



Article Trace Element Analysis of Pyrite and Arsenopyrite Using the LA-ICPMS Technique in Pulai, Central Belt of Peninsular Malaysia

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Abstract: The Pulai gold deposit is one of the most promising gold prospects in the Central Belt of Peninsular Malaysia. It is found within the Permian-Triassic Gua Musang sequence of metasediments and metavolcanics and in a structurally controlled NE-SW major fault. Various ore minerals, including pyrite, arsenopyrite, chalcopyrite, sphalerite, pyrrhotite, and galena are typically associated with this deposit. Four types of pyrite (Pyrite 1, Pyrite 2, Pyrite 3, and Pyrite 4) and two types of arsenopyrite (Arsenopyrite 1 and Arsenopyrite 2) were characterised based on their morphological and textural differences. In this region, gold occurs as refractory gold in the nanoparticle form and in the state of Au⁺ within the structure of sulphides of variable concentrations. Through the detailed laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) trace element mapping analysis of pyrite and arsenopyrite, the main Au-bearing sulphides were found within vein-hosted Pyrite 4 and Arsenopyrite 2 during late phase mineralisation, while Pyrite 3 had the lowest Au concentration. Two phases of Au enrichment were recorded in Pyrite 4, mainly in the core (2 to 11.7 ppm; average 1.4 ppm) and margin of the grain (0.3 to 8.8 ppm; average 1.2 ppm), whereas the highest Au content was detected in the core of Arsenopyrite 2 (0.3 to 137.1 ppm; mean 31.9 ppm). The enrichment of Au is associated with As, forming a zoning elemental pattern distribution. Other trace elements, including Co, Ni, Sb, Pb, Bi, Cu, and Zn, show systematic variation in their composition between the various types of pyrite and arsenopyrite. For early-phase sulphides, the Au enrichment localised at the margin of Pyrite 2 and Arsenopyrite 1, together with Co-Ni, Pb-Bi-Sb, and Ag in the same oriented pattern, suggesting the remobilisation and redistribution of Au in sulfides. Meanwhile, the late crystallisation phase of vein-hosted sulphides formed a rich Au-As ore zoning pattern in the core of Arsenopyrite 2 and Pyrite 4. The second phase of Au enrichment continued at the margin of Pyrite 4 through the remobilisation and precipitation of Au together with Ni, Co, Sb, Pb, Bi, Ag, and Cu. Subsequent deformation then reactivated the late fluid system with the enrichment of Sr, Ba, Rb, Ag, and Zn along the fractures and outermost rim of Pyrite 4 and Rb-Sr-Ba-Pb-Bi along the rim of Arsenopyrite 2. The Pulai gold prospect is interpreted as an orogenic-style gold mineralisation where arsenic can be used as an indicator for proximity to ore mineralisation in exploration.

Keywords: LA-ICPMS; Pulai; pyrite; arsenopyrite; refractory gold; orogenic

1. Introduction

The occurrence of gold as a distinct inclusion smaller and finer than 1000 Å within the crystal lattice of sulphide minerals is defined as 'invisible gold' [1]. Invisible gold is also known as 'refractory gold' due to its complexity, separation, and segregation from ores



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). or sulphides. It can present as non-structural sub-micron-scale particles (0.1 to 0.01 μ m), nanoscale mineral or metallic grain particles (1 to 10 nm), or be structurally bound in solid solution or isomorphic states of the pyrite or arsenopyrite crystal lattice [2–4]. Arsenopyrite and arsenian pyrite are widely found in orogenic gold deposits, mineralised under greenschist facies condition, and become the main sulphide host of invisible gold [5].

The advancement of spectroscopic techniques such as laser-induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) has enhanced the identification of crucial elements including refractory gold and platinum group elements by means of mineral mapping and imaging. LIBS, in particular, is an effective and rapid method that can automatically provide mineralogical information through a LIBS mineral library, which is validated using the advanced technology known as a TESCAN Integrated Mineral Analyzer (TIMA-X), within a few minutes. The utilisation of the LIBS technique enables direct, high-resolution mapping of the chemical and mineralogical composition of ore samples, leading to a significant transformation in the established characterisation of rock minerals for mining exploration and exploitation [6,7] by offering both high-resolution mineralogical imaging and low-resolution core scanning for geological assessment [8].

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is a method for analysing elements within a solid material in situ. It has been extensively applied in the geosciences since its development in 1985 and is commonly used in ore characterisation, geochronology, and provenance studies to analyse trace elements and isotopes [9,10]. LA-ICPMS possesses the capability to measure multiple elements simultaneously, either in a spot analysis or element compositional map, under low detection limits at the ppm to ppb level. This unique in situ and rapid multi-element feature distinguishes LA-ICPMS from alternative methods such as secondary ion mass spectrometry (SIMS) and micro proton-induced X-ray emission (PIXE), as they involve specific operating conditions for each element, thereby reducing the efficiency and impeding the real-time observation of the corresponding elements [11–13]. Over the past decades, LA-ICPMS analysis has been preferred for trace element identification in the exploration and mineral processing industry due to its reliability, sensitivity, flexibility, efficient processing speed, and cost-effectiveness compared to alternative analytical method approaches [9,14].

The concentration of invisible gold in sulphide grains can vary, ranging from less than 0.5 ppm to more than 1000 ppm, depending on the type of deposit. Invisible gold has been discovered in various deposits, including orogenic gold mineralisation [15,16] and sedimentary-rock-hosted gold, such as Carlin-type deposits [15,17–19].

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is widely known as a powerful tool to identify the zone of sulphide growth and stages in hydrothermal mineralisation [17,20–27]. Limited studies have been conducted in the Central Gold Belt of Peninsular Malaysia to relate the quantitative mineralogical and detailed geochemical study of Au and associated trace elements in auriferous pyrite through LA-ICPMS analysis. Ref. [28] identified the variation of gold concentration using LA-ICP-MS analysis across various phases of pyrite in sandstone at the Tersang gold deposit in Malaysia. Through the analysis of trace elements using LA-ICPMS, the Selinsing gold mine in Malaysia has identified five distinct phases of pyrite. These phases have been documented based on the enrichment of trace elements found in different types of pyrite [29]. LA-ICPMS has also been utilised to examine the trace element concentration of pyrite in the magmatic rocks and black shale of the Central Gold Belt [30]. The Au content in the magmatic rock was reported to be up to 800 ppb, indicating a strong genetic correlation between the gold occurrence and the intrusion of the granitoid emplacement. The consistent and strong correlation of Au with Cu, Pb, Ag, Te, and Cd proves the latter very useful as pathfinder elements in the search for intrusion-related gold depositions. In addition to that, the geochemistry of pyritic mudstone in the Singa Formation in Malaysia was also determined using LA-ICPMS analysis. The early-phase enrichment of Au and concentration of other

trace elements in pyritic mudstone ranged up to 62 ppb, which is higher than the crustal level, thus verifying it as a gold-source rock [31].

