

Article

Pyrite-Goethite Alteration in Supergene Oxidation Processes in Till: Elemental Distribution and Evaluation of Goethite Usability as a Fingerprinting Tool for Vectoring Mineral Deposits

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Abstract: In the formerly glaciated terrains in the northern hemisphere and countries such as Finland, till is the most common sediment covering the bedrock. Specifically, indicator or heavy mineral studies utilising till as a vector for mineral deposits undercover have been successful. The pyrite trace-element composition from in situ mineral analyses has been shown to be an effective discriminator between different mineral deposit types, and this has led to research using heavy mineral pyrite in till to identify potential mineral deposits in a given area. However, pyrite is easily oxidised in till beds, and thus, alternative methods should be considered. Goethite pseudomorphs are more commonly found in the till sediments as remnants after pyrite oxidation. This study evaluates trace element compositions of goethitised pyrite recovered in the till beds from central Lapland in northern Finland. Intra-grain trace-elemental variations gathered using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) between the intact pyrite core and oxidised rim demonstrated complex dynamics and variations between different trace-element values. For example, Cu, V and Mn exhibited elevated trace-element values in the goethite rim compared to the pyrite core. However, elemental ratios such as Ni/As and Co/Ni remain stable between the pyrite core and oxidised rim. Therefore, these ratios have the potential to be used as a discriminating tool between the pyrite core and oxidised rim. In addition, nanoscale variabilities using focused ion beam (FIB) and transmission electron microscopy (TEM) were utilised to inspect possible nano inclusions within the studied heavy mineral grain. The FIB and TEM studies revealed a nanocrystalline pyrite nodule observation within the goethite rim.

Keywords: heavy minerals; pyrite; goethite pseudomorph; trace-elements; fingerprinting



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1. Introduction

As the demand for new environmentally friendly and non-invasive exploration methods has increased in the current political climate, surficial geochemical tools such as till geochemistry and till indicator mineral studies are some of the most viable methods, especially in the formerly glaciated terrains in the Nordic countries (e.g., Finland and Sweden), where the bedrock is mostly covered with glacial till. In these environments, geochemical exploration methods, especially indicator mineral exploration, have proven to be valuable [1–10].

Pyrite (FeS₂) is one of the most abundant minerals in various mineral deposits, and they can form under various conditions [11,12]. Understanding pyrite reactivity processes in the natural environment is important for such applications as the production of acid mine waste waters and the flotation processing in the mining industry [13]. All of these processes involve reactions at the surface of the pyrite, and therefore, it is important to understand the fundamentals of these processes [13,14]. Pyrite is a semiconductor, meaning

the electrons are transferred from sulphur atoms at an anodic site, where oxygen atoms form sulphony species via the crystal, to cathodic Fe(II) sites, where they are acquired by the oxidant species [15]. Furthermore, the reaction at the cathodic sites is the rate-determining step for the overall oxidation process. Pyrite occurs in nature and is commonly found in three different crystal forms. These are cubic (1 0 0), octahedral (1 1 1) and pyritohedral (2 1 0). Many studies have been conducted on the simulated oxidation behaviour of pyrite crystal surfaces in laboratory environments including, e.g., density functional theory [16]. In addition, Sit et al. [17] showed that the successive oxidation by O₂ and H₂O of pyrite surfaces (1 0 0) results in the formation of SO₄^{2−}. However, as it is the most studied pyrite surface, it cannot fully represent all the normal oxidation processes in the natural environment.

Multiple previous studies have proven that the pyrite microstructure is complex and can record valuable information about the chemical and isotopic evolution of the precipitation processes of fluids [18–20]. Trace element contents and isotope ratios within sulphide minerals have proven effective in identifying stages of ore mineralisation and delineating geochemical signatures associated with diverse ore deposits [19,21–28]. The concept of mineral fingerprinting is based on trace element and isotope analyses of minerals having different geochemical signatures related to their crystallisation environment. Furthermore, recent studies of gold deposits in northern Finland indicate that sulphide trace elements and isotopic compositions record the mineralisation stages within single deposits [27,29,30].

The pyrite susceptibility to complete or partial oxidation in abiotic environments, as stated by Rosso and Vaughn, 2006 [31], can represent an obstacle to its usefulness as an indicator mineral. However, some studies have demonstrated that pyrite can be preserved locally in till samples [23,32–36]. In many cases, especially in the shallow till beds above the groundwater level, the pyrite grains have been oxidised to goethite (FeOOH), locally preserving the original pyrite core [28]. A comprehensive study of the mechanism of pyrite oxidation and leaching has been reviewed by Chandra and Gerson ([37] and references therein). The oxidation and leaching rates are predominantly influenced by factors such as the solution redox potential (Eh), pH, type and concentration of oxidants, hydrodynamics, grain size, surface area relative to the solution volume, temperature and pressure. Notably, solution redox potential emerges as the primary determinant, consistent with the electrochemically controlled nature of the process, and exhibits a direct correlation with surface area-normalised rates. Furthermore, investigations employing mixed-mineral systems underscore the significance of electrochemical phenomena in driving the oxidation process [37].

This study aimed to determine the trace-element compositions and their mobilisation and or immobilisation within pseudomorphic goethite heavy mineral grains recovered from the till bed from the area of the Petäjäseltä Au occurrence Central Lapland belt (Figure 1: see also [28]). In particular, one grain was selected for a more detailed study. Furthermore, a robust database was created to evaluate the results statistically. Electron microprobe (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were used to achieve the most robust trace-element composition of the grains. In addition, to study possible nanoparticles within the oxidised pyrite rims, focused ion beam (FIB) lamellas were prepared and followed with high-resolution transmission electron microscopy (HR-TEM) studies. Another objective of this study was to analyse the trace-element compositions between the intact pyrite core and the surrounding goethite rim in the grain and evaluate trace-element mobility or immobility for assessing the usability of goethite as a possible additional fingerprinting tool. This could be highly beneficial, as goethite grains are commonly observed in sediments, such as tills, altered from pyrite in the oxidising environment.

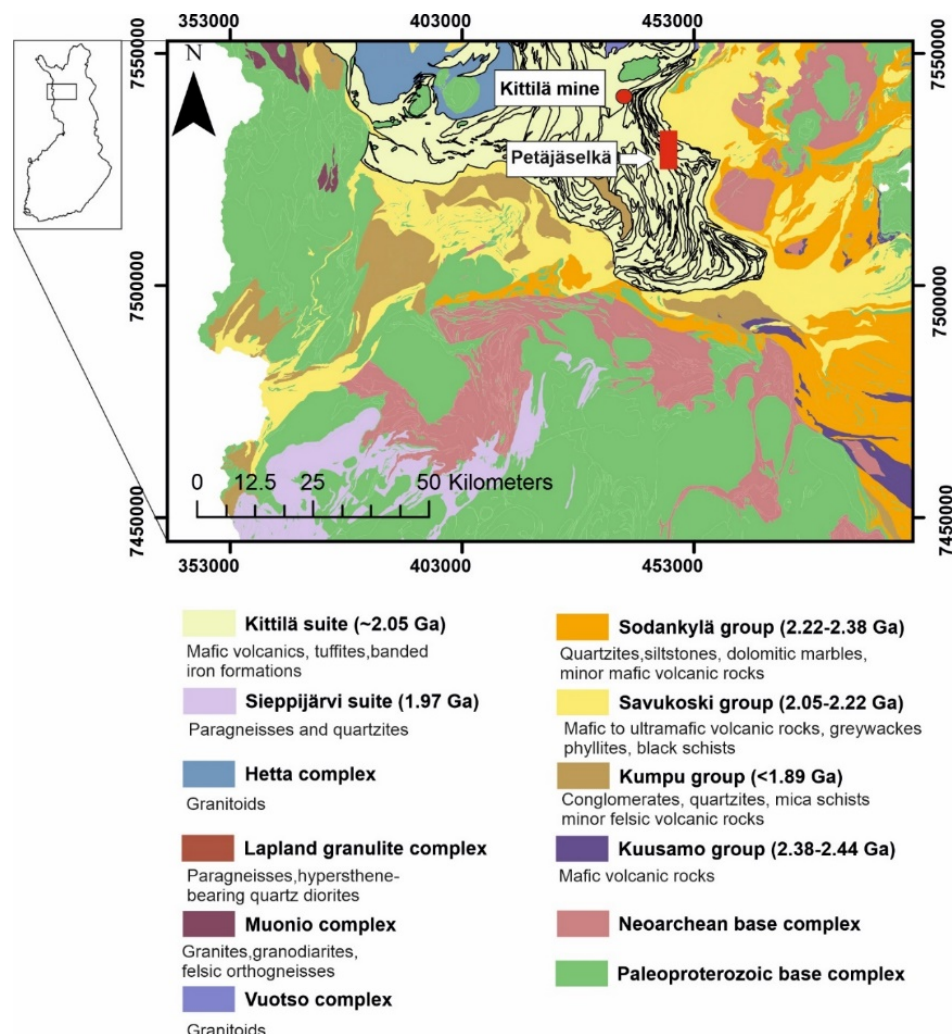


Figure 1. Geological map of the Petäjäselkä study area containing sub-study areas of Selkä-Mäntypää and Kerolaki. DigiKP, digital map database [electronic source], Geological Survey of Finland (Bedrock map 1:100,000 version 1.0 25 April 2022). Geographical coordinate system: EUREF-FIN. Modified after [28].

2. Geological Background

2.1. The Petäjäselkä Au Occurrence in the Central Lapland Belt

The Petäjäselkä study area (EUREF EASTING 446480, EUREF 7522175 NORTHING; Figure 1) is situated geologically in the Paleoproterozoic Central Lapland belt (CLB) within the allochthonous Kittilä suite predominantly composed of mafic metavolcanic rocks [38], positioned approximately 100 km from the Arctic Circle in the Finnish Lapland (Figure 1). The CLB has been the focus of extensive mineral exploration owing to its significant orogenic gold and magmatic sulphide potential [39], along with the known ore potential exemplified by the Suurikuusikko Au deposit (with proven and probable Au reserves of 3.7 Moz [40]) and the Ikkari Au occurrence (indicated as Au ~4.1 Moz [41]). Most of the gold occurrences within the CLB are found along two major crustal-scale shear zones, namely, the Sirkka thrust zone [42] and the Kiistala shear zone, which are nearly perpendicular to each other.

The units hosting the Petäjäselkä Au mineralisation were strongly hydrothermally altered, including albitisation, chloritisation, carbonatisation and sericitisation, along the variable shear/fault zones [43,44]. Gold is enriched in structurally controlled sulphide-carbonate-quartz-rich veinlets. Two gold-bearing zones were discovered at approximately 1 km along the shear/fault zones (Figure 2): (1) the Au occurrence at Kerolaki, which is

hosted by graphite schist with chert interlayers and quartz-bearing rocks with disintegrated sulphidic minerals (pyrrhotite, pyrite and arsenopyrite); and (2) a gold bearing zone in the eastern part of the Selkä-Mäntypää, where the Au occurrence is hosted by carbonate-altered and sericited graphite- and sulphide-bearing mafic tuffs. The gold concentrations in several mineralised veins range from 2.3 to 12.6 ppm in Kerolaki and from 4.3 to 28.2 ppm in Selkä-Mäntypää [43].

