by the plant. The use of regulated plant micronutrients as reference elements gave a small reduction of analytical noise in Tl/Cu and Tl/B concentration ratios at low Tl concentrations which improved identification of the deep mineralization. Pathfinder elements in plants may thus prove useful when combined with a detailed geophysical model. Tl, Zn, Pb and Ag concentrations in topsoil identified the surface mineralization but failed to identify the deep mineralization. This difference between samples of S. glauca and topsoil is probably because target elements from the deep mineralization must be mobile to reach the surface. Mobile elements may be more accessible for ion-exchange and uptake into the plants compared to the calcilcitrant and crystalline fraction in the topsoil.

**Keywords:** Greenland, Thallium, Buried mineralization, Exploration tool, Salix glauca, Element ratios

**1. Introduction**

Organizations that conduct mineral exploration are in urgent need for low-cost, low impact exploration techniques that can be used in the vast, pristine, arctic and subarctic areas where infrastructure is limited or absent. Surficial geochemical techniques are often environmentally friendly, fast and relatively inexpensive, and thus cost-efficient compared to drilling. The primary reason for lacking acceptance is their varying success. The surficial exploration techniques are mostly based on geochemical analyses of soil horizons or plants. The use of plant material rather than surface soil and rocks is not commonly applied, probably because more environmental factors and transport processes contribute to the geochemical signal of plants as compared to soil and rocks. Plant material, however, has the benefit that plants integrate the geochemical signal from the whole root area as well as by taking up only mobile elements, i.e. the fraction of the elements that may originate from deep mineralizations. This was for instance demonstrated by Anand et al. (2007) for five Australian sites with transported overburden where extractions of topsoil showed either no signal from the buried mineralizations or only a weak and ambiguous signal. Their vegetation survey, in contrast, showed a clear multi-element signature from the mineralizations in the tree species Acacia aneura. They concluded that that trees may bring pathfinder elements to surface in dry areas with low water-tables. Middleton et al. (2018) assessed the signal from the Juomauso Au–Co deposit in Finnish Lapland, by element analysis of the circumboreal dwarf-shrubs, Empetrum nigrum, Rhododendron tomentosum and Vaccinium myrtillus and the conifer Juniperus communis. Although the Juomauso deposit is situated more than 200 m below the surface, the biogeochemical signal from the dwarf-shrubs clearly demonstrated a surface anomaly. Reimann et al. (2018a) demonstrated a clear signal in vegetation growing on top of Pb and Mo mineralizations in southern Norway with birch and the dwarf shrub Vaccinium vitis-idaea showing the best compromise for biogeochemical exploration in terms of signal strength and widespread availability. The applicability of plants as matrices for geochemical exploration may, however, be limited by the fact that plants strongly regulate the uptake of most elements (Reimann et al., 2018a).

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The aim of our study was to test whether surficial geochemical techniques are also applicable under arctic conditions where pedogenesis is slow or absent, and where the vegetation is arctic dwarf shrub tundra without trees. In other words, can we detect surface mineralizations or even deeply buried mineralizations in the Arctic simply by analyzing the element content of natural plants and topsoil? To this end, we sampled vegetation and topsoil at a known mineralization at Kangerluarsuk, Northwest Greenland. This Zn-Pb-Ag mineralization surfaces in part of our test area and is deeply buried in other parts. Reflection seismology suggests that a substantial proportion of the Kangerluarsuk area is fractured, which is based on the heavily damped signal from seismic reflectors (Gullbrandsen and Nermark, 2013) and supported by structural geological mapping, which showed several NE-SW dipping fault planes (Marker and van Gool, 2014). The high degree of fracturing suggests that pathfinder elements from the deep mineralization may have migrated to the surface. The Kangerluarsuk test site is therefore ideal for testing the limitations of surficial geochemical exploration methods.