The Pulai gold prospect was discovered southwest of Gua Musang, Kelantan. It is situated in the Central Gold Belt, in the eastern region of the Bentong-Raub Suture Zone (BRSZ), and forms the southern extension of a significant gold belt that extends as far as the southern part of the Kelantan-Thailand border. The Central Gold Belt is recognised as prospective potential zone for gold with various mineralisation types and is known for a long history of the broad and extensive small-scale mining of alluvial gold within Peninsular Malaysia [32–34]. Previous studies in Pulai have brought attention to the alluvial gold and ore geology setting [35–37].

Despite the abundance of the gold prospect in Pulai, no further research has been conducted in this area. This article presents detailed discoveries and a comprehensive analysis of the geochemistry of the major and trace elements in relation to the textures of significant gold-bearing pyrite and arsenopyrite in the Pulai gold prospect, using LA-ICPMS technology. The findings shed light on the mineralisation processes and offer a fresh perspective of the ore genesis.

2. Mining History

The Pulai gold prospect originated as a Hakka Chinese settlement and grew into a vast former gold mining settlement between the late 18th and early 19th centuries. A European company known as Duff Development Company Limited (DDC) Mining continued mining operations in the early 20th century, prior to the start of World War II. From 1979 to 1983, the Malaysia Mining Corporation (MMC) took over the mining and exploration activities covering drilling and bulk testing programmes across a wide area of placer gold potential in a few regions including Sokor, Nenggiri, Galas, and Pergau under a mutual cooperative agreement with the government of Kelantan.

This collaboration proved a sizeable reserve, continuing drilling and bulk testing in Pulai. On 28th February 1998, an agreement was signed between Austral Malaysian Mining Ltd. (AMML) and a private limited company, Kelstone Sendirian Berhad (Sdn. Bhd.), to conduct exploration and mining not only for gold but also other minerals with Pulai Mining Sdn. Bhd. (PMSB), a joint venture company. Exploration activities encompassed geophysical surveys using a high-quality airborne prospecting activity, old workings, and radiometric and magnetic surveys [38].

Pulai Mining Sdn. Bhd. participated in the ongoing exploration through a diamond drilling program with licenses to explore gold, iron, and feldspar over an area of 3700 hectares or 37 km². Between March 2011 and May 2013, the company was successful in producing 206 kg of gold from alluvial mining, which valued at MYR 38 million. In June 2016, CNMC Goldmine Holdings Limited took over Pulai Mining Sdn. Bhd. and further supported the gold exploration and mining activities with the focus on identifying the source of gold and concentrating on processing the alluvial gold.

3. Geological Setting

3.1. Regional Setting

Peninsular Malaysia is an integral component of the Southeast Asian continental core of Sundaland, which is composed of two tectonic blocks or terranes assembled during the Late Triassic, known as the Sibumasu Terrane (the western block) and the Sukhothai Arc or East Malaya Block (the eastern block) [39–42], as illustrated in Figure 1a. Sibumasu drifted away from the NW Australian Gondwana block late during the Early Permian, while the East Malaya Block detached from Gondwana in the Devonian [42–44]. Both terranes originated from the eastern margin of the Gondwana supercontinental block [39,41,42,45,46].



Figure 1. (a) The illustration of principal continental blocks, sutures, and arc terranes of Southeast Asia, modified after [39]; The location of Peninsular Malaysia is marked in the dashed box. (b) The Peninsular Malaysia map indicating the Bentong-Raub Suture Zone NW Domain, and the Western, Central, and Eastern Belts; figure modified from [28,30,47]. Pulai is marked with the red dot and lies in the Gua Musang Formation, Central Belt of Peninsular Malaysia.

The eastward subduction and movement of the Palaeo-Tethys oceanic crust underneath the Sukhothai Arc or Indochina Block resulted in the collision between the Sibumasu and Indochina blocks, forming the Bentong-Raub Suture Zone, which began in the Late Permian, continued to evolve between the Early and Middle Triassic, and ended in the Late Triassic [40,48]. These two continental blocks are divided by the Bentong-Raub Suture Zone, which preserved the remnants and constituents of the Devonian to Late Permian Palaeo-Tethys oceanic basin [42,43,49–51].

Peninsular Malaysia is characterised by three striking belts extending north–south, (Figure 1b), namely, the Eastern Belt, Western Belt, and Central Belt, which resulted from the collision and subduction of the Sibumasu and Indochina blocks [41–43,52]. The Western Belt lies within the Sibumasu Terrane, represented by several stratigraphic sequences: an Early Palaeozoic sequence of continental margin; a Late Palaeozoic to Triassic carbonate platform; Triassic-aged clastic and deep basinal sequences, and a Jurassic to Cretaceous continental sequence [29]. The Quaternary sediments extend from the coastal region to the mountain ranges of the Main Range Granitoid. The northern part of the Western Belt is covered with bedded chert clastic materials including conglomerate and turbidite sandstone of the Permian-Triassic Semanggol Formation, and black shale of the Silurian-Devonian Sungai Patani Formation [29]. The southwest part of the Western Belt comprises Ordovician slate, phyllite, schist, and limestone, whereas the northern part is composed of Cambrian sandstone interbedded with siltstone [29]. The prominent intrusive rocks are

S-type granitoids, emplaced during the Late Triassic to early Jurassic, which are associated with the tin-bearing granitoids in the Main Range [39,41].

The Central Belt, located east of the Bentong-Raub Suture Zone, is composed of metasediment and sequences of deep to shallow marine clastic sediments [29,53], carbonates with abundant intermediate to felsic volcanic rocks, and volcaniclastic turbidites that accumulated in deep basins during the Permian-Triassic period [54–58].

The Eastern Belt is located in the East Malaya Block and forms part of the East Malaya Fold Belt. The oldest rock unit identified is Carboniferous continental margin siliciclastic and carbonate rock [42]. The deformed and highly folded Late Palaeozoic strata are unconformably overlain by the continental conglomerate deposit (Late Permian) and continental sequences of the Jurassic-Cretaceous. Eastern Malaya granitoids have a broad value of compositional range of I-type subduction-related, K-feldspar megacryst granodiorites and calc-alkaline biotite-hornblende, tonalities, and granites. The age of the U–Pb of zircons ranges from the early Middle Permian to the early Late Triassic [59], indicating that the magmatic body was produced by the Palaeo-Tethys subduction beneath the East Malaya-Indochina block and is associated with the Sukhothai Arc [41,60].

The Bentong-Raub Suture Zone (BRSZ) is defined as a main geological feature in Peninsular Malaysia and signifies a NW-SE trending fault system, extending roughly 15–20 km across. Refs. [42,43] described the Bentong-Raub Suture Zone as an accretionary prism comprising pelitic carbonaceous schist, sandstone, conglomerate, amphibole schist, serpentinite, mélange-olistostrome and chert, as well as turbidites, volcanic and volcaniclastic rocks. Active volcanism related to the intrusion of the Permian and Triassic granitoid bodies of the Main Range and Eastern Belt supports the theory [39,61–63]. The Bentong-Raub Suture Zone is also characterised as an imbricated complex of oceanic cherts which document the history of the Palaeo-Tethys Ocean from the Late Devonian to at least the Late Permian.