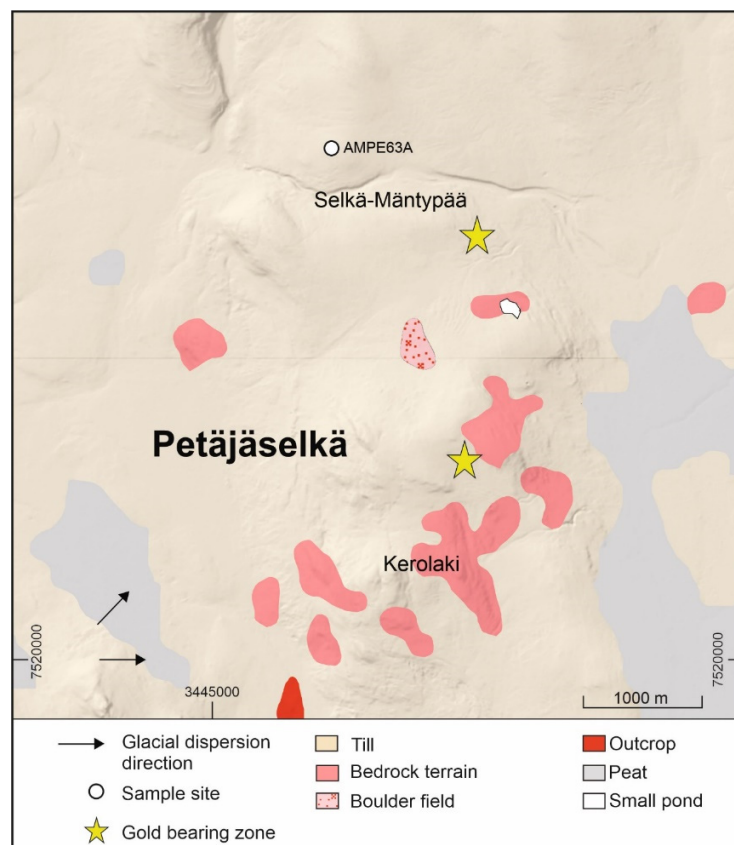


Figure 2. A quaternary map of the study area with sampling localities and the sampling spot of the bulk heavy mineral sample (AMPE 63A) in Selkä-Mäntypää, where the main studied grain was collected. Basemaps: ©National Land Survey of Finland. Geographical coordinate system: Finnish KKJ. Modified after [28].

2.2. Quaternary Geology of Central Lapland and Petäjäselkä

Central Finnish Lapland including the Petäjäselkä area is located in the central part of the Fennoscandian ice sheet—in its latest ice divide zone [45] (Figure 2). The area has been in cold-based, subglacial conditions during many glaciations. Therefore, subglacial erosion has been weak, and the glacial transport distance is relatively short (50–500 m) [46]. Glacigenic sediment cover represents complex till stratigraphy, with two to five different till beds in the area [45,47,48].

Based on the test pit and trench observations in Petäjäselkä, the transported cover comprises three different till units [46,49,50]. The till covers the topographically high areas as a 1–3 m thick layer representing two uppermost till beds [44,50]. The till fabric, high number of angular clasts and preservation of sulphidic mineral grains indicate weak glacial erosion and thus indicate short glacial dispersion. The lowest till unit was deposited during the glacial advance phase, and the uppermost unit is an ablation till representing the melting phase of ice. The third till unit occurs in a lower topographic level under the upper till units [44,46,51]. The intervening organic deposits found between the lowermost till layers at the Petäjäselkä have proven that the area was ice-free at least once during the Middle Weichselian interstadial (55–25 ka [52]). In addition, in some slope areas, the upper

part of the till cover was washed due to wave action during the short glaciolacustrine phase at the last deglaciation. It is seen as a shallow, gravelly layer or washed boulder field on the surface under vegetation cover.

In the Petäjäselkä area, the bedrock surface is typically weathered to a depth of 0.5–3 m [44]. Weak glacial erosion and transportation during glacial phases enabled the preservation of the pre-glacial weathered bedrock [46,47]. However, during the latest melting phases, the changes in the subglacial, ice-marginal conditions and ice-lobe oscillation resulted in some erosion, leading finally to the redeposition of the weathered bedrock and mixing into till material [46,53].

3. Analytical Methods and Sampling

3.1. Heavy Mineral Sampling and Concentration Procedures

The main pseudomorphic goethite grains studied were recovered from the heavy mineral samples collected by the Geological Survey of Finland (GTK) in 2008 during their investigation of the Petäjäselkä gold occurrence in the Finnish Lapland [44]. These samples were obtained from till layers approximately 0.5–1.0 m above the pre-glacial weathered or fresh bedrock. Consistently, a sample size of approximately 12 litres (equivalent to 20–25 kg) was utilised throughout the sampling process. This standard sample size is commonly employed in heavy mineral studies conducted in glaciated regions [5,44,45,54]. In specific localities where till beds were thicker, supplementary samples were collected. For the present study, 39 representative samples were meticulously chosen (i.e., had the highest number of sulphide grains in the preliminary report) from the original 381 heavy mineral samples, comprising 218 till samples and 163 weathered bedrock samples. These 39 samples were deemed to exhibit the highest potential (i.e., had the largest volumes) for the discovery of sulphides within the entire study area, particularly from the Kerolaki and Selkä-Mäntypää sites (Figure 2). Subsequently, the samples underwent wet-sieving to isolate the <2 mm fraction, after which a Knelson concentrator was employed to concentrate the heavy mineral fraction [55]. Additionally, some samples were further concentrated using a spiral concentrator. Post-concentration, methylene iodide separated the remaining light minerals (e.g., feldspar, quartz, mica) from the samples via heavy liquid separation (with a Specific Gravity = 3.3).

In the initial phase, sulphidic mineral grains, particularly fresh pyrite grains, were identified under a stereomicroscope. The concentrates were subsequently sieved to obtain size fractions < 125 µm, under the assumption that the finest fraction might still contain fresh pyrite grains, as evidenced in prior studies [35,53,56]. Although local euhedral pyrite grains were observed, no non-altered pyrites were identified during the present investigation. However, within the coarse fractions (>125 µm), goethite pseudomorphs (Figure 3b) with fresh pyrite cores were identified through manual scanning. In this study, from the 81 identified goethite grains, one grain (Figure 4) was selected for further analysis, including EPMA, LA-ICP-MS and TEM studies. In addition, several other grains were evaluated to give a more robust statistical baseline when evaluating trace-element data (Tables S1 and S2). The main grain studied was selected because it was large enough (>100 µm), its porosity was minimal, it contained different textural zones, and, most importantly, it had an intact pyrite core in the centre. The coordinates of the identified pyrite grain were recorded using copper grids (Figure 3a) and subsequently analysed using laser software (Chromium 2.4.) interfaced with the LA-ICP-MS instrument (Figure 3b).

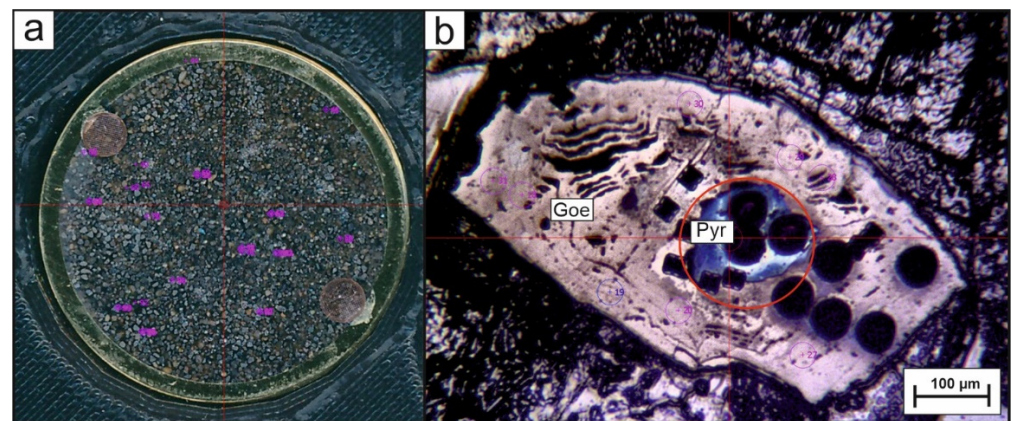


Figure 3. (a) Prepared heavy mineral sample in an epoxy button (~inch diameter) with two TEM copper grids attached for referencing within-sample coordinates of individual mineral grains. (b) Reflected light image of the SEM-located pyrite (Pyr) grain with a goethite (Goe) rim on a laser software within LA-ICP-MS.

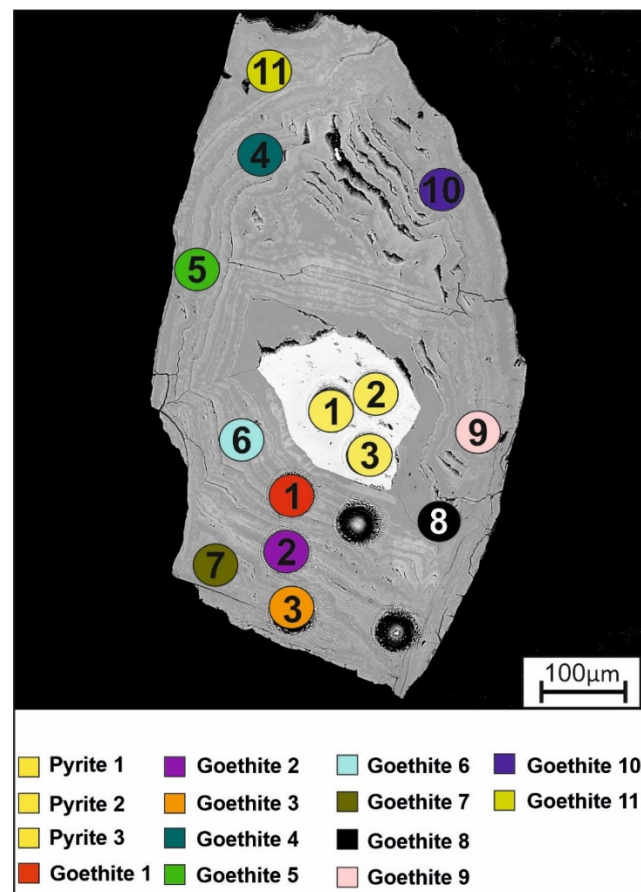


Figure 4. Back-scattered electron image of selected goethite grain with pyrite core.

3.2. EPMA, HR-TEM and FIB

X-ray elemental maps and analytical points were analysed at the Centre for Material Analysis, the University of Oulu, by using a Jeol JXA-8530F Plus field emission electron probe microanalyser (JEOL Ltd., Tokyo, Japan) (FE-EPMA), which is equipped with a 5 WDS (Wavelength Dispersive Spectroscopy) detector and one EDS (Energy-Dispersive X-ray spectroscopy) detector. For WDS elemental map analysis, the following conditions, elements, and elemental lines were used: Si ($K\alpha$), Fe ($K\alpha$), Co ($K\alpha$), Mg ($K\alpha$), Ni ($K\alpha$),

O (K α), Mn (K α), S (K α), Ca (K α), Al (K α), and As (K α). The analytical conditions were focused spot, an accelerating voltage of 20 kV, a current of 35 nA and a dwell time of 35 ms.

HR-TEM observations were carried out using a JEOL JEM-2200FS EFTEM/STEM at the Centre for Material Analysis, the University of Oulu, with an accelerating voltage of 200 kV. X-ray elemental maps were measured using the EDS method during the scanning transmission electron microscopy (STEM) mode. Five cross-sectional thin lamella samples were prepared for TEM using the FIB technique with the FEI Helios instrument (Figure 11).