A general problem in using plant material for mineral exploration is that the concentrations of many elements in plants are close to the analytical quantification limits and consequently give poor data quality. In the present study, we test how analysis of duplicate samples may be used to assess data quality and select suitable elements and element concentration ratios. We hypothesized that ratios of element concentrations in plants may give a reduction of analytical noise and consequently improve data quality compared to absolute concentrations. This is because many analytical errors such as differences in extraction efficiency, weighing errors, pipetting errors, instrument drift, etc. increase noise levels in data sets of absolute concentrations, but may affect the concentration of the target element (numerator) and the reference element (denominator) in the same way and in many instances to the same degree in element ratios. Selection of suitable element ratios has mostly been by trial and error (e.g. Miksova et al., 2019, 2020). In this article, we propose a supervised approach based on exploration target elements (ratio numerators) and plant mineral nutrients as reference elements (ratio denominators). The plant concentration of the target elements should vary according to exposure, i.e., the variation in plant concentrations should identify the mineralizations. The reference elements, in contrast, should show constant concentrations in plants for instance when cellular concentrations of nutrients elements are actively controlled in the plant by heavy metal homeostasis (Williams et al., 2000).

2. Materials and methods

2.1. Regional geology

The Kangerluarsuk test site in Northwest Greenland is part of the Rinkian mobile belt. The area holds the strongest zinc anomaly cluster in stream sediments for all of Greenland (Gullbrandsen, 2013). Most of the area consists of flat-lying and interlayered beds of pyrrhotite-bearing graphitic schist, regional orthogneiss and a mineralized quartzite-carbonate succession. The supracrustal rocks in the area are part of the Lower Proterozoic Karrat Group, that spans several hundreds of kilometers along the coast of Greenland. The Karrat Group is believed to have been deposited in several sub-basins in an extensional fault system along the Rae craton. The pyrrhotite-bearing pelitic schist makes up a part of the Nukavsak formation. The thickness at this locality is unknown, but the Nukavsak Formation is elsewhere up to 5 km in thickness (Rosa et al., 2016). The Nukavsak Formation is underlain by a mineralized quartzite-carbonate succession, the newly defined Qaarsukassak Formation which in turn is underlain by Archean orthogneiss (Fig. S1; Rosa et al., 2016).

Thermal subsidence together with deepening and widening of the basin resulted in a starved basin, in which the shales and semipelites of the Nukavsak formation formed (Rosa et al., 2016). The light grey regional orthogneiss is Archean in age and tonalitic in origin. It often exhibits a sheared contact with the Nukavsak formation. The siliciclastic quartzite carbonate succession of the Qaarsukassak formation is believed to have been the precursor for the thermal subsidence of the Nukavsak formation, in which carbonate platform formed, with interchanging periods of quartzite and pelite deposition (Fig. S1). The Qaarsukassak formation has numerous sulfide-rich zones, which may be followed for tens of kilometers along strike. The Qaarsukassak formation is a 20 m thick succession that marks the boundary to the Nukavsak formation (Rosa et al., 2016). At the top of the formation, a 10 m wide mineralized zone is seen with Zn-Pb-Ag showings in a siliciclastic matrix. In the Kangerluarsuk area, this has been described as the Discovery Zone (Coppard et al., 1992). The area is situated less than 25 km from the famous Black Angel Zn-Pb mine, which was a carbonate hosted Zn-Pb deposit where 11 million tons of ore, averaging 12% Zn, 4% Pb and 29 ppm Ag, where mined from 1972 to 1990 (Thomsen, 2003). The Discovery Zone is regarded as a sediment hosted Zn-Pb-Ag mineralization which is underlain by the regional Archean orthogneiss.