Numerous mineralised vein-hosted gold deposits occur across a 50 km extensive region in the eastern part of the Bentong-Raub Suture Zone, a significant region for hydrothermal fluid systems. These deposits have undergone multiple overprinting mineralising events under a ductile-brittle zone in the Central Gold Belt, such as the Penjom gold deposit [64]. Radar satellite imagery identified a strike-ridge lineament-zone trending NNE to NS on a splay to the NNE of the main Bentong-Raub Suture Zone [65,66]. This zone is where major gold deposits including Penjom, Selinsing, Buffalo Reef, Raub, and Tersang are mineralised, while Pulai, Ulu Sokor, Katok Batu, Sungai Sok, and Batu Melintang are located further north towards the Thailand and Kelantan border.

The accretionary prism, continental margin formation, post-diagenetic deformation, and metamorphism resulted in the mineralisation of vein-hosted gold deposits eastward of the Bentong-Raub suture [29,43,62,63]. The mineralisation of gold can be found in both quartz-carbonate vein systems and dispersed in the altered low-grade greenschist facies of volcanogenic-sedimentary rocks. Extensive magmatic events, deformation, and metamorphism have provided a conducive environment and setting for the trapping and source of the gold. These conditions are typically characterised as orogenic and result in mesothermal-lode-type gold deposits [29,32–34,67,68].

Arsenopyrite and pyrite are the most common sulphide minerals associated with vein-hosted gold mineralisation in the Central Gold Belt of Peninsular Malaysia. At the Tersang gold deposit located within the gold belt, gold mineralisation is corresponded with arsenopyrite and pyrite formed in quartz-sulphide veins within grey, fine-grained sandstone and rhyolitic sills. However, the mineralisation of gold in Penjom is linked to the massive amounts of sulphides in the zone of carbonate-rich dilated quartz veins. Gold can be found both within disseminated stockwork veins of quartz-carbonate in tonalite and with pyrite and arsenopyrite within quartz-carbonate stringers and veins, mainly in shear zones of brittle-ductile nature, and in all type of rocks including rhyodacite. In the Selinsing gold mine, the mineralisation of gold occurs as fine gold particles, mostly correlated with galena and arsenopyrite which has crystallised in mylonite, cataclasite, sandstone, phyllite, and siltstone [29]. According to [69], the gold deposit found in Raub is identified as a quartz

sulphide type. The presence of gold mineralisation in Raub is linked to sulphide minerals such as pyrite, arsenopyrite, stibnite, scheelite, and minor amounts of chalcopyrite and cerussite, which are primarily concentrated within the quartz shear zone, sheeted quartz vein, and quartz breccia. The gold deposition at Buffalo Reef is connected to quartz veins that primarily occur within phyllite and schistose sandstone. The quartz veins consist of a significant amount of sulphide minerals including pyrite, arsenopyrite, stibnite, and galena. An in-depth study of the distribution of gold within the sulphide minerals has revealed that approximately 75% to 80% of the gold is formed as refractory gold within the crystal lattice of arsenopyrite [70].

3.2. Local Setting

Kelantan is one of the main gold-producing states in Peninsular Malaysia (Figure 2a). In the past, about 1.13 t of gold was mined and produced in Kelantan within the years of 1906 and 1912 [38]. (Chu and Singh, 1986). Gold started to be mined during the early times in the Pulai districts of Pergau, Lebir, Galas, and Kelantan River. Refs. [35,38] observed that the mineralisation of gold at Kelantan, which was concentrated in the central part of the state, is related to the Kemahang Granite in the north of Kelantan, the Boundary Range Granite in the east, and the Stong Igneous Complex and Senting Granite in the western part of Kelantan state (Figure 2b). The structures upon the regional scale in the Kelantan gold district are controlled by the north-south and northwest-southeast trending of faults, including the Lebir fault zone with a subsidiary northeast-southwest trending fault.



Figure 2. (a) Map of Peninsular Malaysia, highlighting the state of Kelantan and Pulai area. (b) Geological map of Kelantan, modified after [35,71]: location of Pulai is marked in the red box; (c) Geological map of the Pulai gold prospect: fieldwork, sampling, and drilling (previously by Pulai Mining) were conducted in the area marked with the red box.

The Kelantan gold district is comprised of felsic and intermediate intrusions that were intruded into the Permian and Triassic metasedimentary rocks [35–37]. The mineralisation of gold took place during the Late Triassic to Early Jurassic period [72]. In contrast, the

younger (Cretaceous-Jurassic) and older (Silurian-Ordovician) sedimentary rocks within the state exhibit insignificant levels of gold mineralisation.

The main factors controlling gold mineralisation are the source rock, heating chamber, and depositional structures. According to [67], the main source rocks can be attributed to volcanic rocks from the Permian-Triassic period, which are found associated with sedimentary rocks. The intrusion of granitoid bodies beneath the volcanic-sedimentary rocks served as the heat source, triggering the formation of hydrothermal fluids. The presence of sheared and faulted zones, which originate from deeper layers, creates the suitable conditions for the infiltration and deposition of gold. Gold mineralisation at Kelantan is mostly related with hydrothermal quartz vein systems, volcanogenic massive sulphides, and skarn [35]. In fact, Pulai is associated with a high-sulphide quartz vein [35]. According to [35,73], Kelantan has been identified to have five mineralisation zones, based on the geochemical and geological context and categorised according to the types of ore deposits: the hydrothermal-vein gold mineralisation zone, gold-silver-mercury zone (hydrothermal vein), gold-base metal associated with volcanic exhalative zone, zinc-copper-lead zone, and silver-lead-zinc zone.

Pulai is part of the Gua Musang Group, which is widely distributed in the northern part of the Central Belt of Peninsular Malaysia [74,75]. The Gua Musang Group is composed of shallow marine deposits of Middle Permian-Triassic carbonate sequences and Triassic argillaceous-volcanic facies, later intruded by granodiorite and gabbro [61]. The dominant argillaceous facies of the Gua Musang Group comprise interbedded or lenses of various sedimentary to metamorphic sequences of shale, mudstone, siltstone, slate, and phyllite [76]. Volcanic and pyroclastic facies are identified as agglomerates, tuffaceous material, lapilli, and volcanic agglomerates interbedding with sequences of limestone or black tuffaceous or carbonaceous shale [76–78]. Rhyolitic volcanic rocks are dominant in southwest Kelantan, while andesitic composition dominates the southeast region of Kelantan [76,79]. The various sizes and composition of volcanic rocks in the Gua Musang Group indicate regional volcanism that contributed to the shallow marine topography ideal for limestone deposition [78,80].

