Innovation-critical metals and minerals in greisen-altered Dala granites

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Cover photo: Indium-rich greisen-altered granite at Norra Hållen 1.
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SAMMANFATTNING

I slutrapporten av regeringsuppdraget ”Kartläggning av innovationskritiska metaller och mineral” (SGU:s dnr: 311–2379/2016, Näringsdepartementets dnr. N2016/06368/FÖF) från december 2018 konstaterades att Sverige har geologisk potential för ett flertal innovationskritiska metaller och mineral, samt att det finns ett antal malmberäknade fyndigheter i Sverige där dessa råmaterial ingår. Bergslagen är en av Sveriges viktigaste malmprovinser där gruvdrift har pågått i mer än 1 000 år. Utöver att vara en region med många järn-, basmetall- och ädelmetallfyndigheter, har Bergslagen också potential för innovationskritiska metaller och mineral.

Den globala efterfrågan på innovationskritiska metaller och mineral är rekordhög och förväntas öka även framöver, allt eftersom ny teknik utvecklas. Trots att förekomster av innovationskritiska metaller och mineral inte är ovanliga i berggrunden är utvinningen av dessa koncentrerade till ett fåtal länder, vilket kan innebära störningar i försörjningskedjan vid konflikter.

I samband med SGUs inventering av Dalarnas malm och mineral uppmättes den högsta halten av indium för hela Bergslagen i greisenomvandlad Dalagranit vid Norra Hållen 1 (Ripa m.fl. 2015). Det bestämdes att en provtagning riktad mot Dalagranit med greisen skulle vara intressant generellt sett ur perspektivet förekomster av innovationskritiska metaller och mineral. De flesta bergartskemiska analyser som fanns hos SGU var av äldre datum då dessa grundämnen inte analyserades rutinmässigt eller så var tidigare provtagning av Dalagranit inte fokuserad mot mineraliseringar.

I denna studie av greisenomvandlad Dalagranit, i västra Dalarna, har ett flertal innovationskritiska metaller dokumenterats i höga koncentrationer, till exempel indium, vismut, tenn och volfram. Det påvisades även höga halter av basmetallerna koppar, zink och bly, samt av ädelmetallerna guld och silver. Förutom tenn och volfram har till stora delar Dalagraniterna inte varit föremål för prospektering efter några av de andra metalliska grundämnena. Greisenomvandling med intressanta metallhalter har också upptäckts inom ett helt nytt område med stora volymer Dalagranit.

Uppdatering av SGUs databaser (malmkemi, bergartskemi, geofysiska data) sker kontinuerligt allt eftersom resultat från nya analyser och mätresultat kommer in från SGUs Bergslagsprojekt.

De här i rapporterade undersökningarna tar inte ställning till om förekomsterna är brytvärda, utan detta får eventuella framtida prospekteringsinsatser avgöra.

INTRODUCTION

In connection with the SGU survey of Dalarna's ore and mineral resources, the highest content of indium for the entire Bergslagen at the time, was measured in greisen altered Dala granite in Norra Hållen 1 at 98 ppm (Ripa et al. 2015). It was decided that sampling directed at Dala granite showing greisen would be of general interest, from the perspective of occurrences of innovation-critical metals and minerals. Most of the lithogeochemical analyses that existed at SGU were of earlier dates when these elements were not routinely analysed or previous sampling of Dala granite was not focused on mineralised parts. An article states that there are anomalous levels of indium at Norra Hållen (Cook et al. 2011) and reference is made to Ahl et al. (1999) as the source for this. However, there is no mention of Norra Hållen in the later reference or information that indium was analysed at all, since indium was rarely analysed at that time.

In the past, exploration has primarily been carried out for tin and tungsten of the Dala granites and in their greisen systems, mainly during the 1980s (e.g. Hammergren & Petersson 1982, Hammergren 1984). Many of the elements that are now referred to as innovation-critical were not analysed in the 1980s. There was no provision for them either, since very few products required these innovation-critical metals, compared to modern, digital society.

All lithogeochemical analyses are displayed in the map viewer "Bergartskemi" at <https://apps.sgu.se/kartvisare/kartvisare-bergartskemi.html>.

A shorter version in Swedish is part of a government mission (Claeson et al. 2020).

GREISEN ALTERATION AND ORE-FORMING PROCESSES

There are several different types of ore-forming processes in connection with intrusions of, for example, granites, one of which is referred to as greisen alteration. Mainly hydrothermal alteration occurs in greisen systems. The greisen is formed in granite at the end of the crystallization, when a high concentration of fluids and gas phases have been built up, which during a degassing phase or boiling, transforms the already formed parts that these hot solutions penetrates (e.g. Pirajno 2009). In conjunction with degassing, metal ions are moved as complexes in fluids and gas phases and precipitated when any physical or chemical parameter is changed, or if there is a strong reaction with another rock that is hit by the greisen solution. Examples of such are carbonate and metasedimentary rocks. The solutions also infiltrate surrounding bedrock and can form mineral-isation's in them. Most tin-tungsten-dominated greisen granites are associated with a source material of sedimentary rocks. Greisen-mineralised systems can display zonation, with a lower zone of tin + molybdenum, which upwards or sometimes laterally form tungsten + bismuth, to finally crystallise copper + zinc + lead in the higher lying parts of the system (e.g. Pirajno 2009). Sometimes gold is present in greisen systems.

Ore-forming processes related to granitic intrusions that undergo hydrothermal activity may also include skarn formation, brecciation, dikes, fracture fillings, veins and disseminated deposits in the granite itself and its surroundings. All of these are relatively near-surface phenomena. Boiling of the magma and unmixing of a H_2O-rich phase, the hydrothermal solution, from the volatiles dissolved in the magma only occurs during decompression. The magma starts to boil when it reaches a pressure in the hydrothermal solution corresponding to the surrounding pressure, which cannot be all too high. That is, only near-surface intrusions down to 5–7 km depth can normally exhibit this type of ore formation (e.g. Pirajno 2009).