2.2. Mineralization

The Qaarsukassak formation within the Kangerluarsuk area holds a surficial Zn-Pb-Ag mineralization. The 20 m thick Qaarsukassak formation, consists of interbedded quartzite, metapelite and deformed carbonates (Fig. S1). The surface mineralization can be followed discontinuously for several kilometers in the Kangerluarsuk test area. The lower quartzites show rare crossbedding and the variable thickness along strike is interpreted as deposition in paleo-basins (Rosa et al., 2016). The sediment hosted Zn-Pb-Ag ore zone occurs at the top of the Qaarsukassak formation within a metasedimentary package dominated by sulphides consisting of sphalerite, galena, pyrrhotite and pyrite. Grab samples revealed up to 45% Zn (i.e. essentially sphalerite), 9.3% Pb and 596 g ton⁻¹ Ag (Coppard et al., 1992).

A three-year work program was carried out by Avannaa Resources at the Kangerluarsuk area (Gullbrandsen, 2013). More than 1500 soil sample stations were analyzed by soil-gas- hydrocarbons (SGH), mobile metal ion (MMI), and conventional bulk chemistry. Geophysics, soil chemistry and structural analysis indicated a deep-seated mineral deposit (the deep mineralization), presumably located 500 m below the surface close to regional fault planes. Three positions for drill testing were determined from previous soil chemistry combined with deep penetrating airborne geophysics (ZTEM), and 3D inversion and structural mapping (Gullbrandsen, 2013). Drilling has been postponed to 2021 due to the Covid-19 pandemic, and we therefore do not have absolute proof of the presence of the deep mineralization at the primary drill site which also means that the site is still pristine, so that a signal from the deep mineralization may be picked up without anthropological interference. At least two faults are potential routes for the migration of pathfinder elements from the deep mineralization to the surface which makes the site ideal for testing vegetation and topsoil as indicators of deep mineralizations.

2.3. Sampling and chemical analysis of trace elements

Three parallel sample lines were placed so that each line covered three domains: i) the surface mineralization as positive control stations, ii) the primary drill target and the fault plane (the deep mineralization), and iii) an area in between as a background concentration reference (Fig. 1). Sample lines were separated by 300 m and each line had 50 planned sample stations. The distance between stations within the surface mineralization and the deep mineralization was 50 m whereas the distance between background stations was 400 m, except for background stations that were close to a previously identified redox SGH outline of the secondary drill target and thus sampled every 50 m (for details, see Fig. S1-2). Only 90 stations were sampled as some stations did not have vegetation or a soil cover. Every tenth sample station
was a “duplicate station”, where twice the amount of plant material was sampled and divided in two, a regular sample and a duplicate.

At each sample station, we first collected a soil sample. The soil showed no developed soil horizons, and all stations were therefore sampled at a depth of 20 cm. Approximately 500 g were packed in plastic bags (Fig. SI-3). Specimens of Salix glauca (greyleaf willow) were then sampled as evenly as possible from a circular area within a 3-m radius centered where the soil was sampled. Only twigs with a thickness of approximately 0.3–0.7 mm were selected and cut with ceramic scissors to avoid contamination from scissor steel blades. We sampled only the woody twigs as these have taken up trace elements for several years and may be in semi-equilibrium with average concentrations in the transpiration stream. The twigs were cleared of leaves, washed in deionized water to remove dust, and shortly air-dried (Fig. SI-4). Fifteen to 50 g (dry weight) were sampled at each station. The twigs were packed in cotton bags, immediately air-dried and shipped to the commercial lab ALS Vancouver (Canada) where the dry twigs were milled to less than 1 mm (method VEG-MILL01). The resulting plant pulps were digested in aqua regia and analyzed by ICPAES-ICPMS (analysis package ME-VEG41 with VEG41-REE add-on). Soil samples were processed and analyzed by ALS Loughrea (Ireland). The soil samples were dried and sieved to less than 180 μm (method PREP41), then aqua regia digested and analyzed for the same range of elements by ICP-MS (analysis package ME-MS41L).