3.3. Trace Element LA-ICP-MS

The complete LA-ICP-MS trace-element data (in ppm) of all the pyrite and goethite heavy mineral grain data are shown in Supplementary Tables S1 and S2. The main study was conducted for the single selected goethite grain containing a preserved intact pyrite core. From this grain, eleven successful analyses were gathered from the goethitised rim and three analyses were gathered from the pyrite core (Figure 4) to observe intra-grain compositional variation. Furthermore, two supporting datasets focusing on Cu, As, Ni and Co, which have been shown to be discriminatory elements able to separate different pyrite types [27], were included for a robust baseline statistical review. The first supporting dataset of 24 data points from four goethitised pyrite grains (Supplementary Tables S1 and S2) was chosen because these grains were the only ones that included three pyrite and three goethite analysis spots, ensuring the best comparability and quality. Similarly, the second supporting dataset of five epoxy button samples containing 44 individual grains with 150 data points (Supplementary Tables S1 and S2) included at least two pyrite and goethite analysis spots in each grain.

LA-ICP-MS analysis was conducted using a Nu AttoM double-focusing single collector (SC) ICP-MS coupled with an Excite 193 nm ArF excimer laser at the GTK Research Laboratory, Espoo, Finland. The laser was run at a pulse frequency of 5 Hz and pulse energy of 5 mJ at 30% attenuation to produce an energy flux of 2.17 J/cm² on the sample surface with a 40 μ m spot size. Each analysis was initiated with a 20 s baseline measurement followed by switching on the laser for 40 s for signal acquisition. Analyses were made using a time-resolved analysis (TRA) mode with continuous data acquisition for each set of points following a standard-sample bracketing (SSB) scheme, including a primary standard, two quality controls and 10–15 unknowns. Data reduction was handled using GLITTERTM [57] and Iolite [58].

For the analyses of the goethite rim, GSE-1G glass was used as the primary external standard, and GSD-1G and BIR-1G glasses were used as reference materials for quality control. The isotope ⁵⁷Fe has been used as an internal standard. The measurements were performed on 58 isotopes covering 42 elements at a low resolution ($\Delta M/M = 300$) using the fast-scanning mode.

For pyrite analyses, synthetic pressed nano pellet sulphide standard UQAC FeS-1 [59] was used for external standardisation, and nano pellet sulphide standards FeS-5 and FeS-6 were used for quality control. The isotope ⁵⁷Fe has been used as an internal standard. The measurements were performed on 65 isotopes covering 41 elements at a low resolution ($\Delta M/M = 300$) using the fastscan mode. The following isotopes gave reliable results free of spectral interferences: ²⁹Si, ³⁴S, ⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶²Ni, ⁶⁵Cu, ⁶⁷Zn, ⁷¹Ga, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁹³Nb, ⁹⁵Mo, ¹⁰¹Ru, ¹⁰³Rh, ¹⁰⁶Pd, ¹⁰⁹Ag, ¹¹¹Cd, ¹¹⁵Ln, ¹²⁰Sn, ¹²³Sb, ¹²⁶Te, ¹³⁷Ba, ¹⁸³W, ¹⁸⁷Re, ¹⁹⁰Os, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi and ²³⁸U. For the reported elements, the median limit of detection (LOD) values of the analyses of the primary studied grain were as follows: As = 0.854 ppm, Sn = 0.540 ppm, Cu = 0.354 ppm, Se = 1.097 ppm, Co = 0.544 ppm, Mo = 0.145 ppm, Pb = 0.006 ppm, Cr = 2.399 ppm, Ni = 2.515 ppm, V = 0.176 ppm, Sb = 0.068 ppm, Ga = 0.064 ppm, Ge = 0.829 ppm, Mn = 0.777 ppm and Ti = 2.111 ppm.

4. Results

4.1. Trace Element Characteristics of Pyrite and Goethite

Altogether, 14 spots from the main selected grain were analysed with LA-ICP-MS; the results are shown in Table 1. Three sample points were from pyrite and 11 were from goethite (Figure 4). Specific spots were chosen to represent the entire grain. In the three pyrite samples, the trace-element data are uniform, with little variance except in pyrite spot 2 (Table 1), where Pb (3.24 ppm) and V (2.09 ppm) are slightly higher than the rest of the values. As (287.24–301.97 ppm), Ni (316.86–475.21 ppm), Co (226.84–829.19 ppm) and Se (53.92–58.14 ppm) show the largest trace element concentrations. In the goethite, the variation in trace elements is wider. Co (134.18–5358 ppm), Cu (43.82–744.91 ppm), As (164.65–484.82 ppm) and Ni (181.77–433.25 ppm) show the highest concentrations (Table 1). In addition, some elements such as Cu, Cr, Mo and Mn had significantly higher values locally in goethite than in pyrite. The As, Co and Ni values are the most similar between the pyrite and goethite datasets. Each analysis spot is presented in a parallel coordinate plot in Figure 5. Furthermore, all the specific ratios mentioned above are represented in the box-plot graph Figure 6, showing the goethite trace-element analysis against the pyrite spots.

Table 1. LA-ICP-MS trace-element data (ppm) of the pyrite and goethite in the principal grain.

	As	Sn	Cu	Se	Co	Mo	Pb	Cr	Ni	V	Sb	Ga	Ge	Mn	Ti
Pyrite 1	301.97	0.01	0.16	53.92	829.19	0.07	0.33	1.62	421.71	0.03	0.05	0.01	0.22	0.52	5.78
Pyrite 2	253.63	0.16	0.54	51.87	399.21	0.08	3.24	0.47	316.86	0.37	0.32	0.01	0.34	2.09	5.64
Pyrite 3	287.24	0.12	0.33	58.14	226.84	0.01	0.54	0.72	475.21	0.01	0.06	0.01	0.98	0.45	4.43
Goethite 1	248.53	0.19	43.82	21.92	134.18	3.37	2.27	52.58	433.25	10.94	1.76	0.30	1.21	440.29	0.84
Goethite 2	164.65	0.19	129.07	19.69	252.48	4.32	0.15	10.84	309.72	59.94	2.91	1.51	1.02	657.57	0.54
Goethite 3	187.05	0.17	744.91	18.92	529.52	6.75	0.39	12.56	326.39	95.45	3.42	2.22	0.92	491.73	3.05
Goethite 4	484.82	1.36	700.13	16.71	3561.30	3.43	3.43	7.99	314.62	66.61	4.26	1.95	0.44	993.27	1.57
Goethite 5	418.56	0.38	313.45	17.63	503.70	4.29	0.70	16.81	421.40	146.39	5.70	3.17	2.66	483.32	5.60
Goethite 6	284.82	1.40	64.95	6.33	1324.53	2.21	4.35	91.01	247.63	26.68	2.55	0.32	0.47	377.83	1.67
Goethite 7	325.82	3.46	182.35	15.77	172.65	7.14	0.02	8.75	393.18	105.92	5.04	2.17	0.33	662.99	0.95
Goethite 8	414.70	1.85	174.58	27.52	1091.08	4.07	0.27	142.91	658.93	18.70	1.73	0.50	0.39	297.95	1.29
Goethite 9	317.99	0.34	175.83	8.76	2763.83	3.29	1.36	132.58	181.77	35.26	2.57	0.94	0.37	395.70	1.39
Goethite 10	475.87	0.45	389.07	29.71	3115.81	1.80	3.46	7.01	404.74	171.55	3.55	2.71	2.05	671.60	1.53
Goethite 11	474.36	0.38	371.64	23.01	5357.98	4.80	5.45	12.32	242.18	107.21	4.44	3.77	0.54	519.29	4.80

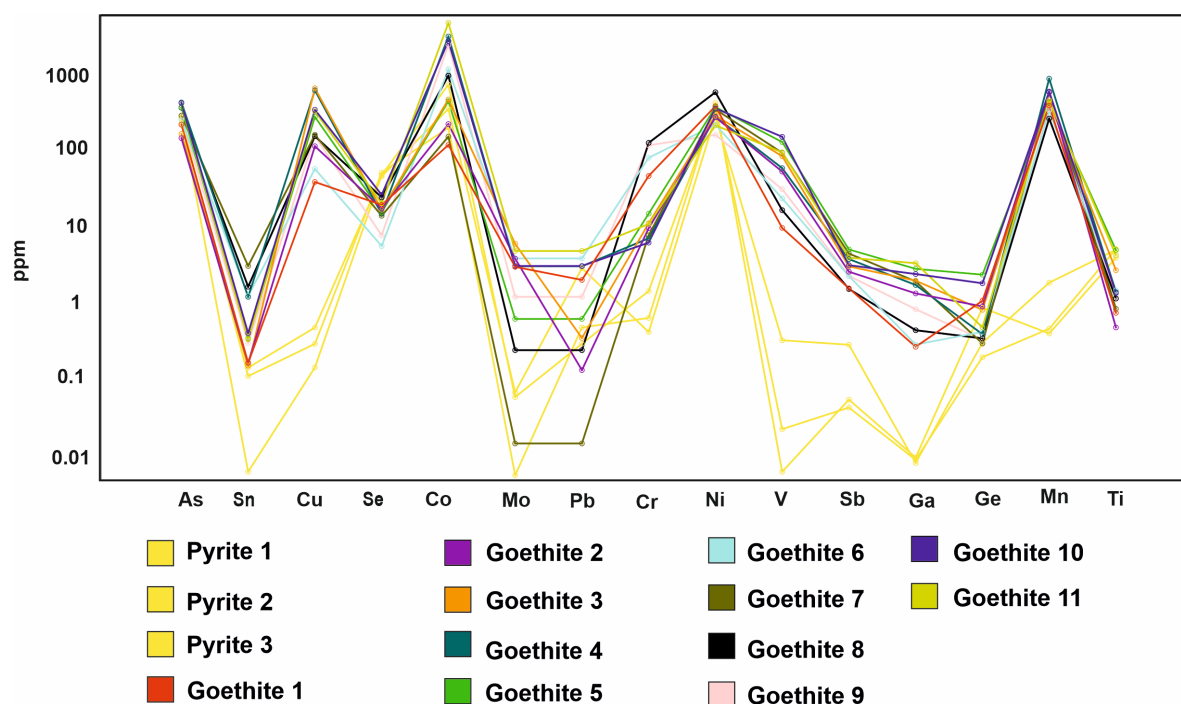


Figure 5. Parallel coordinate plot (log-Y scale) of the LA-ICP-MS trace-element data, with individual spots demonstrated in Figure 4 and Table 1.