THE DALA GRANITES

The Dala granites are usually divided into three types; Järna-, Siljan- and Garberg granite and the older Järna granite is separated from the younger intrusions of Siljan- and Garberg granite (Ahl et al. 1999, Lundqvist & Persson 1999, Högdahl et al. 2004). All types are considered to belong to different phases of the Transscandinavian magmatic belt (e.g. Högdahl et al. 2004). Järna granite is the oldest and is considered to have intruded at significant depth in the crust about 1.79 Ga ago (e.g. Persson & Ripa 1993, Ahl et al. 1999, Lundqvist & Persson 1999). It follows that Järna granite will probably never exhibit any greisen alteration that can be related to its own magmatic stage. Siljan and Garberg granites are more fractionated granites and intruded at relatively shallow levels about 1.70 to 1.68 Ga ago (e.g. Ahl et al. 1999, Lundqvist & Persson 1999, Ripa et al. 2008). They are associated with the contemporary volcanic Dala porphyries, in spatial position and their petrogenesis (e.g. Ahl et al. 1999, Lundqvist & Persson 1999, Högdahl et al. 2004). It is known that there are smaller, polymetallic greisen mineralisations in Siljan and Garberg granite (e.g. Ahl & Sundblad 1997, Högdahl et al. 2004, Ripa et al. 2015). Rätan granite, which is not included among the Dala granites, is located north and northeast of these and is contemporary with the Siljan and Garberg granite (e.g. Ahl et al. 1999, Lundqvist & Persson 1999). Rätan granite is in some publications not considered to have any gresien associated with its magmatic stage (e.g. Ahl et al. 1999, Lundqvist & Persson 1999, Högdahl et al. 2004), whereas the opposite is stated in others (e.g. Ahl & Sundblad 1997). Most likely there are late-magmatic H_2O-rich solutions in all of them and that it is only the extent of greisen alteration, and the trace-element content that differs. However, the near-surface intrusions should have better well-developed greisen systems.

Sampling

The sampling was focused on mineralised parts where greisen alteration was noted in Dala granite during previous exploration of the bedrock. Even in some cases of this study, the rock has been analysed in the vicinity of or in older volcanic rocks, where granite and greisen solutions from Dala granite and skarn formation have been noted. This selection means that sampling took place outside the Bergslagen area, since Dala granite also occurs north of it (fig. 2). A sample of Rätan granite was analysed (fig. 2). A variety of innovation-critical metals and minerals are found in elevated levels as well as gold and base metals in the currently investigated rocks (Table 2, see *Lithogeochemistry and petrophysical properties*). Known greisen of some visited outcrops were too thin to sample for lithogeochemical analysis (fig. 1). The weight of samples collected in this study varies from 2.33 to 4.40 kg.

Figure 1. Thin, grey, fracture-filling greisen in unaltered red Dala granite (6747689/469758). Photo: Dick Claeson.

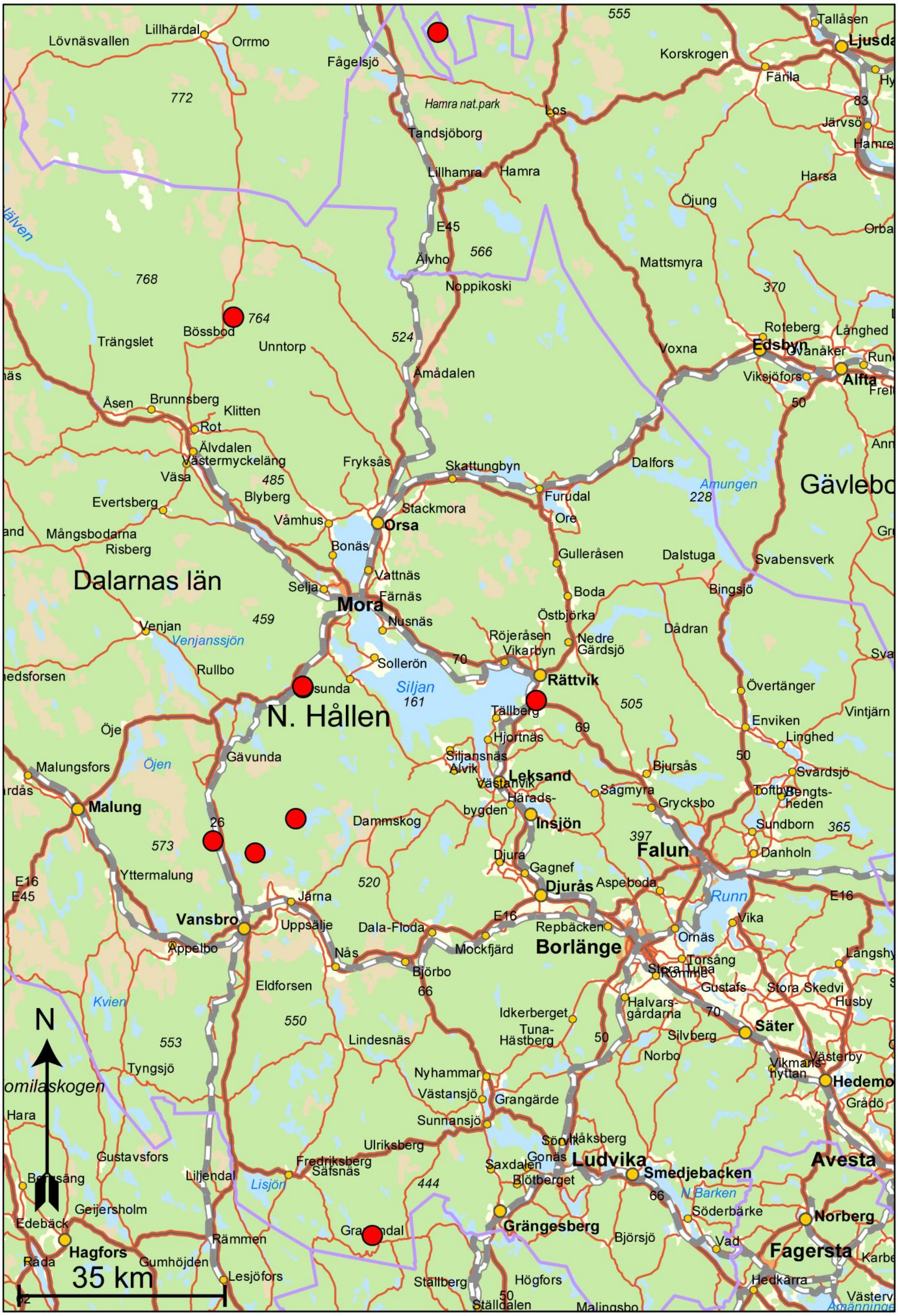

Figure 2. Sampling sites shown as red circles of greisen-altered rocks and Rätan granite furthest to the north.

Norra Hållen

Norra Hållen 1 and 2 are mineralogically distinctly different, where the former shows much higher contents of chalcopyrite and much lesser amounts of epidote than the latter, judging from the waste rock seen at the outcrops (fig. 3). The greisen altered granite is grey to green and red to greyish red when unaltered. Blue-coloured fluorite is present at both locations.