3.3. Geological Setting of the Pulai Gold Mine

Thick Quaternary sediments in the Pulai gold mine form alluvial deposits along the main rivers, namely, the Sungai Galas and Sungai Tan See. Overall, the Pulai gold mine geology is comprised of north-south blocks of Lower Permian metasedimentary rocks, limestone, and pyroclastic and volcanic rocks that strike in the NNE direction (Figure 2c). The western part of Pulai is made of limestone, interbedded tuff with slate, and andesite that dip 23°–72° to the west-northwest. Andesite along with andesitic and rhyolitic tuff are distributed in the central part of Pulai, while the southern part of the area is covered with andesite and andesitic tuff.

The eastern and central zones of the mine are dominated by various volcanic and volcaniclastic rocks. Pyroclastic rocks are characterised as stratified, structureless, and massive bodies. The rock unit is dominated by the mixture of crystal lithic tuff, agglomerate, breccia, quartz grain, siltstone, and mudstone. The most common volcaniclastic rock observed is matrix-supported with greenish to greyish felsic volcanic ash, medium- to coarse-grained crystal lithic tuff, and tuffaceous breccia or conglomerate. Based on the borehole section, volcanic occurrences in Pulai exhibit a broad spectrum, with rhyolitic to andesitic composition and trace amounts of ferro-magnesium minerals. The rhyolitic composition of subduction-related rock is associated with the Middle-Upper Triassic, while andesite is more common during the Permian [42]. Sulphide mineralisation in the tuffaceous materials is common and most of the rock is slightly to strongly chloritised and sericitised.

Metasedimentary rocks of the Pulai gold mine are generally observed along the western margin to the east of the Sungai Tan See and close to the north-south trend of the Sungai Galas. The degree of metamorphism affecting the sedimentary rocks is variable at various localities and depths, ranging from shale, slate, and phyllite, while some is associated with tuffaceous materials. The metasedimentary rock comprises mainly greenish to greyish, fine-grained slate to phyllite and metatuff. The upper section of Pulai is strongly oxidised and dominated by argillaceous and highly sericitised rock, covering up to 20 m in depth of the host rock.

Exposed carbonate bodies, mainly limestone hills and pinnacles, are extensively developed as dominant topographic landscapes, trending approximately north-south alongside the Sungai Tan See in the western part of Pulai. At various localities, the limestone is interbedded with thin bands of metasedimentary, volcanic, and tuffaceous materials. The limestone is identified as whitish to light grey crystallised and compacted calcite, typically well-bedded and jointed. Impurities also cause the variation of the limestone, due to the argillaceous and arenaceous materials present in the surrounding host rock.

The dominant structural features of the Pulai gold mine are the north-south- and north-northeast-oriented fault zones that control mineralisation and stream formation. The north-south fault zone dominates the western part of the Pulai gold mine, forming a north-south valley, where the eastern side is covered with pyroclastic material, and the western side is composed of limestone hills. Medium- to coarse-grained mylonitic granite is exposed at the riverbed, representing the north-northeast striking fault zone distributed along the central valley. Granodiorite is found as small intrusive bodies throughout the Pulai area.

The Pulai gold mine is well known for its alluvial gold in fluvial placer deposits that extend along 17 km of the Sungai Galas, Gua Musang [74]. The bedrock morphology of the Sungai Galas is typically narrow, small, and surrounded by hilly ground, which expands to form alluvial plains varying in width between 120 m and 1200 m, with an average thickness of 6 m to 20 m. The alluvium consists of poorly sorted sandy and clayey gravels, known as the basal gravelly horizon, and is overlain by sandy clay and silt. According to [74], the detrital gold is mostly accumulated at the basal gravelly horizon and usually near the surface silt and stream gravel, whereas the coarse detrital gold is highly concentrated in the slope interruption zone at the convergence of the Sungai Galas and Sungai Tuang. The finer gold, however, is concentrated further downstream in the potholes of limestone bedrock surfaces [74].

Hydrothermal activities have resulted in the wide distribution of quartz veins, veinlets, and stockworks. When partially combined with gold mineralisation in Pulai, these activities have caused various types of host rock alteration, including silicification, carbonation, chloritisation, and argillic and potassic alteration. The gold mineralisation in Pulai is closely linked to silicification, argillic alteration, and limonitic quartz. The primary gold mineralisation at the Pulai gold mine occurs in the western part of Pulai, along the north-south major fault zone. This is revealed by the limonitic quartz vein in the metasedimentary and metavolcanic rock. The mineralisation zone of the primary gold involves millimetre- to centimetre-thick quartz-pyrite stringers and the surrounding altered host rocks. Silicification is widely developed and represented by quartz veins, stockworks, or veinlets, mainly distributed in the host rocks, ranging from tens of centimetres to tens of metres in width. However, carbonation is distributed as veinlets of carbonate which are intergrown with quartz and associated with sulphide mineralisation. Chloritisation and epidotisation also occur to varying degrees, altering the andesitic slate and tuff.

4. Methodology

We conducted fieldwork to document the lithology, mineralogy, and geological features in the Pulai area and also extract representative samples of mineralised and unmineralised rocks. Locations for mapping and sampling at the Pulai gold mine were marked using GPS and a topographic map. From the collected samples, selected blocks were chosen to prepare polished blocks and thin sections. A detailed microscopy study was carried out by examining 41 polished blocks of sulphide samples under a reflected microscope to discuss the mineralogy and paragenesis of sulphides in the Pulai gold mine related to gold mineralisation. Out of the 41 polished blocks, 5 were chosen to represent the best sulphide samples for examining the geochemistry of pyrite and arsenopyrite in Pulai. The sampling was concentrated in the western part of Pulai, as marked on the map (Figure 2c), since exploration and drilling work have been established and localised in that area. The outcrops and hand specimens for rock samples consisting of sulphides from the Pulai gold prospect are presented in Figure 3a–f.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at the Centre for Ore Deposit and Earth Sciences (CODES), University of Tasmania, Australia, was utilised to analyse the trace element composition and the imaging and mapping of the trace element pattern for the selected arsenopyrite from the Pulai gold mine. The LA-ICPMS combines a Resolution 193 nm excimer laser, together with an Agilent 7700x ICP-MS. The mapping of the element composition required a time-resolved signal mode with a laser beam of 5 μ m, ~3.5 J/cm² of laser fluence, and 5 Hz of repetition rate. The carrier gas signal with no ablation was monitored and acquired regularly for the correction of instrumental background.

Spot analysis was conducted using a laser beam size of either 19 μ m or 29 μ m based on the size of sulphide grains and 5 Hz of firing rate, moving speed of 3 μ /s with laser energy of 3.5 J/cm². A spot size of 51 μ m was applied on the standard STDGL3 and GSD-1G; however, a 19 μ m spot size was used on the standard PeruPy. Primary assessment and calibration of elemental contents were conducted using the following reference materials (standards): STDGL3 [81,82], mainly for chalcophile and siderophile elements, while GSD-1G [83] for lithophile elements, and PeruPy. The images were programmed using spot sizes of 19 μ m to draw lines across the sulphide grain. The analytical detection limit of the elements is 0.001 ppm or 1 ppb.