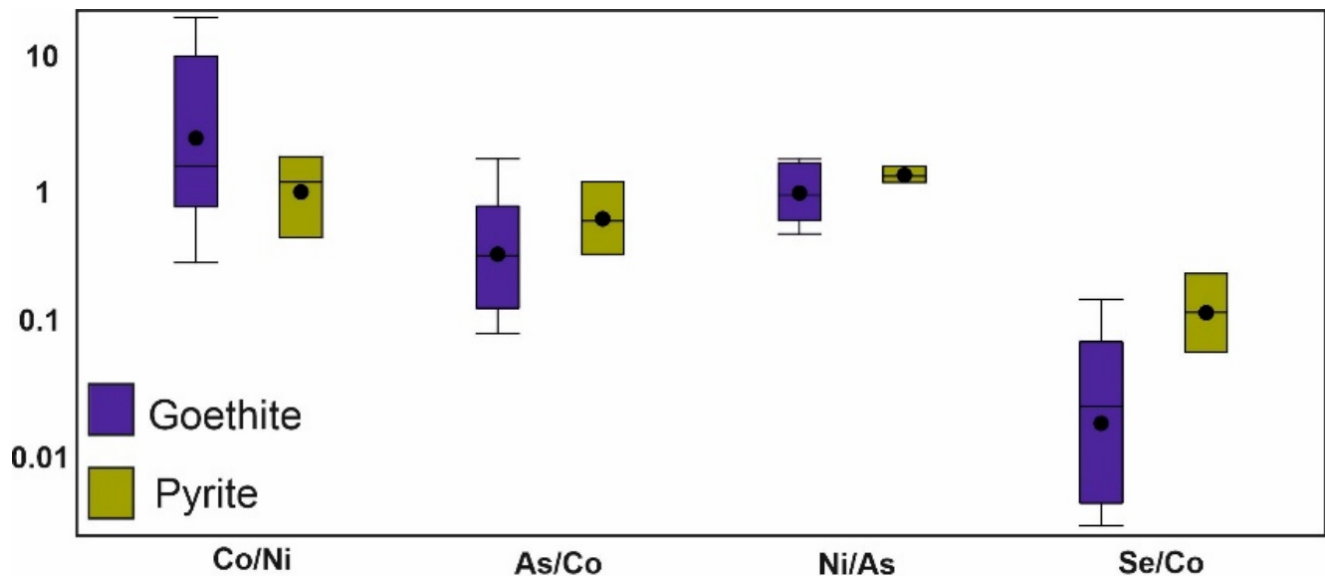


Figure 6. Box-and-whiskers plots (log-Y scale) based on mass basis ratios of Co/Ni, As/Co, Ni/As and Se/Co in the trace-element data.

The Co/Ni ratios varied from pyrite 0.48–1.97 to goethite 0.31–22.12 in the main grain (Figure 7a). The variance in other ratios was as follows: As/Co pyrite 0.36–1.27 vs. goethite 0.09–1.89; Ni/As pyrite 1.25–1.65 vs. goethite 0.51–1.88 and Se/Co pyrite 0.07–0.26 vs. goethite <0.00–0.16 (Figure 7a). When comparing trace-elemental ratios between the pyrite core and goethite rims in the one selected main grain with calculated statistics, Co/Ni shows the most similar values, with median results of 1.26 in pyrite vs. 1.66 in the goethite rim (Table 2b). The second-best median similarity is shown by the Ni/As (median of 1.39 in pyrite vs. 1.00 in goethite) and As/Co median of 0.64 in pyrite vs. 0.35 in goethite, respectively. The Se/Co median varies the most, with 0.13 in pyrite vs. 0.26 in goethite.

Table 2. (a) Trace-element ratios of Co/Ni, As/Co, Ni/As and Se/Co for analysed pyrite and goethite spots in the main grain. (b) The calculated statistical values of the main grain's measured Co/Ni, As/Co, Ni/As and Se/Co.

(a)				
	Co/Ni	As/Co	Ni/As	Se/Co
Pyrite 1	1.97	0.36	1.40	0.07
Pyrite 2	1.26	0.64	1.25	0.13
Pyrite 3	0.48	1.27	1.65	0.26
Goethite 1	0.31	1.85	1.74	0.16
Goethite 2	0.82	0.65	1.88	0.08
Goethite 3	1.62	0.35	1.74	0.04
Goethite 4	11.32	0.14	0.65	0.00
Goethite 5	1.20	0.83	1.01	0.04
Goethite 6	5.35	0.22	0.87	0.00
Goethite 7	0.44	1.89	1.21	0.09
Goethite 8	1.66	0.38	1.59	0.03
Goethite 9	15.21	0.12	0.57	0.00
Goethite 10	7.70	0.15	0.85	0.01
Goethite 11	22.12	0.09	0.51	0.00

Table 2. Cont.

	(b)			
	Co/Ni	As/Co	Ni/As	Se/Co
Pyrite: Unique Values	3	3	3	3
Pyrite: Minimum	0.48	0.36	1.25	0.07
Pyrite: Maximum	1.97	1.27	1.65	0.26
Pyrite: Mean	1.24	0.76	1.43	0.15
Pyrite: Median	1.26	0.64	1.40	0.13
Pyrite: Geometric Mean	1.06	0.66	1.42	0.13
Pyrite: Geometric Mean	1.06	0.66	1.42	0.13
Goethite: Unique Values	11	11	11.00	11.00
Goethite: Minimum	0.31	0.09	0.51	0.00
Goethite: Maximum	22.12	1.89	1.88	0.16
Goethite: Mean	6.16	0.61	1.15	0.04
Goethite: Median	1.66	0.35	1.01	0.03
Goethite: Geometric Mean	2.70	0.36	1.04	0.02
Goethite: Standard Deviation	7.26	0.67	0.51	0.05

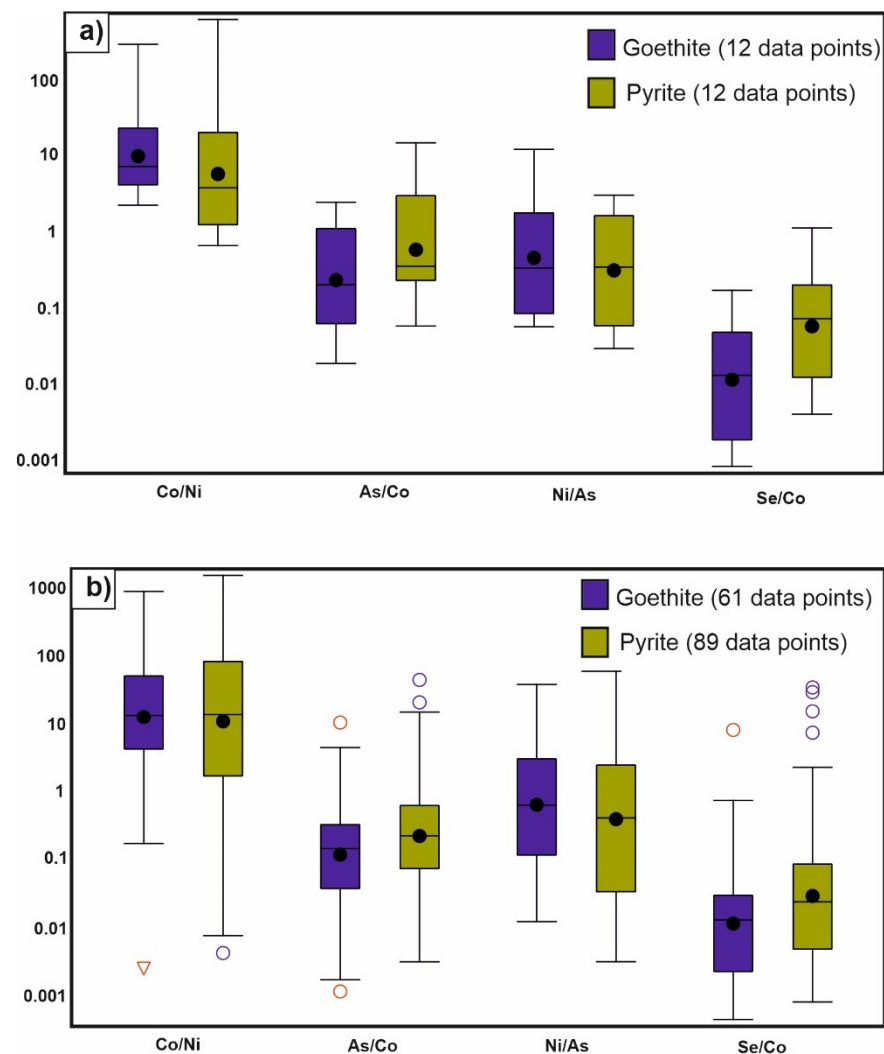


Figure 7. Box-and-whiskers plots (log-Y scale) of the trace-element data. (a) Co/Ni, As/Co, Ni/As and Se/Co ratios from the combined results of four individual grains with pyrite (12) and goethite (12) data points. (b) Co/Ni, As/Co, Ni/As and Se/Co ratios from the combined results of five heavy mineral epoxy samples with 61 goethite and 89 pyrite data points.

In addition to the two supporting datasets, all trace-element (ppm) analysis results for the pyrite and goethite are shown in Supplementary Tables S1 and S2. The calculated statistical results with only Co, Ni, As and Se (ppm) and their ratios are reviewed. In the first datasets of four individual grains, the calculated statistical values are shown with boxplots in Figure 7a. Furthermore, the median of pyrite vs. goethite ppm results for the four individual grain datasets was as follows (Table 3a): Co 756.9 ppm vs. 495.3 ppm; Ni 95.1 ppm vs. 90.8 ppm; As 292.8 ppm vs. 244.8 ppm and Se 20.8 ppm vs. 34.7 ppm. The same values with the second dataset of five epoxy buttons (containing 44 grain values) are demonstrated with boxplots in Figure 7b. The pyrite vs. goethite ppm results are shown in Table 4a and were as follows: Co 1202.4 ppm vs. 1617.9 ppm; Ni 126.09 ppm vs. 108.41 ppm; As 377.85 ppm vs. 164.65 ppm and Se 42.68 ppm vs. 17.85 ppm.

Table 3. Calculated statistics of (a) Co, Ni, As and Se trace-element (ppm) values from the combined results of four individual grains' pyrite and goethite datapoints. (b) Co/Ni, As/Co, Ni/As and Se/Co ratios from the combined results of four individual grains' pyrite and goethite datapoints.

(a)				
	Co	Ni	As	Se
Pyrite: Unique Values	12	12	12	12
Pyrite: Minimum	160.24	39.00	15.64	0.53
Pyrite: Maximum	12,902.07	271.55	1232.54	41.75
Pyrite: Mean	2370.88	115.94	429.25	19.26
Pyrite: Median	756.99	95.10	292.81	20.88
Pyrite: Geometric Mean	915.46	94.31	209.82	10.33
Pyrite: Standard Deviation	3869.83	76.15	426.42	13.79
Goethite: Unique Values	12	12	12	12
Goethite: Minimum	121.16	14.01	60.30	3.05
Goethite: Maximum	8447.09	333.41	2045.31	136.70
Goethite: Mean	1208.58	118.49	637.16	52.29
Goethite: Median	407.51	90.82	244.90	34.72
Goethite: Geometric Mean	495.31	87.56	284.51	28.14
Goethite: Standard Deviation	2328.54	96.18	790.60	47.51
(b)				
	Co/Ni	As/Co	Ni/As	Se/Co
Pyrite: Unique Values	12	12	12	12
Pyrite: Minimum	2.200	0.018	0.056	8.24×10^{-4}
Pyrite: Maximum	285.255	2.407	11.940	0.168
Pyrite: Mean	33.684	0.609	2.015	0.035
Pyrite: Median	7.098	0.203	0.340	0.013
Pyrite: Geometric Mean	9.707	0.229	0.449	0.011
Pyrite: Standard Deviation	80.060	0.803	3.742	0.050
Goethite: Unique Values	12	12	12	12
Goethite: Minimum	0.649	0.057	0.029	0.004
Goethite: Maximum	602.933	14.547	2.978	1.111
Goethite: Mean	57.252	2.350	0.893	0.171
Goethite: Median	3.739	0.351	0.434	0.072
Goethite: Geometric Mean	5.657	0.574	0.308	0.057
Goethite: Standard Deviation	172.077	4.339	1.112	0.307

Furthermore, the analyses from the four individual grains and their statistical trace-element distribution for the Co/Ni, As/Co, Ni/As and Se/Co median ratios between pyrite and goethite were as follows (Table 3b): Co/Ni 7.1 vs. 3.73, As/Co 0.2 vs. 0.35, Ni/As: 0.33 vs. 0.43 and Se/Co 0.01 vs. 0.07. The five epoxy buttons data for the Co/Ni, As/Co, Ni/As and Se/Co median ratios between pyrite and goethite were as follows (Table 4b): Co/Ni 13.8 vs. 13.3, As/Co 0.2 vs. 0.15, Ni/As: 0.42 vs. 0.64 and Se/Co 0.02 vs. 0.01. All the specific ratios mentioned above are represented in the box-plot graphs (Figure 7a,b), showing the goethite trace-element analysis against the pyrite spots.