3. Results and discussion

We chose Salix glauca (greyleaf willow) as our indicator species as this species is present almost everywhere in Greenland and was found at all the sampled stations. The first challenge was to select target elements in S. glauca that could be used to identify areas of explorational interest. Many elements could not be used simply because the concentrations were low and rounded or below the quantification limit. We therefore chose supervised data analysis of few selected elements rather than unsupervised data analysis of a many elements. Target elements for the mineralization were Zn, Pb and Ag. Other elements may be chosen as pathfinder elements if they occur in close association with the target elements and show increased geochemical dispersion halos. We therefore included Tl in the target elements as Tl seems to be an efficient pathfinder element for Zn-Pb-Ag mineralizations (Graham et al., 2009).

3.1. Target elements in S. glauca

The first evaluation of data quality came from biplots of target element concentrations in duplicate S. glauca samples. Ideally, duplicate biplots should show a straight line with a slope of 1. None of the target elements did this (Fig. 2), which demonstrated poor data quality. Tl had the best data quality with some linearity especially at low concentrations (Fig. SI-5). The high-concentration duplicates were also clearly separated from the rest of the Tl duplicates (Fig. 2), suggesting considerable Tl variation in S. glauca and thus a potential for identifying the mineralizations. Pb and Ag duplicates were like Tl except that data quality was poorer and high-concentration duplicates were less separated from low-concentration duplicates (Fig. 2). Pb and Ag were therefore of lower quality with respect to identification of the mineralizations. Zn duplicates showed a different pattern as the high-end extremes were missing (Fig. 2). The low variation in concentration is probably because Zn, in contrast to Pb, Ag and Tl, is also an essential plant nutrient, where the concentrations in S. glauca are within certain limits (homeostasis) as hypothesized in the introduction.

To identify the mineralizations, good target elements should furthermore show a large difference between samples with high concentrations (mineralization) and samples with low concentrations (background) in the complete dataset. This was first evaluated by comparing the 0.1-fractile and the 0.9-fractile for all sample stations. Tl had a high 0.9-fractile/0.1-fractile ratio of 26 (Table 1), Ag had a lower 0.9-fractile/0.1-fractile ratio of 13 and the ratio was rather low for Pb.
(3.3) and Zn (2.2). The fractile ratios were in line with the duplicate results. The data structure of Tl and to a smaller extend Pb and Ag, therefore indicated that these elements in S. glauca may be useful for visualizing the mineralizations, whereas Zn would probably fail to identify the mineralizations because of too little separation of highs and lows.

The fractile ratios in Table 1 do not say anything about the actual spatial distributions. The distribution of the target element concentrations in S. glauca is therefore compared in Fig. 3 and in Fig. SI-6. Tl gave the best results that very clearly identified the surface mineralization. Tl also showed increased concentrations in some of the background stations close to the surface mineralization which indicates a secondary dispersion halo where Tl has migrated down-slope from the surface mineralization. Increased Tl concentrations close to the primary drill target also gave hints of the presence of the presumed deep buried mineralization (Fig. 3). Some background stations closer to the primary drill target also showed increased Tl concentrations. These stations are situated close to a melt water river at low elevation and likely represent a seepage anomaly from the buried mineralization. Ag, and especially Pb, showed weak spatial signals from the mineralizations (Fig. SI-6). The small Pb signal was surprising given that Pb showed clear mineralization-related signals in many of the tested species in a previous study (Reimann et al., 2018a). It is furthermore interesting that Ba and Mn did not show the surface mineralization as these elements have been suggested as pathfinder elements for metasedimentary Zn-Pb-Ag mineralizations of the Eagle Bay Assemblage (Lett et al., 1998). For Mn, this is probably because Mn is also an essential plant nutrient that may show homeostasis in S. glauca as seen for Zn. The reason is less obvious for Ba, but the Ba anion is probably too mobile in the topsoil. Ba may also precipitate with oxidized S during the aqua regia extraction which may explain that the Ba concentration is also an essential plant nutrient that may show homeostasis in S. glauca (ppm) as suggested by the fractile ratio, the duplicate biplot and previous studies (Reimann et al., 2018a).