The backgrounds were recorded prior to each trace element image [17]. Ca, Si, Ti, V, Cr, Fe, Mn, Ni, Co, Cu, Zn, Cd, Se, As, Mo, Sb, Sn, Ag, Te, W, Pt, Au, Tl, Hg, Pb, Bi, Th, and U. Maps of the trace element images were generated and transformed from counts per second (cps) to parts per million (ppm) in a .CSV file to convert into a visible output of the elemental composition in pyrite and arsenopyrite. The data in .CSV files were then imported into ioGASTM, an advanced software programme for geochemical exploratory data analysis and interpretation. Using ioGASTM, each pyrite and arsenopyrite grain is loaded as x and y coordinates for presentation and visualisation, followed by quantitative analyses of all the trace elements within the sulphides.

Sulphur isotope analysis was performed on six sulphide samples: two vein-hosted pyrite samples and four pyrite with arsenopyrite hosted in tuffaceous metasediment samples. Approximately 0.3 to 0.4 mg of finely powdered sulphide was weighted in tin capsules and tested for stable sulphur isotopes. Flash combustion isotope ratio mass spectrometry (varioPYRO cube paired to Isoprime100 mass spectrometer) at the Central Science Laboratory, University of Tasmania, Australia, was used to analyse the sulphur isotope of the sulphides. The product of SO₂ during the combustion was captured in a trap, isolated from other by-products of the combustion, and later fed into a mass spectrometer, where the sample's isotopic ratio was compared against the reference gas. The abundance of the stable isotope was recorded as delta (δ), represented by the deviation from conventional standards in parts per million (‰) based on the following equation:

δ 34S (‰) = [(R_{sample}/R_{standard} - 1) × 1000]

where R is reported as the ratio of ${}^{34}\text{S}/{}^{32}\text{S}$, and the $\delta^{34}\text{S}$ values are recorded respective to the Canyon Diablo Troilite (CDT). After every fifth sample, two international standard references with known isotopic composition (IAEA-S-1, -S-2, -S-3, and -SO5, as well as NBS-123 and -127) were analysed for quality assurance and instrument calibration. The instrumentation's analytical performance, linearity, and drift correction was determined by the repetitive testing of these reference standards. For isotopic measurement, the precision was 0.2%.



Figure 3. Outcrop and hand specimens as rock samples containing sulphides from the Pulai gold prospect: (**a**,**b**) show the limonitic, brittle, and oxidised quartz vein marked with the dotted yellow line on the trenching wall, hosted in argillaceous rock; (**c**(**i**)) displays the limonitic quartz vein with sulphide, mainly pyrite, with a close-up image; (**c**(**i**),**d**(**i**)) a borehole sample of the quartz vein hosted in carbonaceous tuff with arsenopyrite mineralisation, as shown in the close-up image of the polished mount; (**d**(**ii**),**e**,**f**) are the borehole samples of tuffaceous volcaniclastic rock with sulphide mineralisation, mainly pyrite and arsenopyrite.

5. Results

5.1. Mineralogy and Paragenesis

The samples of sulphide and gangue minerals underwent petrography and microscopy studies to establish the lithological, mineralogical, paragenetic, and host rock alteration of the Pulai gold mine. Our findings reveal that the hydrothermal assemblages in Pulai are mainly composed of quartz, limonite, ankerite, talc, sericite, kaolinite, calcite, chlorite, and sulphide. Gold mineralisation is related to the quartz-sulphide-limonite and quartz-carbonate-sulphide veining systems. Furthermore, sulphides found in the Pulai gold mine include pyrite, arsenopyrite, pyrrhotite, galena, sphalerite, and chalcopyrite (Figure 4a–h). The detailed mineralogy of Pulai ores is important to determine the paragenesis sequence connected to gold mineralisation. The mineralisation phase of Pulai is simplified in a paragenesis sequence table, which summarises the sulphide and gangue mineral formation in this localised area (Figure 5).

Pyrite was the most common sulphide ore in all the mineralised regions in Pulai. It is generally coarse- to fine-grained and disseminated in quartz veins and host rocks. Four types of pyrite were identified in Pulai, based on their morphology and composition, which were categorised as framboidal pyrite (Pyrite 1), anhedral to subhedral inclusion-rich, porous pyrite (Pyrite 2), euhedral to subhedral clean pyrite (Pyrite 3), and coarse euhedral to subhedral pyrite (Pyrite 4).

Pyrite 1 formed aggregates of discrete equigranular shapes of euhedral microcrystalline pyrite in the carbonaceous slate host rock (Figure 4a). Pyrite 1 was commonly observed with Pyrite 2, sphalerite, and chalcopyrite. Pyrite 2 was the most abundant pyrite discovered in Pulai. Pyrite 2, mostly documented in volcanic and pyroclastic rocks, consisted of inclusion-rich chalcopyrite, pyrrhotite, sphalerite, galena, and matrix inclusion. Pyrite 2 was an early-phase pyrite frequently found in corroded, porous, anhedral, irregular forms, frequently replaced or rimmed by pyrrhotite. Pyrite 2 could be found together with Pyrite 3 in the tuffaceous volcanic- or metasedimentary-hosted material. Pyrite 2 contained a low concentration of refractory gold, and no visible gold was recorded (Figure 4b-e). Relatively, Pyrite 3 is younger than Pyrite 2 and found as intergrowth, as the former grew on the latter (Figure 4b). Pyrite 3 was recognised as a euhedral, clean pyrite grain and was not associated with the gold mineralisation phase. Pyrite 3 was also found in andesite as a single sulphide mineral along the fracture. Late-phase pyrite identified as Pyrite 4 is described as a clean and coarse euhedral to subhedral pyrite grain (Figure 4f). Pyrite 4 was mainly found in the milky quartz vein or limonitic quartz vein in metasedimentary or volcanic-hosted rock. The largest grain reached up to 1.7 mm, sometimes seen as a fractured grain or vein indicating a post-deformation stage from the cross-cutting of the volcanic host. Pyrite 4 usually occurred as a single grain and contained a high composition of refractory gold and arsenic.

Arsenopyrite was easily recognised by its euhedral, rhombohedral, coarse to fine aggregates or disseminated around a thinly bedded parallel network of carbonaceous quartz veinlets in silicified tuffaceous rock or tuffaceous volcaniclastic rock. Inclusions of sphalerite (10–30 μ m) and pyrrhotite (30–80 μ m) were found in the arsenopyrite grain. Two types of arsenopyrite were identified in Pulai: Arsenopyrite 1 and Arsenopyrite 2. Intergrowth of pyrrhotite in Pyrite 2 and Pyrite 3 could be observed together with Arsenopyrite 1 during the early phase of sulphide crystallisation in the silicified tuffaceous metasediment, as shown in Figure 4g. However, Arsenopyrite 2 was often found as a single mineral formed in a carbonaceous quartz vein during the late phase of sulphide crystallisation in Pulai, Figure 4h. A high detection of refractory gold in Arsenopyrite 2 compared to Arsenopyrite 1 was documented based on the LA-ICPMS analysis. However, no visible or gold inclusion was detected in the arsenopyrite grains.