Table 4. Calculated statistics of (a) Co, Ni, As and Se trace-element (ppm) values from the combined results of five heavy mineral epoxy bulk samples (44 grains) with pyrite and goethite datapoints. (b) Co/Ni, As/Co, Ni/As and Se/Co ratios from the combined results of four individual grains with pyrite and goethite datapoints.

(a)				
	Co	Ni	As	Se
Pyrite: Unique Values	89	89	89	88
Pyrite: Minimum	2.41	0.74	2.23	0.27
Pyrite: Maximum	23,356.89	4729.75	19,908.95	157.57
Pyrite: Mean	5083.7301	329.54	1751.90	52.61
Pyrite: Median	1202.41	126.09	377.85	42.68
Pyrite: Geometric Mean	1300.31	118.42	295.51	38.84
Pyrite: Standard Deviation	6787.2801	655.94	3870.71	34.02
Goethite: Unique Values	62	62	62	62
Goethite: Minimum	3.05	6.44	2.84	1.22
Goethite: Maximum	26,279.48	1344.88	4869.6	67.92
Goethite: Mean	4426.09	208.93	559.63	21.74
Goethite: Median	1617.9	108.41	164.65	17.88
Goethite: Geometric Mean	1328.57	109.00	168.97	17.18
Goethite: Standard Deviation	6104.1497	266.78	888.68	14.62
(b)				
	Co/Ni	As/Co	Ni/As	Se/Co
Pyrite: Unique Values	89	89	89	89
Pyrite: Minimum	0.004	0.003	0.003	8.31×10^{-4}
Pyrite: Maximum	1521.238	44.473	59.486	34.452
Pyrite: Mean	120.814	1.726	4.895	1.094
Pyrite: Median	13.752	0.229	0.419	0.025
Pyrite: Geometric Mean	10.980	0.227	0.401	0.030
Pyrite: Standard Deviation	254.564	5.652	11.059	5.054
Goethite: Unique Values	61	61	60	58
Goethite: Minimum	0.002	0.001	0.013	4.6×10^{-4}
Goethite: Maximum	888.120	10.525	38.033	8.180
Goethite: Mean	73.929	0.640	3.388	0.187
Goethite: Median	13.320	0.148	0.644	0.013
Goethite: Geometric Mean	12.650	0.121	0.653	0.012
Goethite: Standard Deviation	160.877	1.581	6.693	1.075

4.2. EPMA

The back-scattered electron (BSE) images of the selected pyrite-goethite grains are presented in Figures 8a, 9a and 10a with selected areas for further detailed studies. The three specific areas were chosen in the contact of the pyrite core and oxidised goethite rim, as well as two other areas, to see the elemental variation within the grain. The BSE images show rhythmic zonations within the goethitised/oxidised part of the grain (Figures 8a, 9a and 10a). In addition, small cracks or fissures from the surface to the core can be seen in the BSE images.

In Figure 8b–l, Figures 9b–l and 10b–l, elemental maps based on WDS scan analyses show elevated Si, O, Al, Fe, Mg and Mn levels in the brighter cyclical zones. A higher concentration of Mn is seen in one of the brighter cyclical zoned areas in Figure 8f. The Co content follows the zonation (e.g., Figure 9d) but also crosscuts the zonation perpendicularly (Figures 9d and 10d). The distribution of Ni and As within the goethite alteration rim is more homogeneous in the analysis seen in Figure 8i,k, Figure 9i,k and Figure 10i,k, except in the small area in Figure 9e, where Ni has an elevated concentration area in the lower right side of the image. In Figure 8b, a small circular area with a high concentration of Si is seen. Furthermore, slightly elevated values of Mg and Al are seen in the same spot in Figure 8e,j. In addition, in Figure 8g, Ca has a small area of a high-concentration spot inside the pyrite inclusion.

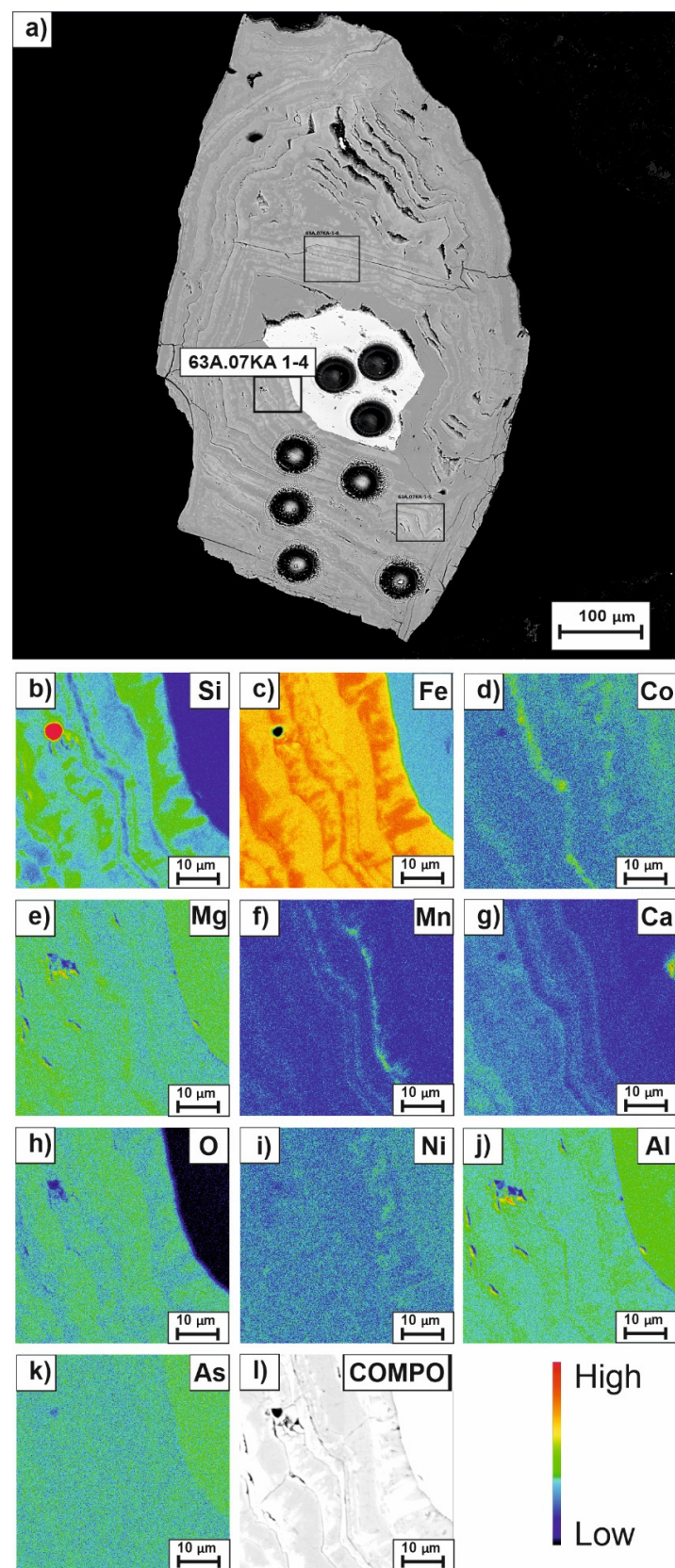


Figure 8. EPMA-WDS elemental scans of the first study spot (63A.07KA 1-4 (a)), including Si (b), Fe (c), Co (d), Mg (e), Mn (f), Ca (g), O (h), Ni (i), Al (j), As (k) and Bse Compo maps (l).

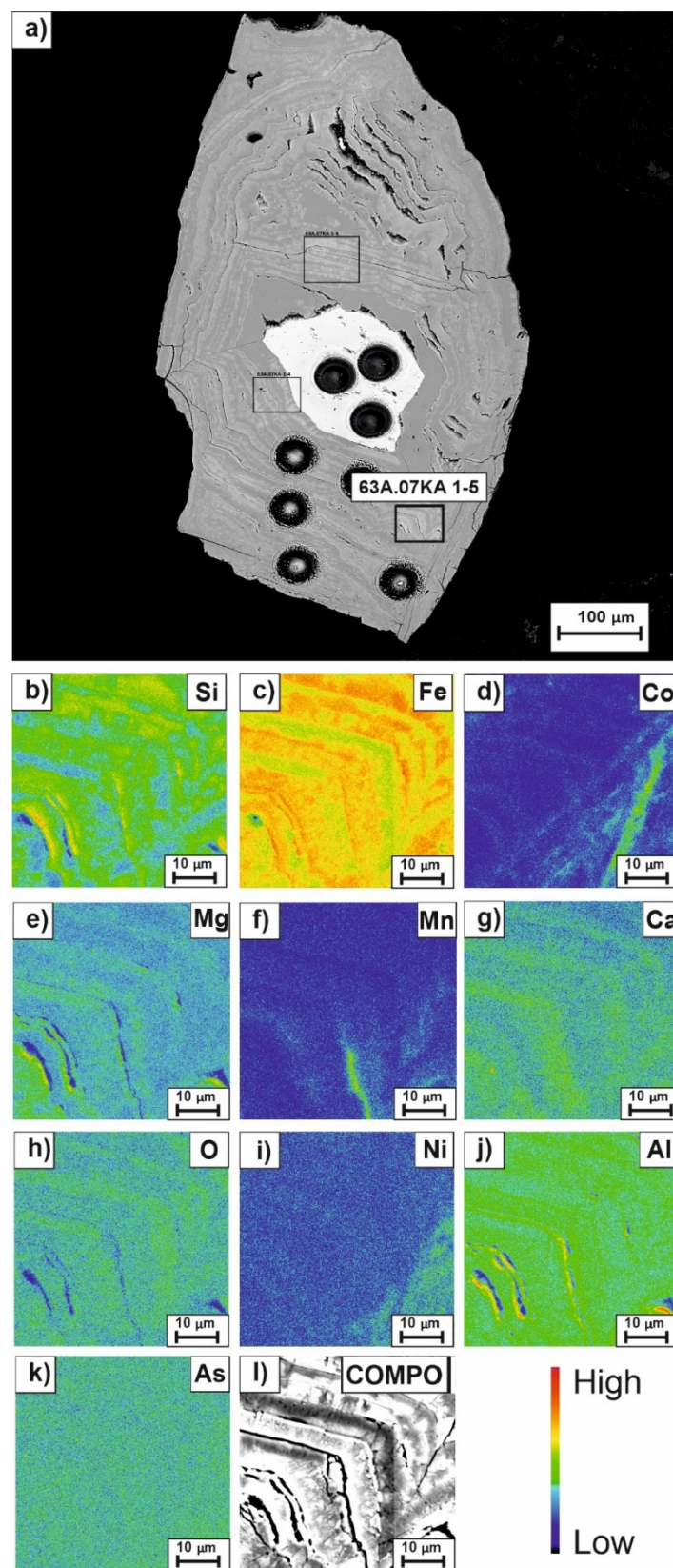


Figure 9. EPMA-WDS elemental scans of the second study spot (63A.07KA 1-5 (a)), including Si (b), Fe (c), Co (d), Mg (e), Mn (f), Ca (g), O (h), Ni (i), Al (j), As (k) and Bse Compo maps (l).