The lithogeochemical analyses show that the area at Norra Hållen has high anomalous levels of indium. Four different samples have levels from 24 to 98 ppm of indium, which are significant in comparison with an estimate of the content of the Earth's crust of 0.05 to 0.20 ppm (Alfantazi & Moskalyk 2003). There is no background value for Dala granite since indium has not been analysed until the last decades. There are also enriched levels of tantalum 7.6–12 ppm, copper 0.7–1.51 percent and zinc 0.5–1.57 percent at Norra Hållen (Table 2). Norra Hållen 1 shows anomalous levels of silver, 36–67 ppm and of bismuth, 287–462 ppm.

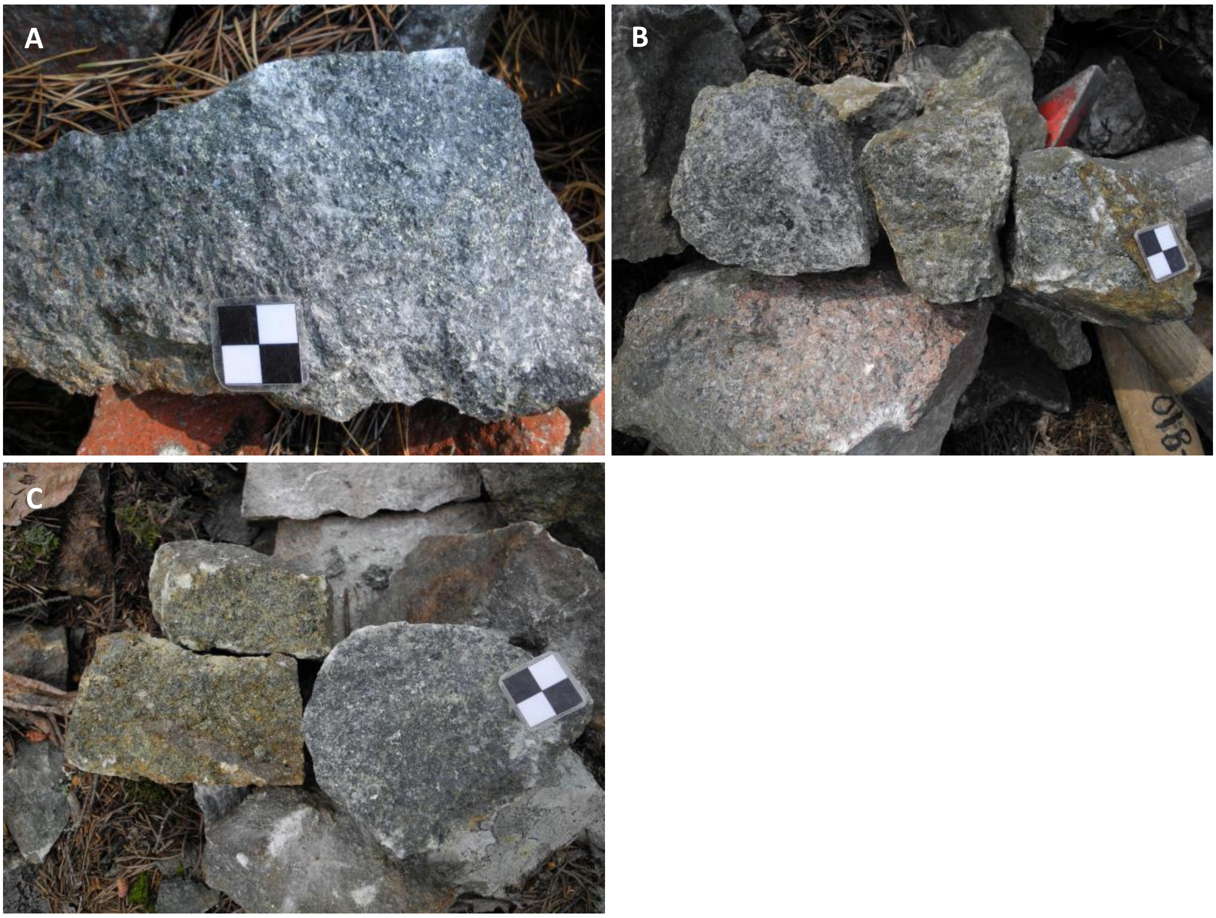

Figure 3. Waste rock at Norra Hållen 1, **A.** and **B.** indium-rich greisen-altered granite with chalcopyrite and sphalerite (6748687/467370), and **C.** at Norra Hållen 2 indium-rich greisen-altered granite with mostly sphalerite and epidote (6748496/467427). Photo: Dick Claeson.

Eldberget-Van

Several studies and prospecting efforts have been performed at the Eldberget-Van area (Edberg & Edlund 1984). The granite is massive, red, finely medium- to medium-grained, and equigranular, whereas the greisen is grey, fine-grained to medium-grained (fig. 4).

Very high concentrations of gold appeared in the analysis, 8.17 ppm at Eldberget, with anomalous levels of silver 80 ppm, arsenic >10000 ppm, and interesting concentrations of the base metals zinc and lead, up to 2.97 and 2.3 percent respectively (Table 2).

Fagerberget

Red to greenish red, massive, equigranular granite occurs at Fagerberget. The greisen alteration has turned the granite grey (fig. 5).

High levels of bismuth were measured at Fagerberget, 162 ppm, with elevated levels of tungsten ta 170 ppm and tin 136 ppm (Table 2).