Before the survey, the stations were assigned to one of three domains based on previous soil measurements and geophysical data, i.e., the surface mineralization, the deep mineralization and the background domain. We could therefore test if the domains were recognizable from the S. glauca concentrations of the target elements. The surface mineralization could easily be identified from the mean concentration of Tl, that was enriched 12-fold compared to the background mean (Table 2). Pb and Ag, on the other hand, were only slightly enriched in the surface mineralization (enrichment factors of 2.1 and 2.4), and Zn was not enriched at all. The high Ag 0.9-fractile/0.1-fractile ratio (Table 1) was therefore mostly random noise. Zn concentrations did not hold any information, as expected from the biplot (Fig. 3) and the 0.9-fractile/0.1-fractile ratios (Table 1). One-tailed t-tests on log-transformed concentrations confirmed that the surface mineralization mean was larger than the background mean at the 1% level for Tl (p = 2.2E-7), Ag (p = 0.8.64E-7) and Pb (p = 0.0004), but not for Zn (p = 0.012).

The presumed deep mineralization had enrichments of only 1.6 to 1.7 compared to the background for Tl, Ag and Pb (Table 2). t-test of log-transformed data showed that only TI (p = 0.0009) and Pb (p = 0.0003) means were significantly different from the background domain, whereas Ag (p = 0.013) and especially Zn (p = 0.081) means were not. The comparison of domains is, however, to some extend blurred by the likely signals from the down-slope halo and the seepage anomaly within the background domain as discussed above. The differences between the target elements in the three domains were also evident when all measurements were visualized in boxplots (Fig. SI-7). Overall, the mean values for the three domains therefore led to similar conclusions as would have been reached by simple visual inspection of the spatial distributions (Fig. 3 and Fig. SI-6).

Other elements also showed high 0.9-fractile/0.1-fractile ratios indicating high spatial variation and possibly enrichment in the mineralization domains. The ten with the highest ratios were Er (18.8), Y (18.1), Dy (17.6), Tb (17.6), Gd (16.7), Eu (16.2), Ho (16.1), La (15.7), Ba (15.5) and Rb (15.1). None of these, however, could be used as pathfinder elements as they either failed completely to visualize the surface mineralization in spatial distribution plots (Er, Y, Dy, Tb, Gd, Eu and Ba, data not shown), or showed only small indications of the surface mineralization (Ho, La and Rb, data not shown). The 0.9-fractile/0.1-fractile ratio is therefore a poor indicator of good pathfinder elements, but sufficient to eliminate a large number of non-relevant elements in the initial data analysis.

It is furthermore interesting that Ba and Mn did not show the surface mineralization as these elements have been suggested as pathfinder element for metasedimentary Zn-Pb-Ag mineralizations of the Eagle Bay Assemblage (Lett et al., 1998). For Mn, this is probably because Mn is also an essential plant nutrient that may show homeostasis in S. glauca as seen for Zn. The reason is less obvious for Ba, but the Ba anion is probably too mobile in the topsoil. Ba may also precipitate with oxidized S during the aqua regia extraction which may explain that the Ba signal was actually lower in S. glauca from the surface mineralization (high in S) compared to the background signal. The plant Ba concentration is also to some degree regulated by plants (Reimann et al., 2018b).

### 3.2. Element ratios in S. glauca

The reference elements (ratio denominators) should not be elements with increased prevalence within the mineralization area, or if they are, the plants should limit uptake to constant levels (homeostasis). Such tuning of element concentrations in plants was previously demonstrated for B, K, Ca, S, Mg, P, Ba, and Cu (Reimann et al., 2018b). Plant concentrations of suitable reference elements should therefore show tight clusters as suggested by the fractile ratio, the duplicate biplot and previous studies (Reimann et al., 2018a).
The plant macronutrients N, P, K and S are probably poor reference elements as they are found in very high concentrations compared to the trace concentrations of target elements, and may consequently show analytical variation that is different from the target elements. The target elements are furthermore present in the plants as complexed cations, whereas N, P and S are mostly present in biological macromolecules such as DNA and proteins. The ratio analysis was therefore limited to the macronutrients Mg and Ca, and the micronutrients Mn, B, Fe, Cu and Mo as reference elements. The micronutrient Zn was not used as reference because it was also a target element.