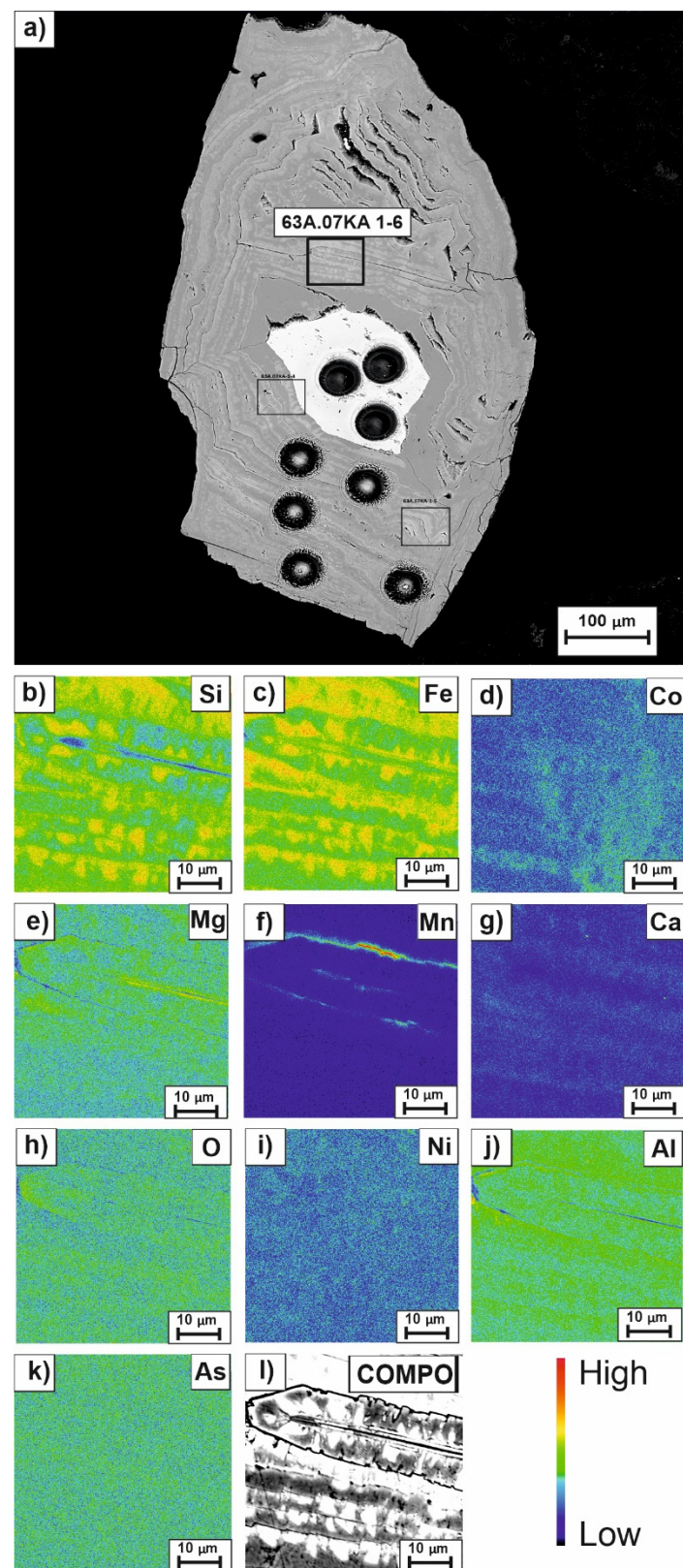


Figure 10. EPMA-WDS elemental scans of the third study spot (63A.07KA 1–6 (a)), including Si (b), Fe (c), Co (d), Mg (e), Mn (f), Ca (g), O (h), Ni (i), Al (j), As (k) and Bse Compo maps (l).

4.3. TEM

HR-TEM was used to analyse the five FIB lamellas. The lamella's (a–d) locations are shown in Figure 11. Lamella A represents the contact between pyrite and goethite in the bright field image (Figure 12a). The bright field (BF) image shows that goethite is characterised by tubular channels perpendicular to the pyrite (Figure 12a). The pyrite–goethite contact zone is clearly visible, characterised by an open fracture surface, visible as a bright outline (Figure 12a). Furthermore, from the border towards pyrite, a narrow alteration halo separates the minerals with a more porous texture (Figure 12a). Lamella B (Figure 12b) represents the area of the goethite rim where cyclical zoning patterns were not observed earlier with EPMA. Within this type of texture of goethite, nano nodules/inclusions of pyrite were observed (Figure 12b). Lamellas C, D and E represent homogeneous parts of the goethite with tubular and zoned textures (Figure 12c–e).

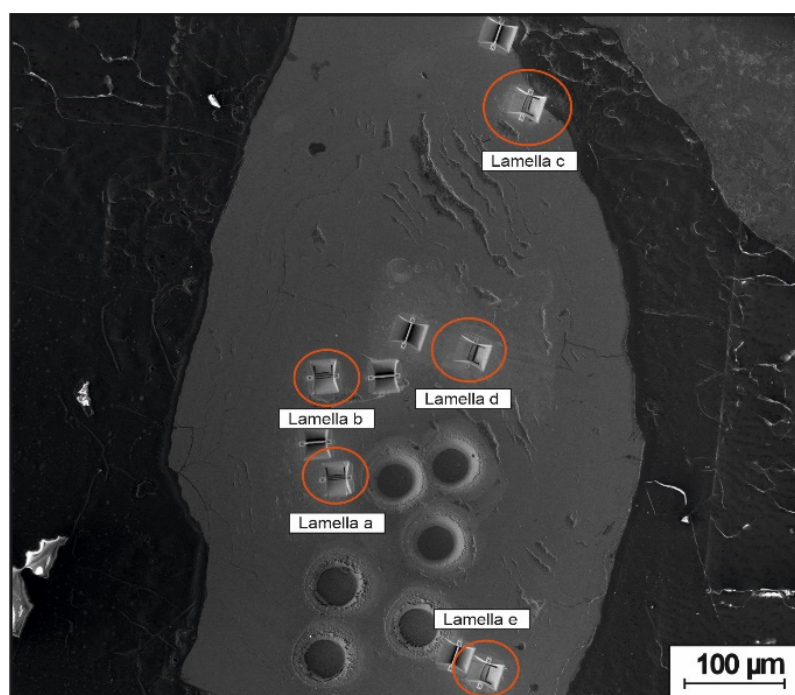


Figure 11. Secondary electron image with five lamella positions.

TEM-EDS scans (Figure 13a–d) from the Lamella A show uniform Fe, S and O values without any observed zonation in the pyrite–goethite contact. In lamella B (Figure 14a–d), three pyrite nodules are seen in the BF image (Figure 14a) and with the enrichment of the S and O deficit of O in Figure 14c,d. In the lamella C (Figure 15a–e), the BF image in Figure 15a revealed brighter areas where the elevated concentrations of Fe, Si and Co are observed (Figure 15b,c,e). Also, Mg and Al are moderately observed following the zonation (Figure 15d,f). In the lamella D, the Fe, Co, Zr and Mo (Figure 16b,d,e,f) overlap perpendicularly with the lighter zone boundary. Furthermore, the Si spectrum is homogenous in lamella D. Finally, in the lamella E (Figure 17a–e), Fe, Co and Si form tooth-like patterns perpendicular to the main zoning, especially seen with Fe and Si images (Figure 17b,c), but they are also seen moderately with Mg and Co (Figure 17d,e). The phenomenon can also be seen in the BF image, which has textures different from the surrounding area (Figure 17a). Moreover, the Mg spectrum was analysed and has a more sporadic distribution than the previous elements mentioned (Figure 17d).

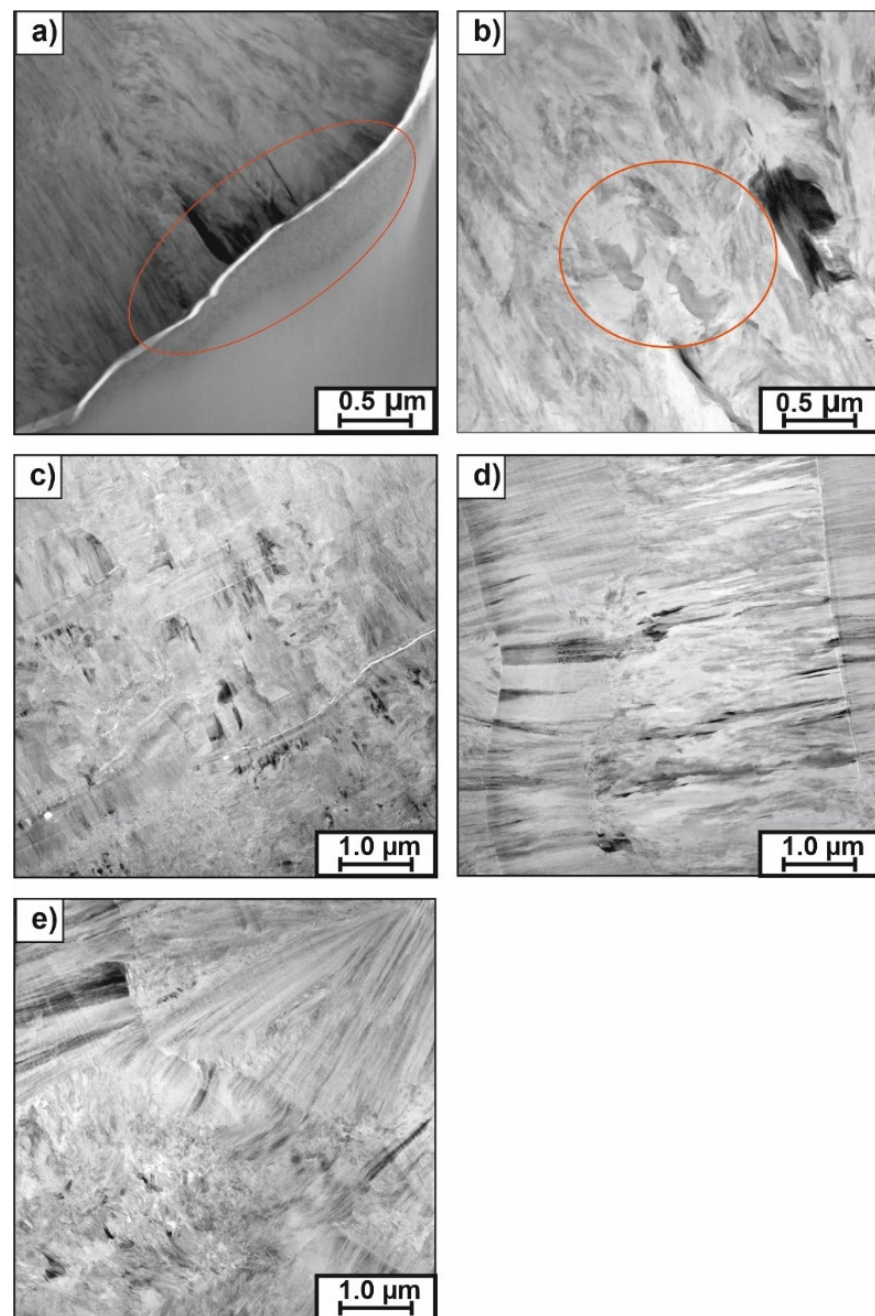


Figure 12. Five nano-scale lamellas (a–e) bright field TEM images. (a) Lamella A from the contact between the pyrite core and surrounding goethite rim. (b) Lamella B from the goethite rim with pyrite nano nodules. (c) Lamella C from the edge of the goethite showing cyclical rims. (d) Lamella D from within the goethite rim displaying cyclical zoning. (e) Lamella E from within the goethite rim displaying cyclical zoning.