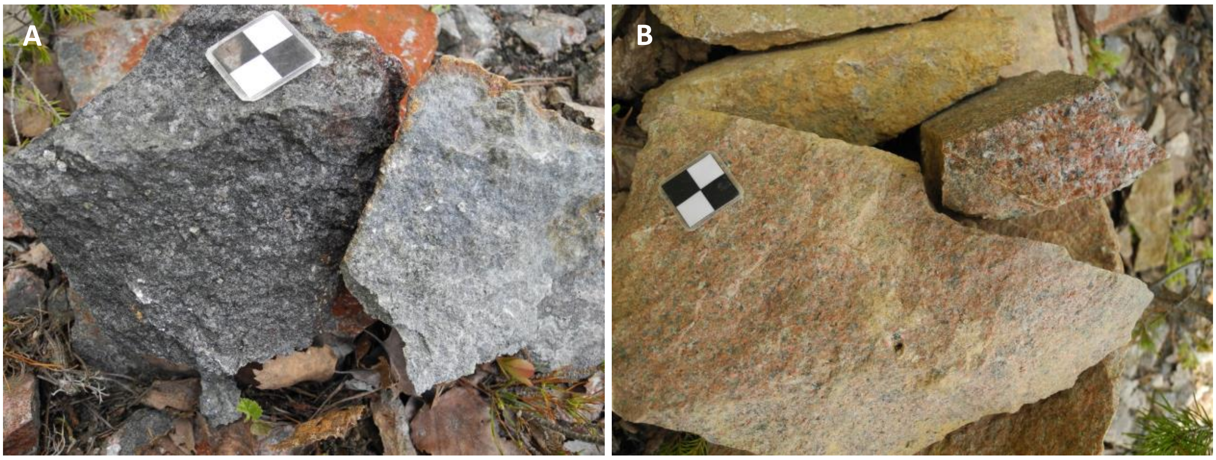

Figure 4. Waste rock at Eldsberget. **A.** Gold-rich, arsenopyrite-bearing greisen-altered granite with sphalerite and galena. **B.** Red unaltered granite (6722645/452299). Photo: Dick Claeson.

Figure 5. Waste rock at Fagerberget. **A.** Tungsten and bismuth anomalous greisen-altered granite. **B.** Close-up of greisen-altered granite (6720769/459428). Photo: Dick Claeson.

Flatberget

Red, massive, equigranular granite occurs at Flatberget. The greisen is seen as grey to greenish grey alteration with some epidote (fig. 6A). Miarolitic cavities are present with infilling of quartz and purple fluorite (fig. 6B). Fluorite also occurs as fracture filling and in the groundmass.

The sample from Flatberget showed anomalous content of tin at 1310 ppm (Table 2).

Getgruvan

Massive, medium-grained, equigranular, red granite occurs at Getgruvan. The greisen is grey (fig. 7).

The Getgruvan shows elevated total amount of rare earth metals + yttrium at 1060 ppm, where yttrium makes up more than a third (Table 1). The sample had elevated content of tin at 200 ppm (Table 2).

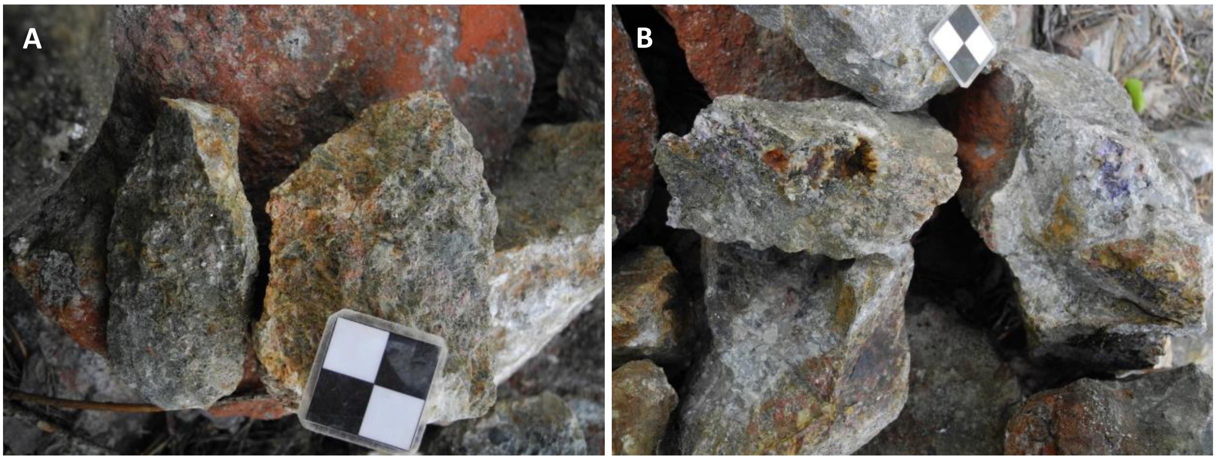

Figure 6. Waste rock at Flatberget. **A.** Greisen-altered granite. **B.** Greisen-altered granite with quartz and fluorite in miarolitic cavities (6726562/466221). Photo: Dick Claeson.

Table 1. REE and Y content in ppm of sample from Getgruvan.

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
107	262	30.3	116	27.3	0.45	28.7	5.16	38.1	9.47	33.5	5.4	37.5	354

Figure 7. Waste rock of grey, greisen-altered granite at Getgruvan (6746355/506470). Photo: Dick Claeson.

Skråckbäcken

A meter-wide dike showing greisen alteration was found at Skråckbäcken next to Gyrisberget, in an area that had not previously been subjected to exploration of the Dala granite. An old find from the Mineraljakten at 6810492/455789 was the target for sampling but at these coordinates no outcrops could be found. Therefore, a wider area was searched in order to prove or disprove the reported greisen system at this location. The present outcrop was found c. 400 m southwest and if they are identical is not known. Sphalerite and galena are clearly observed in the greisen-altered part of the granite. The granite is fine-grained to finely medium-grained, massive, equigranular, red (fig. 8). The alteration is clearly seen as unaltered pale red to red granite versus its often grey to greenish-grey greisen part (fig. 8). The contacts between greisen-altered and unaltered granite, varies from razor-sharp to fuzzy in appearance.

The sample shows interesting levels of the base metals zinc and lead, 1.8 and 1.72 percent, respectively, as well as 16 ppm silver and 21 ppm bismuth (Table 2). The magnetic susceptibility of the mineralised greisen is very low and the unaltered granite higher (Table 3).