Fe and Mo duplicates covered a large concentration range with high-end outliers (Fig. SI-8) resembling the target elements and were therefore poor reference elements. In our case, the plant micronutrients Cu and B seem to be good reference elements. Cu and B were the reference elements with the most constant plant concentration in duplicates (Fig. 4), but B concentrations were, unfortunately, rounded to two digits. Cu and B furthermore showed no enrichments in the mineralizations (Table 2). Ca and Mg might also have been used (Fig. SI-8), but they were present in very high concentrations compared to Tl.

Biplots of the Tl/B and Tl/Cu duplicates showed more noise than Tl itself for the highest values (Fig. 4). Data quality was, on the other hand, increased for the low values by using the ratios instead of

| Element (ppm) | Background (ppm) | Presumed deep mineralization (ppm) | Surface mineralization (ppm) |
|---------------|------------------|-----------------------------------|-----------------------------|
| Target elements in S. glauca | Zn | 227 | 254 (1.1) | 278 (1.2) |
| Pb | 0.104 | 0.180 (1.7) | 0.218 (2.1) |
| Ag | 0.0046 | 0.0073 (1.6) | 0.0108 (2.4) |
| Tl | 0.0063 | 0.0106 (1.7) | 0.0762 (12) |
| Target elements in topsoil | Zn | 200 | 117 (0.6) | 727 (3.6) |
| Pb | 12.5 | 15.6 (1.2) | 40.9 (3.3) |
| Ag | 0.179 | 0.213 (1.2) | 0.647 (3.6) |
| Tl | 0.61 | 0.55 (0.9) | 2.44 (4.0) |
| Reference elements in S. glauca | Cu | 5.80 | 5.73 (0.99) | 5.09 (0.98) |
| Ti | 5.80 | 5.73 (0.99) | 5.09 (0.98) |
| Element ratios in S. glauca | Tl/B | 0.000574 | 0.00123 (2.1) | 0.00588 (14) |
| Tl/Cu | 0.0011 | 0.0018 (1.7) | 0.0160 (15) |

Fig. 3. Spatial distributions of relative Tl and Zn concentrations in S. glauca (n = 90). The arrow indicates a possible seepage anomaly from the deep mineralization.

Fig. 4. Duplicate biplots of selected reference elements and target/reference element ratios in S. glauca (n = 15).
absolute Tl concentrations (Fig. SI-5). The correlation coefficient ($R^2$) between the duplicates was 0.53 for Tl when the four largest concentrations were excluded but increased to 0.59 with B as reference (Tl/B, Fig. SI-5) and further to 0.75 with Cu as reference (Tl/Cu, Fig. SI-5). Overall, the Tl/Cu ratio showed the same spatial distributions (Fig. 5) as the absolute Tl concentration (Fig. 3), but with more precise data for the low concentrations, i.e. the background and the deep mineralization domains. This was also reflected in slightly increased enrichment factors for the ratios compared to absolute Tl concentrations (Table 2).

The relatively small effect of using ratios rather than absolute concentrations suggests that much of the signal noise was completely random, for instance from the ICPMS instrument when close to the quantification limit, and only a small proportion was caused by varying extraction efficiency, pipetting, weighing etc.

3.3. Target elements in topsoil

We did not collect duplicate samples of topsoil as our main focus was on *S. glauca*. This means that we could not evaluate soil data quality as rigorously as for *S. glauca*. The soil dataset furthermore had one outlier that was extremely enriched in Pb (3050 ppm), Ag (90.8 ppm) and Bi (144 ppm), slightly enriched in Zn (145 ppm), and not enriched in Tl (145 ppm). The enrichments were not seen in *S. glauca* from this station. This soil sample might represent a true nugget distribution of Pb, Ag and Bi, but the results are more likely caused by a fragment of lead shot that may contain Ag, Bi and other elements (Gillespie and Krishnan, 1969; Peters et al., 1988). Data from the outlier station was therefore excluded from the data analysis.