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Figure 4. Textural and mineralogical characteristics of sulphide identified at the Pulai gold prospect: (a) aggregates of discrete equigranular shapes of euhedral microcrystalline Pyrite 1 in the host rock of carbonaceous slate; (b) intergrowth of Pyrite 2 over Pyrite 3 and pyrrhotite in tuffaceous volcanic rock; (**c**–**e**) association of Pyrite 2 sphalerite, chalcopyrite, and galena in tuffaceous phyllite (chalcopyrite form inclusions, known as chalcopyrite disease on the surface of sphalerite; galena crystallises irregularly or fills the spaces between Pyrite 2 and sphalerite); (**f**) quartz-vein-hosted of subhedral and clean Pyrite 4, occurs as disseminated grain; (**g**) Arsenopyrite 1 with intergrowth of Pyrite 2, Pyrite 3, and pyrrhotite inclusion in tuffaceous metasediment; (**h**) Arsenopyrite 2 grain as disseminated, euhedral grain in a carbonaceous quartz vein.



Figure 5. Paragenesis sequences of sulphides and gangue minerals in Pulai, based on the mineralogical study.

Pyrrhotite was found predominantly as a rim and replaced Pyrite 2 in the silicified pyroclastic host, as well as being intergrown with pyrite and arsenopyrite, as observed in Figure 4b–g. Pyrrhotite also can be identified as inclusions in Pyrite 2, ranging in size between 40 μ m and 120 μ m, and varied in size from 20 μ m to 40 μ m. Pyrrhotite was also observed to be a massive, elongated, irregular-shaped mineral up to 2 mm long and associated with chalcopyrite. The massive grain of sphalerite has a close relationship with Pyrite 2, galena, and chalcopyrite in the pyroclastic or tuffaceous materials (Figure 4c–e). Chalcopyrite and galena were documented as overgrown or forming fine aggregates occupying sphalerite interstitial spaces. Chalcopyrite diseases appeared as exsolution blebs or inclusions on the surface of sphalerite (Figure 4c–e). However, sphalerite can be found partially rimmed or replaced by galena and chalcopyrite, and also observed as an inclusion in Pyrite 2 and arsenopyrite grain.

Galena was mainly present late in paragenesis. Galena was hosted within the altered zone of tuffaceous material and was primarily abundant along with sphalerite, pyrite, and chalcopyrite. Galena is easily identified by its triangular pits along the cleavage lines (Figure 4c) and is mineralised in the late phase as fine-grain aggregates. Galena was found as either disseminated, fine grains or as aggregate of massive fracture filling in brecciated Pyrite 2, intergrown with sphalerite and Pyrite 2, or as a late inclusion of pyrite. Overall, only alluvial gold has been discovered as visible gold in Pulai. The alluvial gold was widely distributed along the north-south Galas Valley. No visible gold could be observed within sulphide minerals in the petrography study. However, the LA-ICPMS trace element mapping revealed the existence of invisible or refractory gold in sulphides of pyrite and arsenopyrite in the Pulai area.

5.2. Trace Element Geochemistry of Pyrite and Arsenopyrite

LA-ICPMS determined the chemical composition of gold-bearing arsenopyrite and pyrite on a suite of five representative polished blocks. Six pyrite and four arsenopyrite grains of Pulai sulphides were subjected to LA-ICPMS analysis for mineral grain mapping. For this study, the LA-ICPMS trace element mapping was focused on Pyrite 2 intergrown with Pyrite 3 in silicified tuffaceous rock, Pyrite 4 in quartz-vein-hosted pyrite, Arsenopyrite 1 in volcaniclastic rock, and Arsenopyrite 2 in a carbonaceous quartz vein. Pyrite 1 was excluded from this study as it was highly oxidised due to weathering which may cause misleading results. The analysis was combined with a detailed petrographic study to produce the sulphides' geochemical details and elemental distribution. The trace element mapping demonstrated significant variation between the core and margin of pyrite and arsenopyrite grains, with the core being richer in some trace elements compared to the margin and vice versa. As a result, the details on the trace element composition of pyrite and arsenopyrite in Pulai have been evaluated separately for the core and margin of the grains as indicated in Tables 1 and 2, respectively, for a better understanding and interpretation of the mineralisation event in the Pulai gold deposit.

5.2.1. Pyrite Types and Their Composition of Trace Elements

The LA-ICPMS trace element mapping revealed the composition and distribution of trace elements in three types of pyrite: Pyrite 2 (Figure 6), Pyrite 3 (Figure 6), and Pyrite 4 (Figure 7A,B). The key trace elements of pyrite, including Au, As, Co, Ni, Pb, Bi, Sb, Cu, and Ag, were chosen to understand spatial element zoning and enrichment features better. However, other elements including Ba, Rb, Sr, and Zn were reported as minor trace elements in the Pulai pyrite grain. Arsenic is an essential constituent in most of the pyrites in Pulai, with a maximum concentration of 323,858 ppm.

In general, Pyrite 2 and Pyrite 3 were commonly found intergrown together as two pyrite generations in silicified metasediment or metavolcanic rock. The distinct trace element composition of the zoned pyrite reflects the multi-stage paragenesis of pyrite in a single grain. Pyrite 2 formed as the core of the pyrite grain, identified by its inclusion-rich texture, and was followed by the intergrowth of inclusion-free Pyrite 3 at the margin of the grain. The Au–As enrichment band identified on the margin of Pyrite 2 and the same pattern of high Pb–Bi–Sb–Ag concentration clearly defined a boundary between Pyrite 2 and Pyrite 3.

Pyrite 2 had a higher content of Co and Ni elements, with values ranging from 0.1 ppm to 403 ppm (mean: 42 ppm) and 1 ppm to 398 ppm (mean: 49 ppm), respectively. Au was only concentrated at the margin of the grain and varied from 0.01 ppm to 5.6 ppm (average: 0.6 ppm), forming Au-barren zone at the core of Pyrite 2. Major trace elements were preferentially concentrated at the rim of the Pyrite 2 grain as compared to the core. Overall, the concentration of the trace element in Pyrite 2 varied from 876 ppm to 13,127 ppm (mean: 4026 ppm) for arsenic, 0.2 ppm to 226 ppm for Sb (mean: 28 ppm), 0.2 ppm to 377 ppm for Pb (mean: 57 ppm), and 0.03 ppm to 76 ppm for Bi (mean: 15 ppm), which were mainly concentrated and occurred as inclusions at the margin of Pyrite 2. The As/Au and Ag/Au ratio for Pyrite 2 ranged from 1003 to 1,057,353 (mean: 199,339) and 0.004 to 523.13 (mean: 9.46), respectively. However, the Co/Ni ratio of Pyrite 2 varied between 0.01 and 7.3 (mean: 1.12).