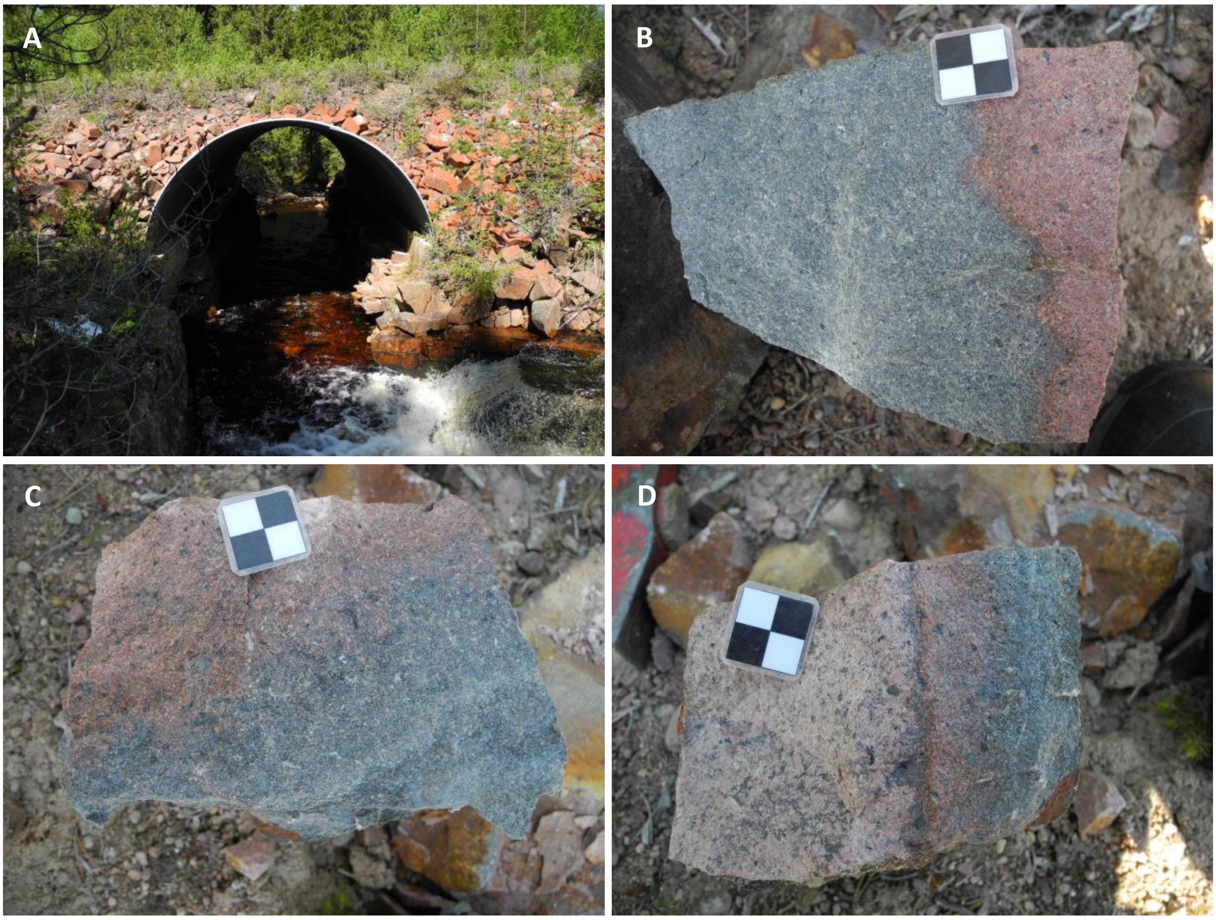

Figure 8. A. Road tunnel with blasted rock fragments of the Dala granite displaying greisen-altered granite at Skråckbäcken. **B–D.** Different appearance of contacts between greisen-altered and unaltered granite, razor-sharp to fuzzy (6810303/455432). Photo: Dick Claeson.

Örnbotjärnen (Garpkölen södra)

The Rätan granite was sampled at a known mineralisation, Garpkölen södra, about 400 m east of Örnbotjärnen. The sampled granite is fine-grained, equigranular, red to light red, whereas in the surrounding outcrops a coarser, darker, and K-feldspar phenocryst-bearing granite is present. The mineralisation mainly consists of molybdenite in Rätan granite (fig. 9). The aggregates of molybdenite show subordinate amounts of pyrite, pyrrhotite, and chalcopyrite.

The lithogeochemical analysis shows unusually high rhenium levels. The sample has 1120 ppm molybdenum and 3.33 ppm rhenium, respectively (Table 2). Normally, rhenium resides in columbite, tantalite, or molybdenite (and of course in PGE associations), the only element that is elevated in the analysis is Mo, Nb and Ta are at normal levels for these granites. If all rhenium is allocated to molybdenite, it is c. 0.30 percent, which is a very high content for that mineral (Berzina et al. 2005). However, nothing is known about the volume of the molybdenite-bearing Rätan granite at the site (Bjurstedt 1979).

Sörbergshöjden

Sörbergshöjden is located within an area of Järna granite (Persson & Ripa 1993). A mix of pyroxene-rich garnet-bearing skarn, metavolcanic rock, and granite was sampled among the waste rock (fig. 10). Strings of chalcopyrite were noted. Pyroxene, garnet, epidote, amphibole, and other skarn minerals are present. Exactly how much greisen solutions have contributed to the content or redistribution of metals is not known, if any. Bismuth and bismuthinite were reported by Igelström (1884). Anomalous amounts of gold have been reported prior to this work (Hammergren 1987, Bergman 1990, T. Bergman pers. comm. 2020). Mineralogical studies show opaque minerals dominated by chalcopyrite, pyrite, bismuthinite, and sphalerite, with minor amounts of chalcocite, bornite, and covellite (Bergman 1988). Most chalcocite was rimmed by emplectite ($CuBiS_2$). Analyses using SEM-EDS indicate that tellurobismuthite (Bi_2Te_3) is present, a mineral close to carrollite ($CuCo_2S_4$) in composition of the solid solution series between carrollite and linnaeite ($Co^{+2}Co^{+3}{}_2S_4$) with some analyses showing minor Ni substitution, and some sulfosalts were also present (T. Bergman pers. comm. 2020).

Figure 9. Waste rock at Örnbotjärnen. **A.** Aggregates of molybdenite in Rätan granite. **B.** Close-up of molybdenite aggregates (6858128/489930). Photo: Dick Claeson.

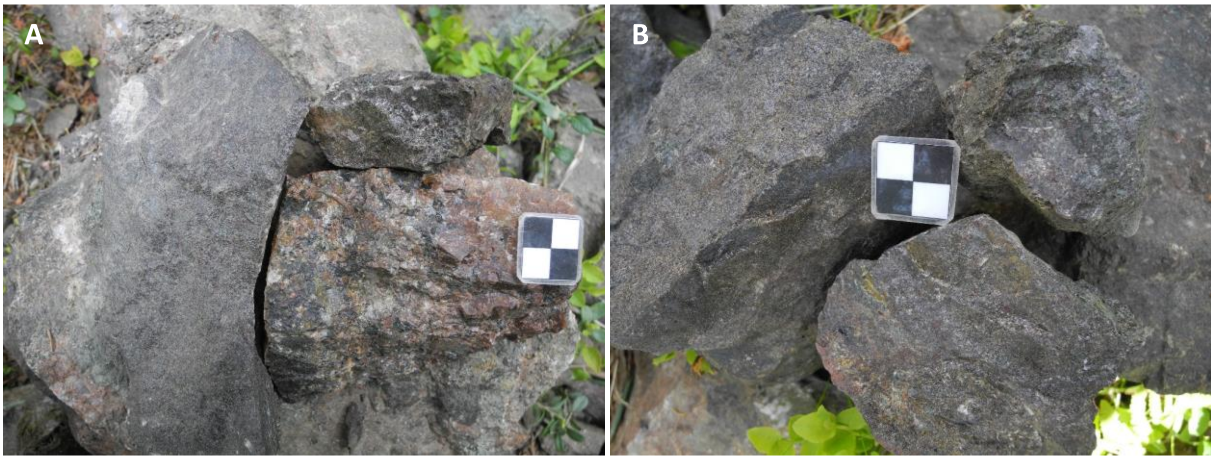

Figure 10. Waste rock at Sörbergshöjden. **A.** Granite, pyroxene skarn, and a metavolcanic rock. **B.** Pyroxene skarn (6656718/479036). Photo: Dick Claeson.