The soil Zn 0.9-fractile/0.1-fractile ratio of 5.2 was increased (Table 1) compared to concentrations in *S. glauca*, again probably a consequence of Zn being a regulated plant nutrient. Zn may therefore
be a suitable pathfinder element in soil. The Pb 0.9-fractile/0.1-fractile ratio of 2.9 (Table 1) was low and similar to S. glauca. Ag and Tl had 0.9-fractile/0.1-fractile ratios of 7.8 and 6.1 (Table 1) which shows considerable variation in the soil concentrations of these elements. The Ag and especially the Tl fractile ratios were, however, much smaller than in S. glauca (Table 1).

All four target elements identified the surface mineralization from enrichments factors (3.3 to 4.0, Table 2), spatial distributions (Fig. 6 and Fig SI-9) and boxplots (Fig. SI-10). One-tailed t-tests on log-concentrations also showed that the surface mineralization mean was significantly larger than the background mean at the 1% level for all four target elements. The enrichment factors were, however, smaller than in S. glauca. The Zn signal was also rather low and variable (Fig. 6). Unexpectedly, the deep mineralization could not be recognized from enrichment factors (0.6 to 1.2, Table 2) or spatial distributions (Fig. 6 and Fig. SI-9) for any of the target elements. This was confirmed by boxplots for Zn, Ag and Tl, but the Pb boxplot indicated some separation from the background (Fig. SI-10). One-tailed t-tests on log-concentrations confirmed that the deep mineralization mean was not different from the background mean at the 1% level for Zn (p = 0.014), Ag (p = 0.17) and Tl (p = 0.15), but slightly higher for Pb (p = 0.0008).

3.4. Differences between topsoil and plant signals

The S. glauca roots are shallow and mostly present in- or above the sampled soil layer, but the plant concentrations of target elements do not simply reflect the concentrations of the topsoil. This is probably because plants “see” only the bioaccessible fraction of the target elements, which may be a drawback in the case of surface mineralizations where target elements are bound in recalcitrant crystalline material. It may on the other hand be an advantage when aiming for deeply buried mineralizations. The target elements of such mineralizations must be mobile to reach surface layers. Being mobile means that they probably are present in the topsoil in a state where they are accessible for ion-exchange and thus uptake into the plants. At the same time, the recalcitrant, crystalline minerals of the topsoil will interfere less with the signal from the subsurface mineralization when plants rather than soil are used as the exploration medium. This may be why we could detect a weak signal from the presumed deep mineralization in the S. glauca data, but not in the soil data. A similar observation was reported by Anand et al. (2007). It is questionable whether the deep mineralization would be recognizable only from the plant concentrations without preknowledge of the domains, but plant concentrations may prove useful when combined with geophysical and structural mapping.

The signal from plants and soil also differs in that the plant signal is highly dependent on the different uptake mechanisms into the plant roots and the allocation within the plant. Some plants are hyperaccumulators of various elements and as such good indicator species. Tl hyperaccumulators may for instance access some Tl pools that are not simply reflect the concentrations of the topsoil. This is probably because plants “see” only the bioaccessible fraction of the target elements, which may be a drawback in the case of surface mineralizations where target elements are bound in recalcitrant crystalline material. It may on the other hand be an advantage when aiming for deeply buried mineralizations. The target elements of such mineralizations must be mobile to reach surface layers. Being mobile means that they probably are present in the topsoil in a state where they are accessible for ion-exchange and thus uptake into the plants. At the same time, the recalcitrant, crystalline minerals of the topsoil will interfere less with the signal from the subsurface mineralization when plants rather than soil are used as the exploration medium. This may be why we could detect a weak signal from the presumed deep mineralization in the S. glauca data, but not in the soil data. A similar observation was reported by Anand et al. (2007). It is questionable whether the deep mineralization would be recognizable only from the plant concentrations without preknowledge of the domains, but plant concentrations may prove useful when combined with geophysical and structural mapping.