Pyrite 3 contained lower Co and Ni concentrations compared to Pyrite 2, with values ranging from 0.1 ppm to 111 ppm (mean: 7 ppm) and 0.9 ppm to 86 ppm (average: 10 ppm), respectively, while the ratio of Co/Ni for Pyrite 3 ranged from 0.005 to 5.7 (mean: 1.0). Au concentration was very low in Pyrite 3, only up to 1.12 ppm (mean: 0.07 ppm). Arsenic was also detected in low concentrations from 1431 ppm to 6492 ppm (mean: 3870 ppm). The As/Au ratio for Pyrite 3 varied from 3989 to 741,863 (mean: 393,898), while the Ag/Au ratio fell between 0.04 and 523.13 (mean: 22.82). There was no indication of the significant enrichment of other trace elements in Pyrite 3 mineral formation, as observed in the LA-ICPMS trace element mapping.

Minerals	Element (ppm)	As	Au	Ni	Co	Sb	Pb	Bi	Rb	Sr	Ba	Ag	Cu	Zn	As/Au	Ag/Au	Co/Ni
Pyrite 2	Minimum	875.5126	0.008752	0.914056	0.124547	0.166966	0.219604	0.027948	0.036279	0.005797	0.014022	0.022733	1.670181	0.876008	1002.8092	0.004085	0.006677
	Maximum	13,126.78	5.565245	398.0231	402.8428	226.117	377.4368	76.36598	15.09278	28.10147	69.39259	4.578416	40.020441	98.62157	105,7352.5	523.128	7.316678
	Mean	4025.523	0.572877	48.7811	41.62942	27.92246	57.37764	14.67409	0.405848	1.24255	2.358685	0.268457	6.9916967	2.428775	199,339.36	9.458289	1.124381
	Median	3839.977	0.008752	32.53811	25.9273	8.762911	21.33459	7.036974	0.036279	0.005797	0.014022	0.022733	3.72904	0.876008	218,554.88	2.597463	0.758435
	Standard Deviation	1747.474	0.986757	49.0894	49.61695	40.66558	76.93855	16.61982	1.479143	2.880893	7.618886	0.707193	8.2616502	7.387671	196,004.15	46.95918	1.187133
	Minimum	1431.719	0.008752	0.914056	0.124547	0.166966	2.564584	0.027948	0.036279	0.005797	0.014022	0.022733	1.670181	0.876008	3989.0484	0.040723	0.005
	Maximum	6492.788	1.116488	86.21947	110.6214	159.9688	306.2989	59.31093	15.09278	51.68063	69.39259	4.578416	38.565203	414.5025	741,863.39	523.128	5.699315
Pyrite 3	Mean	3870.227	0.067667	10.13978	7.468502	18.1978	45.52324	8.497963	0.539567	0.531254	2.006845	0.243683	5.0982302	3.392135	393,897.96	22.82145	1.000715
	Median	3980.094	0.008752	6.217371	3.785058	10.09349	29.59871	6.45011	0.036279	0.005797	0.014022	0.022733	3.274285	0.876008	446,222.05	2.597463	0.570743
	Standard Deviation	740.2362	0.173264	10.60753	11.64654	26.30521	49.66266	7.20975	1.777206	2.691696	7.425777	0.649396	5.6123847	26.56162	156,094.13	67.63494	1.235696
	Minimum	1185.703	0.181959	0.08736	0.009341	0.03732	0.014009	bdl	bdl	bdl	bdl	bdl	0.929679	0.111792	287.66017	0.000303	0.002
	Maximum	6326.242	11.69149	116.521	30.35347	1753.55	636.7568	35.03213	1.309842	1.890307	312.7561	228.3681	31774.445	25.05898	22,655.944	817.8465	1.995192
Pyrite 4 Core	Mean	2716.418	1.447866	1.712607	0.241855	12.66616	14.86365	0.639219	0.044029	0.096132	2.525599	1.387968	58.346854	0.89571	3881.7382	3.250824	0.205242
	Median	2588.965	0.890961	0.549191	0.016663	2.271188	7.722599	0.1008	0.006158	0.001191	0.002379	0.257806	9.920386	0.215126	2916.6537	0.222251	0.103886
	Standard Deviation	722.2518	1.498466	7.876297	1.431014	86.91491	30.03519	1.999302	0.118292	0.24287	17.62948	10.34631	1054.0105	2.015316	3454.2801	32.87833	0.330821
Margin/Rim	Minimum	546.1231	0.325801	0.150474	0.017228	0.087293	0.16585	bdl	bdl	bdl	bdl	bdl	0.909897	0.183283	367.00818	0.003257	0.020244
	Maximum	323,858.2	8.831484	559.5409	53.19705	194.5393	6187.396	8.893333	13.22643	19.83836	5071.792	111.1635	654.15847	110.449	294,120.56	44.74188	0.810323
	Mean	13,844.41	1.156559	51.7326	5.821004	36.80185	139.1087	1.227883	0.209939	0.618412	58.84502	4.227447	42.68588	4.043433	7242.5454	2.260234	0.162475
	Median	1409.014	0.825742	26.69594	3.694144	15.94069	22.06939	0.646591	0.00691	0.09127	0.404563	0.622394	14.995271	0.468112	1886.3079	0.945154	0.12988
	Standard Deviation	49,334.95	1.123101	70.64892	7.399387	42.42451	585.5555	1.470975	1.080264	2.072867	362.074	12.8507	92.689493	11.96903	23,895.428	4.816078	0.129584

Table 1. The summary of LA-ICPMS data on trace element composition and concentration of pyrite in the Pulai gold prospect area: bdl—below detection limit.