The lithogeochemical analysis shows very high concentrations of gold at 5.14 ppm, high levels of bismuth at 2970 ppm, and anomalous cobalt content of 280 ppm at Sörbergshöjden (Table 2).

The suggestion in Ripa et al. (2015) that scheelite is present at Sörbergshöjden is not substantiated by the observations made during this work (2 ppm W) or mentioned in Igelström (1884), Hjelmqvist (1966), nor Bergman (1988, 1990).

Lithogeochemistry and petrophysical properties

The samples from this study and some additional, older samples from Dala granite with indication of some greisen alteration were plotted in different diagrams to document the variability among them (fig. 11–13). CIPW-normative calculations indicate that most samples are of either alkali feldspar granite composition or quartz-rich granitoid composition, some of syenogranite (fig. 11). In the plot of modified alkali–lime index versus SiO_2 (Frost et al. 2001) the samples spread all over and no trend can be imagined (fig. 12A). Most samples plot in the ferroan field (fig. 12B). Those samples with suitable compositions plot within the peraluminous field (fig. 13). Some of the scatter in these plots is probably due to the greisen alteration that remobilise elements and redeposit them in other parts of the greisen system (e.g. Pirajno 2009).

The multi-element diagram shows the granites signatures with negative anomalies for Ba and Nb, troughs for Sr-P and Eu -Ti, mostly distinct positive anomalies for Pb (fig. 14). In the multi-element diagram several samples have P_2O_5 below detection limit of <0.01 ppm and is thus not accurately displayed, they should have a distinct trough for Sr and P as the rest of the samples (fig. 14). The pyroxene skarn-dominated sample from Sörbergshöjden differs with significantly lower content of Cs, Rb, K, and higher Eu, therefore showing a dissimilar pattern in the multi-element diagram.

In the REE diagram, all greisen-altered granite and Rätan granite samples show significant negative Eu-anomalies, enriched LREE, and rather flat HREE patterns (fig. 15). This may be due to the influence from magmatic hydrothermal fluids (Yang 2019) or to fractionation of the granite magma, or a combination of the two. The pyroxene skarn-dominated sample from Sörbergshöjden differs with a weak negative Eu-anomaly and lesser enriched LREE pattern.

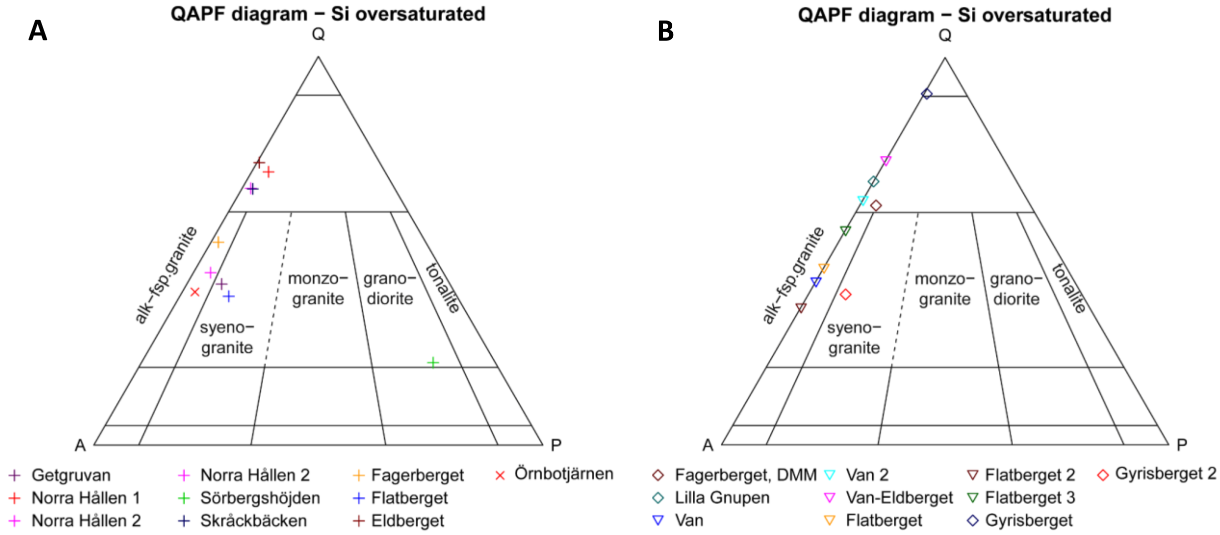

Figure 11. CIPW-normative calculations plotted in Q-A-P-diagram (Le Maitre et al. 2002). **A.** Samples from this study and **B.** older samples of Dala granite with indication of greisen.