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The signal from plants and soil also differs in that the plant signal is highly dependent on the different uptake mechanisms into the plant roots and the allocation within the plant. Some plants are hyperaccumulators of various elements and as such good indicator species. Tl hyperaccumulators may for instance access some Tl pools that are generally considered non-available to plants (Al-Najar et al., 2003) with reported shoot Tl concentrations (dry weight) of 1.2 ± 0.2 ppm in Brassica oleracea and 2.9 ± 0.5 ppm in Iberis intermedia (Al-Najar et al., 2003). Within the surface mineralization domain, S. glauca in our study had a mean Tl concentration of 0.076 ppm and a maximum concentration of 0.218 ppm. S. glauca therefore is probably not a hyperaccumulator but was nevertheless a reasonable indicator plant. The signal from deep mineralizations may possibly be improved if hyperaccumulators are used in prospecting, but it is unlikely that such species will have a sufficiently broad distribution within the Kangerluarsuk area or in the Arctic in general where the vegetation is often discontinuous and dominated by few common species.

3.5. Subsurface transport mechanisms

Uptake in S. glauca requires that suitable target- and pathfinder elements are present in the shallow root zone, but how are these ions mobilized from a deep orebody and transported to the ground surface? The surface signals from some deeply buried bedrock mineralizations, such as the Kangerluarsuk mineralization, are presumably caused by transfer of pathfinder ions from deep, oxidizing orebodies via water infiltration and convection. The underlying processes are poorly understood, but supposedly, water may enter deep orebodies by a network of cracks in metasedimentary rocks, that have been subjected to regional shear and faulting (Palcsu et al., 2007). The infiltrating water may oxidize the orebody, a process that generates heat. Oxidation of crystalline zinc sulphide to zinc- and sulphate ions, for instance, generates 795 kJ per mole (Mann et al., 2005). From this reaction, one gram of zinc sulphide, will generate sufficient heat for a 2 °C increase of one liter of water which may drive the upwards convection of water and ions towards the surface and eventually to the root zone.

Iion transport may also occur from deep mineralizations by electrochemical processes. Sulphide ore bodies are reducing agents, which create spontaneous potentials associated with surrounding country rocks (Sato and Mooney, 1960). The potential gradient between the reducing sulphide orebody and the country rocks, may result in upward movement of the charged pathfinder ions, leading to geochemical surface anomalies (Hamilton, 1998). Such electrochemical transport may take place where background redox gradients are coupled to strong redox anisotropy. Lithological boundaries, with contrasting redox potentials such as between sulphide ores and metasedimentary rocks, coupled with regional fault planes and fault gouge (Hamilton, 1998), could suffice in creating electrochemical mass transport in unsaturated environments such as bedrocks. We would therefore expect detectable signals along faults, even from deeply buried orebodies as demonstrated in the present study for the deep Kangerluarsuk mineralization.

4. Conclusions

The surface mineralization could readily be identified by element analysis of the omnipresent plant S. glauca. The strongest signal came from the pathfinder element Tl. The target elements Pb and Ag gave only weak signals. The target element Zn gave no signal, probably because Zn is also an essential plant nutrient under active regulation of the cellular concentrations by the plant. The use of mineral plant micronutrients as reference elements gave a small reduction of analytical noise in Ti/Cu and Ti/B ratios at low Tl concentrations, and consequently improved data quality slightly compared to absolute Tl concentrations. The small effect of using ratios rather than absolute concentrations indicated that most of the signal noise was completely random and only a small proportion was caused by varying extraction efficiency, pipetting, weighing etc. The presumed deep mineralization probably would not be recognized solely from the weak signal in S. glauca, but plant concentrations may prove useful in combination with a detailed geophysical model. Tl, Zn, Pb and Ag concentrations in topsoil showed the surface mineralization but failed to identify the deep mineralization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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