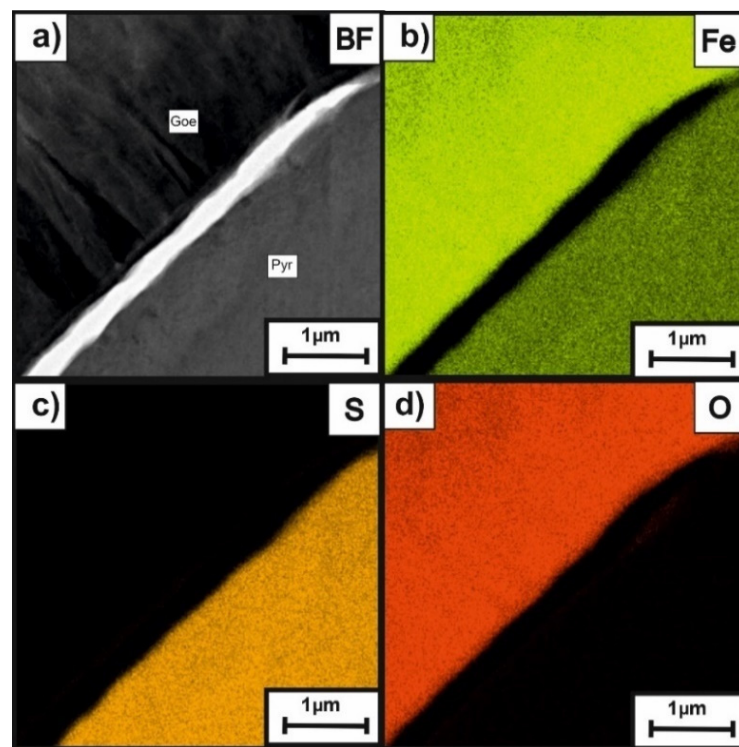


Figure 13. TEM-EDS elemental maps from lamella A from the contact between the pyrite and goethite rim with a bright field (BF) image (a) and Fe (b), S (c) and O (d).

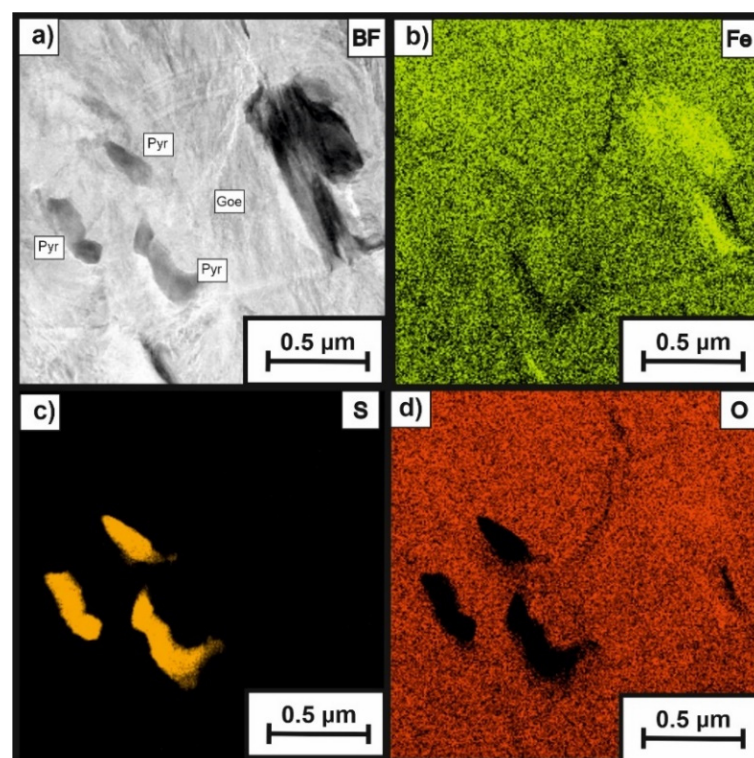


Figure 14. TEM-EDS elemental maps from lamella B with a bright field (BF) image (a) and Fe (b), S (c) and O (d) with pyrite nano nodules displayed.

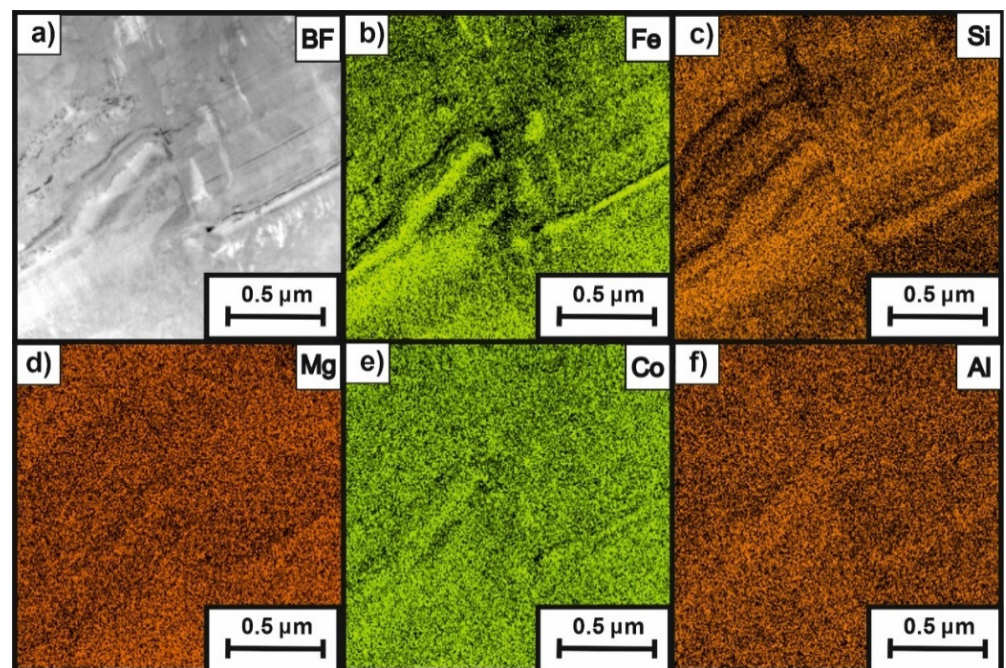


Figure 15. TEM-EDS elemental maps from lamella C with a bright field (BF) image (a) and Fe (b), Si (c), Mg (d), Co (e) and Al (f).

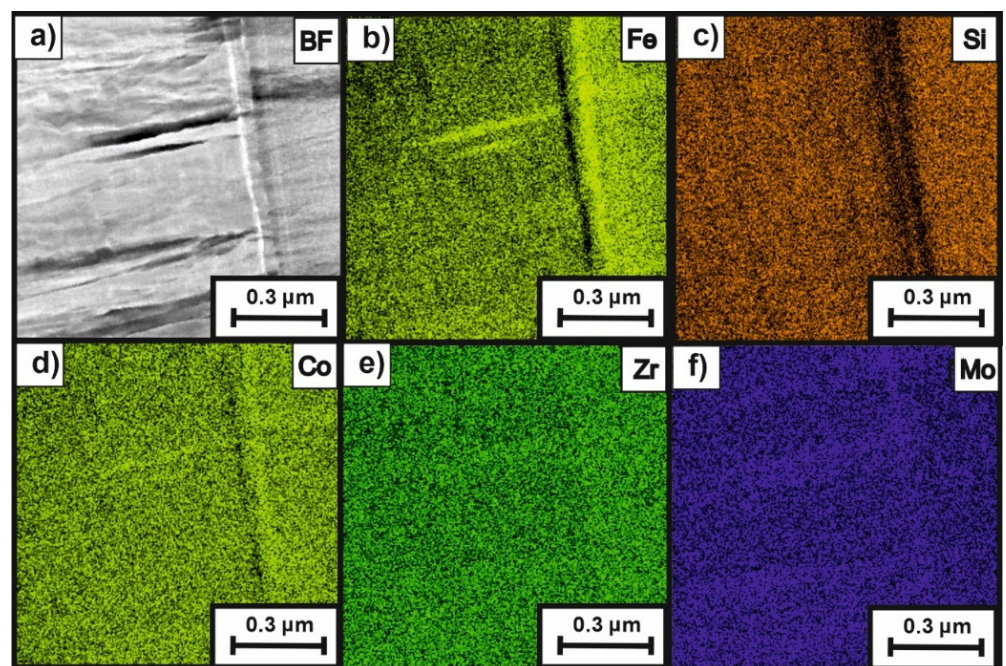


Figure 16. TEM-EDS elemental maps from lamella D with a bright field (BF) image (a) and Fe (b), Si (c), Co (d), Zr (e) and Mo (f).

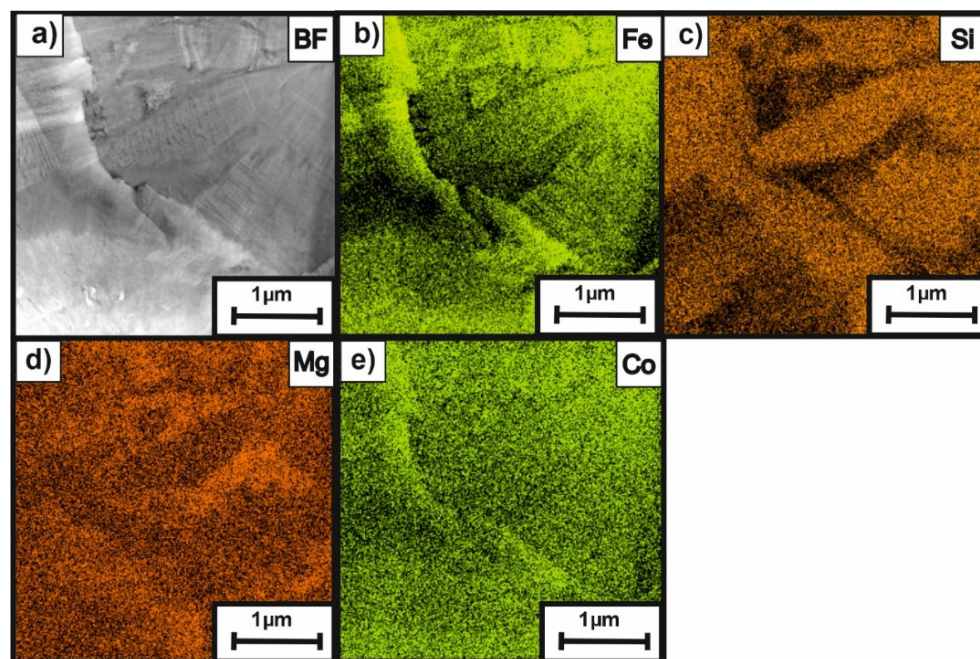


Figure 17. TEM-EDS elemental maps from lamella E with a bright field (BF) image (a) and Fe (b), Si (c), Mg (d) and Co (e).