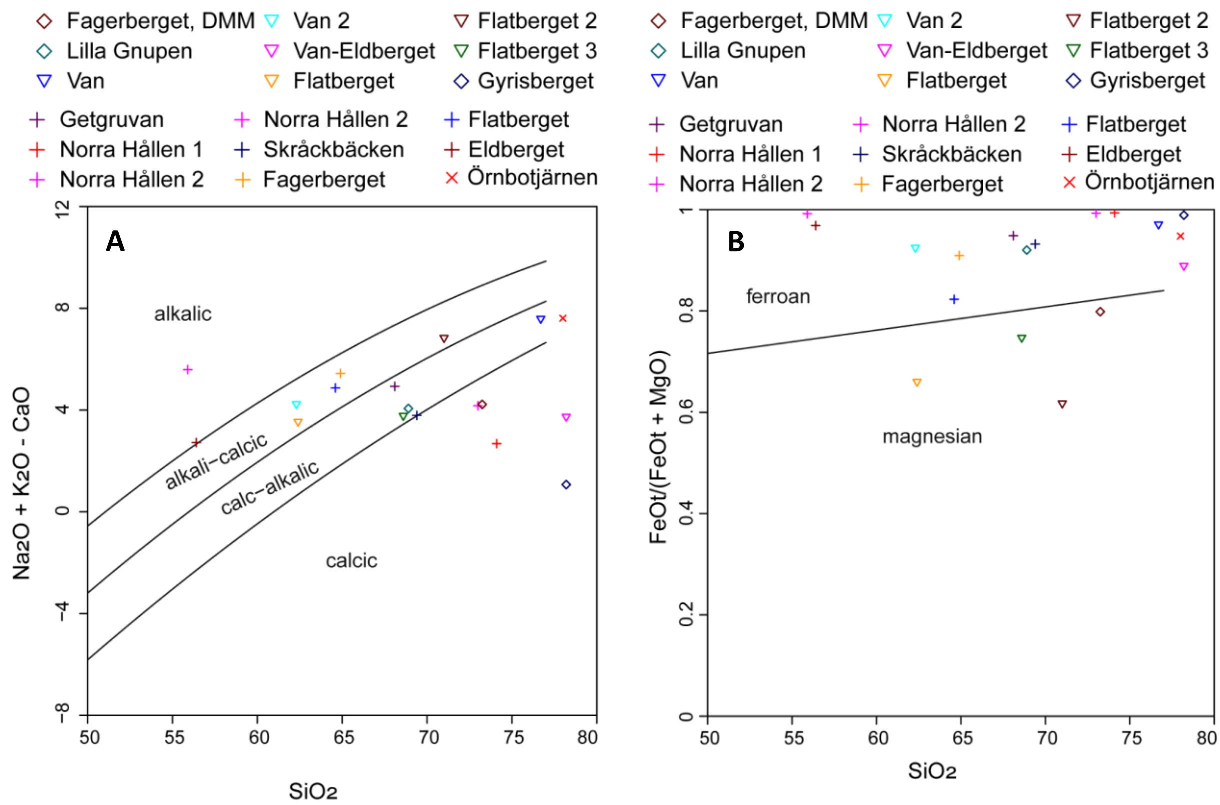

Figure 12. A. Plot of modified alkali–lime index versus SiO_2 (Frost et al. 2001). **B.** Plot of Fe* versus SiO_2 (Frost et al. 2001).

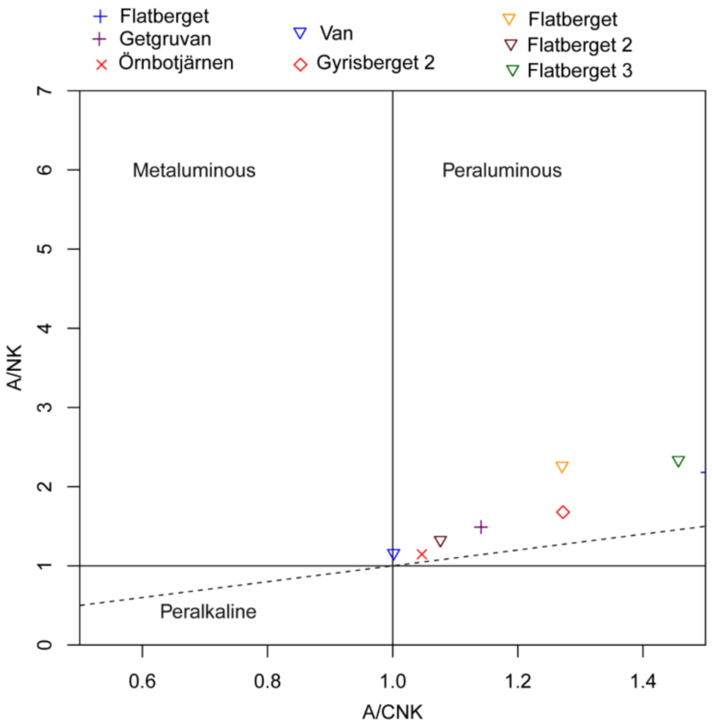

Figure 13. Plot of molecular $Al_2O_3/(Na_2O + K_2O)$ versus molecular $Al_2O_3/(Na_2O + K_2O + CaO - 1.67P_2O_5)$ (Shand 1943).

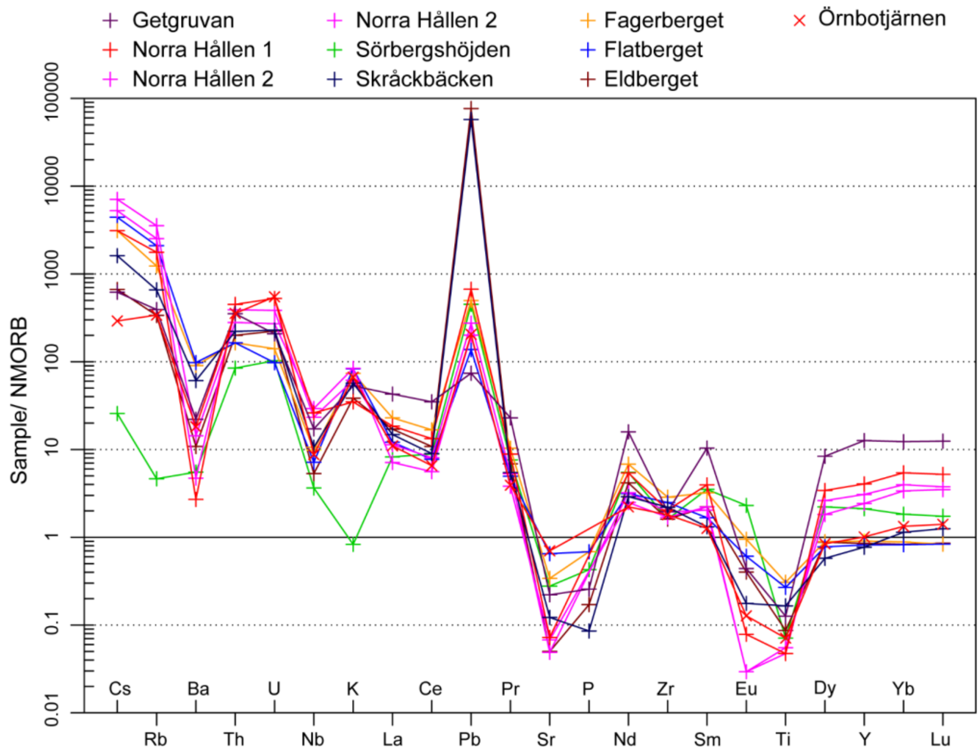

Figure 14. Multi-element diagram of greisen-altered samples and Rätan granite. Normalized to N-MORB (Sun & McDonough 1989).

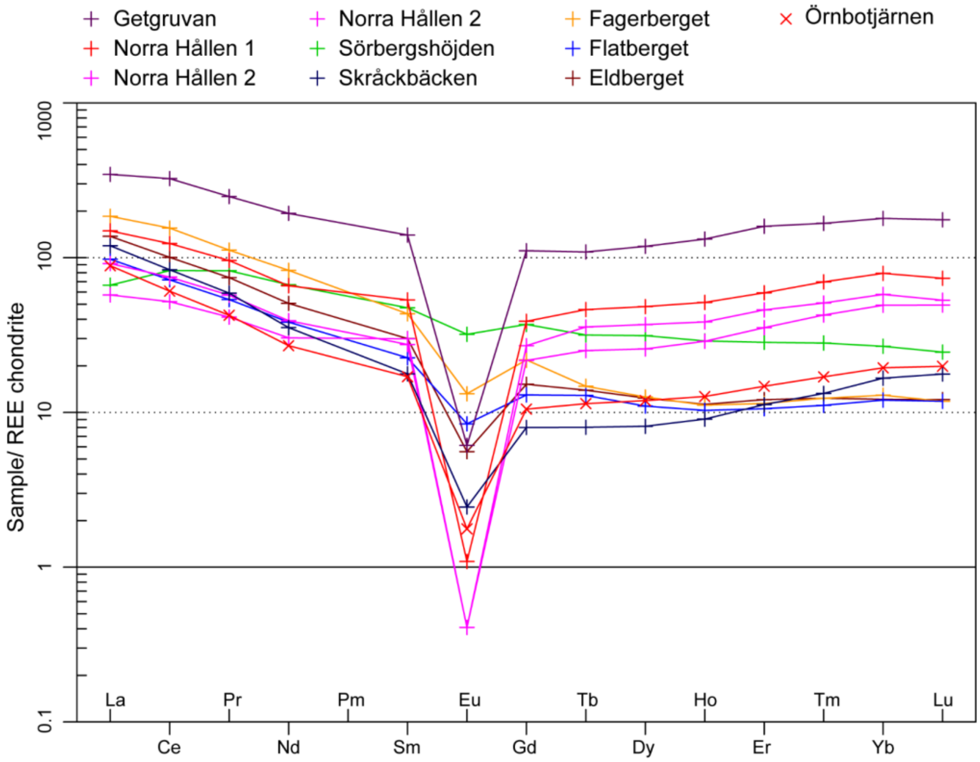

Figure 15. REE diagram of greisen-altered samples and Rätan granite. Normalized to chondrite (Boynton 1984).

The survey shows that there are opportunities to find a variety of innovation-critical metals in greisen-altered Dala granite. In order to evaluate whether there are enough volumes of greisen-altered granite for an ore deposit, or how the shown variations between the different metals occur within the greisen systems, a much greater effort is needed and other methodologies must be used. In Finland, exploration related to greisen systems in large, anorogenic granitic intrusions has resulted in ore deposits (e.g. Cook et al. 2011, Valkama et al. 2016).

Petrophysical samples were taken in connection with the field work in order to characterize the greisen-altered mineralisations and for future use in geophysical work (Table 3). An increased content of metals results in a significantly higher density in most of the samples, where Fagerberget, Getgruvan and Örnbotjärn are more comparable to ordinary granite. All have low magnetic susceptibility and natural remanent magnetisation.

Table 2. Selection of values from lithogeochmical analyses of greisen-altered and molybdenite-bearing granite, this study. All in ppm but S in percent.

	Sörberget 1	Eldberget 2	Fagerberget 3	Flatberget 4	Norra Hållen 2 5A	Norra Hållen 2 5C	Norra Hållen 1 7	Getgruvan 8	Skråck-bäcken 9	Örnbo-tjärnen 10	Norra Hållen 1 Dalarna malm och mineral
Au	**5.14**	**8.17**	0.009	0.004	0.001	0.003	0.003	0.001	0.001	0.001	<0.2
Cu	**1 960**	719	264	281	449	264	**7 120**	32	225	87	**15 100**
Pb	136	**23 000**	150	41.3	60.2	82.6	201	22.2	**17 250**	61.5	409
Zn	387	**29 700**	66	1 240	**9 860**	**8 030**	**4 640**	38	**18 000**	100	**15 700**
S	0.2	4.64	1.11	0.29	0.79	0.84	1.05	2.32	1.05	0.44	–
Sn	44	12	136	**1 310**	50	46	170	200	4	2	12.4
W	2	9	**170**	21	19	10	21	19	5	2	6.61
Ag	**17.9**	**80.1**	0.87	5.79	1.13	0.78	**36**	0.29	**15.5**	0.3	**66.8**
As	79.6	**>10 000**	127	3.1	8.3	7	1.9	2.5	0.6	5.7	2.6
Bi	**2970**	3.4	**162**	**26.9**	6.99	6.03	**287**	1.48	**20.7**	0.39	**462**
Co	**280**	<1	2	1	2	2	2	2	5	7	4.6
In	0.206	0.119	0.082	0.353	**32.1**	**23.6**	**48.5**	0.075	0.13	0.118	**98**
Mo	2.43	**249**	3.7	0.83	45.9	13.4	9.66	30.9	0.49	**1 120**	13.1
Te	**11.4**	0.02	0.35	0.04	0.02	0.03	0.84	0.12	0.33	0.02	1.6
Re	<0.001	0.004	0.001	<0.001	0.003	0.005	0.006	0.011	0.001	**3.33**	0.001
REE+Y	245	209	298	160	224	231	386	**1 060**	171	146	–

Table 3. Petrophysical properties of greisen-altered and molybdenite-bearing granite

Provpunkt	Density (kg/m3)	Magnetic susceptibility (µSI)	Natural remanent magnetisation (mA/m)
Sörberget	3 653	1 941	19.7
Eldberget	2 774	230	13.8
Fagerberget	2 563	318	36.0
Flatberget	2 727	212	10.0
Norra Hållen 1	2 739	271	24.9
Norra Hållen 2A	2 931	1 006	8.7
Norra Hållen 2B, green, epidote-rich	2 761	432	15.4
Getgruvan	2 642	117	46.2
Skråckbäcken	2 767	292	26.6
Örnbotjärnen	2 607	183	28.9

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