5. Discussion

Till is the most common sediment covering the bedrock in formerly glaciated areas such as Finland and, therefore, one of the most used mediums in the early stages of exploration projects. The highly oxidising environment proved challenging in recovering suitable unaltered pyrite grains in the study areas till beds. In this kind of environment, goethite pyrite remnants with large enough intact pyrite cores are the alternative way to analyse pyrite trace-element signatures, as they are more commonly found in heavy mineral samples [28]. The trace-element results of this study highlighted the main differences between the intact pyrite core and the surrounding layer of goethite within a single grain (Table 1 and Figure 5). Trace-elements such as As, Ni and Co had the highest values in both the pyrite core and goethite rim data. Furthermore, Ni, As and Se were the most immobile trace-elements between the two datasets (Table 1). However, Cu, Cr, V and Mn values were enriched in the goethite compared to in the pyrite core (Table 1). In some cases, the ppm values deviated significantly in the datasets between different analysis spots within the grain. For example, Co pyrite analysis ranged between 226.8 and 829.2, and the goethite ranged between 134.18 and 5358 ppm (Table 1 and Figure 5). Therefore, the ratios between certain trace elements (Co/Ni, As/Co, Ni/As and Se/Co) were utilised to compare possible similar trends in both the pyrite core and the goethite rim datasets. Co, Ni, As and Se and their ratios have been successfully used to distinguish different pyrite generations and mineralising stages in multiple deposit types [60–62]. With these four ratio pairings, Ni/As and Co/Ni were the most similar in the main studied grain between pyrite and goethite's 14 data points (Table 2b and Figure 6). The same trend is observed in the two larger datasets of four goethite grains with 24 data points and the largest datasets with five heavy mineral epoxy buttons with 150 data points (Table 4b and Figure 7b.)

Iron(III)-(oxy)hydroxides, including ferrihydrite and goethite, have been documented to exhibit adsorption capacities for Cu and Ni, as evidenced by studies conducted by [63,64]. Furthermore, the occurrence of sulphate (SO₄) on the surface of ferrihydrite or goethite has been demonstrated to enhance the adsorption of toxic trace metals, including Pb, Cu and Zn [65]. Chowdhury and Singer [66] elucidated that the partitioning of Mn, Cr, Ni and Co during oxidative pyrite dissolution is influenced, in part, by the timing of subsequent Fe(III) precipitation. Specifically, there is the question of whether the precipitation occurs

immediately, such as the pseudomorphic replacement of pyrite, or after transportation in pore water, such as the formation of Fe(III) coatings on primary grains or discrete Fe(III)-bearing phases. Additionally, factors such as the sulphur content and maturity also play a role in this partitioning process.

Moreover, all of the Fe-bearing mineral phases, including goethite, and their transformation to other more mature phases depend largely on pH levels, and they play an important role in the fate of trace-metals in the pore waters [67,68]. Furthermore, the previously mentioned studies demonstrated that, e.g., Mn, Cr, Cu and Zn can be sequestered by Fe(III)-oxyhydrosulphates such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) and therefore could act as a comparison tool or guideline for what is also happening in the pyrite transformation to goethite.

The studied goethite pseudomorph grain BSE image (Figure 4) revealed rhythmic compositional geochemical patterns along the core-to-rim profile. The same rhythmic zones with enriched elements such as Si, O, Al, Fe, Mg and Mn can also be observed in the EPMA WDS images in Figures 8–10. These chemical zoning patterns might represent oscillatory zoning. Oscillatory zoning has been observed in all mineral classes in various geological environments [69]. Shore and Fowler [70] and L'Heureux [69] proposed two broad mechanisms for explaining the formation of oscillatory zoning. Within the 'extrinsic' mechanisms, fluctuations in the chemical composition result from alterations in external conditions such as the pressure, temperature and pH. Conversely, 'intrinsic' mechanisms suggest that oscillatory zoning emerges from self-organisation within a nonlinear growth environment, i.e., the intrinsic nonlinear dynamics of the system, characterised by positive feedback among variables independent of fluctuation. Notably, both mechanisms could occur simultaneously, generating fluctuating patterns with a rich spectral content. In our study, the first mechanism is most probable, as the grain is exposed to external conditions in the till beds. Furthermore, compositional zoning was reported in the precipitated iron oxides by Herbert [71], and the study suggested that the zoning may arise from the cyclic complexation of silicate and Al at the ferrihydrite and goethite surfaces, followed by periods of goethite growth.

The FIB and TEM nanoscale studies revealed in the contact zone of lamella a (Figure 11) between the pyrite core and the goethite rim (Figure 12a) a porous zone that could potentially be the precursor stage of ferrihydrite or feroxhyte ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) (FH) before the goethite stage. The study of mechanisms of pyrite weathering by Gu et al. [72] reported a similar observation conducted by TEM of a more porous zone in the sharp interface between pyrite and goethite zones within oxidised framboidal pyrite grains (approximately 5 μm in radius). Ferrihydrite is the precursor stage for most iron oxides in soils, and it will ultimately transform into more stable phases such as goethite [73]. Due to its complex surface, it has a large surface area and a high reactivity, making it a significant adsorbent of metals and organic species in natural waters [74]. Therefore, if the ferrihydrite phase is present in the grain of our studies, it could explain the variations in certain trace-element values within the goethite grain. However, in our case, the Fast Fourier Transform (FFT) method was not used to discriminate or verify the two possible phases.

The discovered pyrite nodules found in the nanoscale lamellas (Figures 12b and 13a) could be considered as newly formed nanocrystalline pyrite domains. [75] reported a similar type of nanocrystalline pyrite during their investigation of pyrite mineral transformation relating to FH and speculated that it might have formed by oriented aggregation. Hellige et al. [76] proposed that pyrite formation is linked to an excess of Fe(II) in the system. Furthermore, According to Hellige et al. [76], the mechanism excess of Fe(II) is a reductant for S^0 , promoting the formation of pyrite via the generation of polysulphides, which have been regarded as a key precursor for the formation of pyrite [77].

Evaluating the Usability of the Pseudomorphic Goethite Grains as a Mineral Fingerprinting Tool

Other iron oxide minerals similar to goethite, e.g., magnetite and hematite, have already been studied in the last decade for their ability to record the chemical compositions

as an exploration tool for various mineral deposit types [78–83]. The ability of Fe oxides to incorporate a wide range of cations that substitute for Fe^{2+} and Fe^{3+} into their crystallographic structure enables them to record the chemical composition of the deposit and the parental fluid [83]. Furthermore, in aquatic settings, iron(III) hydrous oxides assume a pivotal role in the conveyance and mitigation of trace metals, effectively modulating the concentrations of dissolved trace metals via adsorption mechanisms [65].

Despite the promising preliminary calculated statistical results of the trace-elemental Ni/As and Co/Ni ratios being similar between the intact core and the surrounding goethite, this study also demonstrates possible limitations to this approach. For example, the EPMA WDS element analysis images of the selected grain revealed a Co-rich pervasive zone perpendicular to the main zoning shown in Figure 9d. This phenomenon is most likely caused by a secondary pulse of the Co-rich aqueous solution after the initial cycles of the goethite oscillating precipitation of elements or remobilisation events, adding to the complexity of the dynamic system of the oxidation process within the grain. Furthermore, the microfractures or fissures seen on the edges of the goethite outer rim (e.g., Figure 4) could also provide pathways of metal-rich fluid entering the grain's oxidation system.

Additional factors potentially controlling the transformation of pyrite into goethite are clay silicates. Refs. [84,85] proved that pyrite oxidation can be linked to clay–mineral interaction. Furthermore, the previously mentioned studies reported that clay silicates and related minerals influence the formation of iron oxide in the weathering environment, especially in the transformation of ferrihydrite into goethite. Weathered bedrock till samples from the central Lapland ice-divide zones are reported to be clay-rich and have high amounts of adsorption water attached to them [86,87]. Consequently, as the till bed where the studied grain was recovered is shallow (1–2 m) and is deposited above weathered bedrock, it is also likely that the studied main grain is derived from the weathered bedrock and clay minerals were present when the pyrite oxidised into goethite.

Finally, local climatic conditions can control the formation of secondary minerals because the chemical composition of the draining water can vary with the season [68,88–90]. Chemical changes in water composition vary due to changes in temperature and precipitation. In the northern latitudes, these chemical changes may also be due to snowmelt and the subsequent infiltration and wash-off of sulphide weathering products in the springtime [71,90].

In future studies of pyrite pseudomorph (goethite) grains found in tills, a more robust dataset is needed to fully assess the usability of the goethite grain in mineral deposit fingerprinting. Moreover, advanced statistical methods, such as self-organising maps (SOM) and Principal Component Analysis (PCA), could be added to assess more detailed trace-element signature variations. One possible starting point for further studies could be to identify fully oxidised goethite grains from the heavy mineral till samples with the distinct euhedral shape of pyrite (to be clear about the grain's original state of the grain). Otherwise, the grains could even be completely oxidised.

6. Conclusions

Based on the LA-ICP-MS trace-elemental, EPMA and TEM studies of the pseudomorph goethite grain, the following conclusions can be drawn:

- (1) The mass balance ratios of Ni/As and Co/Ni in the goethite rim could potentially be linked to the intact pyrite core, as demonstrated by the three different-sized trace-elemental datasets between the pyrite core and goethite rim.
- (2) The oxidation process of pyrite to the goethite pseudomorph is complex and involves many factors, such as the effects of the possible precursor stages of ferrihydrite, Ph and Eh fluctuations and the presence of silica-rich pore waters in the abiotic environment of the till beds.
- (3) Pseudomorphosed goethite grains contain oscillatory zone-type cyclical rims enriched in certain trace elements (Fe, Si, Co, Mn, Al). The zones' genesis could be derived from the system's extrinsic or intrinsic dynamics or both of them combined.

- (4) Possible nanocrystalline nodules of pyrite were observed in the goethite rim, which could be derived from the ferrihydrite transformation phase caused by oriented aggregation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14070668/s1>, Table S1: All the heavy mineral LA-ICP-MS pyrite results (ppm). The red highlighted results are from the five epoxy button datasets, and all the red (bolded) results are from the four individual grains dataset. Table S2: All the heavy mineral LA-ICP-MS goethite results (ppm). The red highlighted results are from the five epoxy button datasets, and all the red (bolded) results are from the four individual grains dataset.

Author Contributions: Conceptualization, A.T. and J.-P.R.; methodology, A.T. and J.-P.R.; validation, P.N. and M.M.; formal analysis, A.T.; investigation, A.T., P.N., M.M. and T.S.; resources, P.S.; data curation, A.T., P.N. and M.M.; writing—original draft preparation, A.T.; writing—review and editing, J.-P.R., P.S., P.N. and M.M.; visualization, A.T.; supervision, P.S. and J.-P.R.; project administration, P.S.; funding acquisition, P.S. and A.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article and Supplementary Materials, further inquiries can be directed to the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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