											_				
Mineral		Element (ppm)	As	Au	Ni	Со	Sb	Pb	Bi	Rb	Sr	Ba	Ag	Cu	Zn
Arsenopyrite 1	Core	Minimum Maximum Mean Median Standard Deviation	147,715.2 647,746.3 445,769.2 446,833.2 42,105.96	$\begin{array}{c} 0.01 \\ 8.09037 \\ 0.595056 \\ 0.28969 \\ 0.766755 \end{array}$	$\begin{array}{c} 0.270616\\ 2609.11\\ 163.4468\\ 31.44705\\ 289.3454 \end{array}$	0.035383 3240.641 185.2653 69.65092 316.5946	62.46316 742.9067 327.3336 323.8355 139.1831	$\begin{array}{c} 0.180196\\ 326.2957\\ 35.95442\\ 18.44897\\ 42.50602 \end{array}$	0.016762 142.7171 29.73462 23.56737 29.78226	0.012262 48.33404 1.46917 0.027719 3.73276	0.001139 42.90599 0.497222 0.002556 1.801985	0.000483 220.4094 6.770163 1.061115 17.33855	0.011431 8.543954 0.400718 0.037786 0.707449	0.379408 1193.487 11.82745 3.427284 51.0557	0.18629 30.90141 0.555323 0.205942 1.155353
	Margin/Rim	Minimum Maximum Mean Median Standard Deviation	74,012.25 573,262.2 435,781.8 452,524.8 70,498.62	$\begin{array}{c} 0.137091 \\ 14.97858 \\ 3.662126 \\ 3.186889 \\ 2.341259 \end{array}$	0.270616 3340.014 277.6651 44.41733 485.4634	0.309225 5273.879 447.3669 123.5262 702.3528	6.528173 594.1372 150.4241 136.3995 75.35164	0.169033 177.158 28.7493 18.12413 32.0484	0.016762 150.9966 19.81568 10.77917 24.97925	0.012262 45.55278 0.665146 0.013524 2.79952	0.001139 58.37319 0.370644 0.002556 1.604939	$\begin{array}{c} 0.000483\\ 321.6794\\ 2.625556\\ 0.016\\ 12.20009 \end{array}$	$\begin{array}{c} 0.011431 \\ 5.306475 \\ 0.316314 \\ 0.014488 \\ 0.596007 \end{array}$	$\begin{array}{c} 0.379408 \\ 509.4985 \\ 12.12164 \\ 5.309415 \\ 36.3568 \end{array}$	0.18629 3727.486 6.159907 0.205942 109.6361
Arsenopyrite 2	Core	Minimum Maximum Mean Median Standard Deviation	175,999.9 598,918.4 479,049.1 481,941.8 47,541.49	0.32819 137.0898 31.86071 27.11095 22.64965	$\begin{array}{c} 1.115864\\ 1026.7\\ 65.75164\\ 26.21923\\ 120.2277\end{array}$	$\begin{array}{c} 0.108662 \\ 2416.825 \\ 129.0999 \\ 48.69148 \\ 241.2973 \end{array}$	27.88119 2378.447 201.9119 92.56669 316.1286	0.19509 65.6499 3.374499 0.833821 7.198533	0.03118 25.54358 1.666939 0.518571 3.588948	0.018997 1.778832 0.048173 0.018997 0.163514	$\begin{array}{c} 0.009838\\ 4.546702\\ 0.085663\\ 0.009838\\ 0.435458\end{array}$	$\begin{array}{c} 0.024654\\ 8.365597\\ 0.174813\\ 0.024654\\ 0.882888\end{array}$	$\begin{array}{c} 0.021675\\ 11.09364\\ 0.064795\\ 0.021675\\ 0.484941 \end{array}$	1.612447 9892.779 51.12353 2.653599 506.2063	0.998036 260.388 1.577542 0.998036 9.954066
	Margin/Rim	Minimum Maximum Mean Median Standard Deviation	14,4137.7 609,336 443,961.9 464,883.8 83,154.34	$\begin{array}{c} 0.317604\\ 23.72111\\ 4.343974\\ 3.03851\\ 4.229689\end{array}$	1.115864 242.2287 10.78748 4.484793 27.16952	0.108662 882.364 41.31036 8.788623 103.4931	25.29699 701.7397 120.9874 115.7217 57.1468	0.19509 3187.987 30.66859 5.225544 179.803	$\begin{array}{c} 0.03118\\ 59.55579\\ 4.40868\\ 2.027731\\ 6.528839\end{array}$	0.018997 97.02415 8.905787 0.861602 17.20723	0.009838 337.9647 8.696148 0.652406 23.38688	0.024654 606.1292 25.50651 0.024654 69.31208	0.021675 22.25789 0.214217 0.021675 1.43437	$\begin{array}{r} 1.612447 \\ 9892.779 \\ 68.74183 \\ 2.506165 \\ 569.7294 \end{array}$	0.998036 260.388 2.628831 0.998036 12.4524

Table 2. The summary of LA-ICPMS data on trace element composition and concentration of arsenopyrite in the Pulai gold prospect area.



Figure 6. LA-ICPMS element mapping of Pyrite 2 and Pyrite 3 grains marked with a dashed line, mineralised in tuffaceous metasediment: (**a**) tuffaceous metasediment mineralised with sulphide; (**b**,**c**) ore textural and morphological features of the pyrite under reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm).

Euhedral to subhedral, gold-bearing Pyrite 4 mineralised along the northeast-southwest (NE-SW) quartz vein of the tuffaceous host rock. The gangue mineral is mainly quartz, with disseminated pyrite grains found as fractured and slightly deformed entities. Based on the elemental mapping of Pyrite 4, there was a huge compositional difference between the core and margin of the grain. There are two zones of high Au content in Pyrite 4. The first enrichment was concentrated at the core of the pyrite and varied from 0.2 ppm to 11.7 ppm (mean: 1.5 ppm), while the enrichment of the margin of Pyrite 4 fell between 0.3 ppm and 8.8 ppm (mean: 1.2 ppm). The core of the pyrite grain had less enrichment of trace elements except for Au and As. A Au–As enrichment band marked the earliest precipitation stage at the core of the grain, and As continued to form oscillatory zonation. As enrichment at the core was between 1186 ppm and 6326 ppm (mean: 2716 ppm). The

As/Au and Ag/Au ratios for the core of Pyrite 4 varied from 288 to 22,656 (mean: 3882) and 0.0003 to 817.85 (mean: 3.25), respectively.

The Co and Ni zoning patterns were used as proxies to monitor the primary growth of Au and As, with both Co and Ni depleted when Au and As were highly concentrated at the core of Pyrite 4. Co composition at the core varied between 0.01 ppm and 30.4 ppm (mean: 0.25 ppm), while Ni varied between 0.1 ppm and 117 ppm (mean: 1.7 ppm). The ratio of Co/Ni for the core of Pyrite 4 ranged from 0.002 to 2.0, with an average of 0.21. The elements of Zn, Se, Te, and Sb were concentrated and distributed evenly in the interior of the grain during early pyrite formation. In contrast, Cu, Pb, and Bi were concentrated as nanoinclusions in the pyrite. Chalcopyrite and antimony inclusion were also present at the core of Pyrite 4, based on the extremely high Cu and Sb value at the core of the grain.



Figure 7. Cont.



(B)

Figure 7. (**A**) LA-ICPMS element mapping of Pyrite 4: (**a**) polished block of a limonitic quartz vein, mineralised with Pyrite 4 (the grain underwent deformation, forming cracks and fractures on the grain); (**b**,**c**) ore textural and morphological features of the pyrite under reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn (Au–As zoning is marked at the core of the grain). Scales are displayed in parts per million (ppm). (**B**) LA-ICPMS element mapping of Pyrite 4: (**a**) polished block of the quartz vein, mineralised with Pyrite 4; (**b**,**c**) ore textural and morphological features of the pyrite under reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and margin, based on the trace element distribution.

Au enrichment at the margin of Pyrite 4 was accompanied by elevated levels of As up to 323,858 ppm (mean: 13,844 ppm) with other trace elements, including Ni, Co, Sb, Pb, Bi, Ag, and Cu. The trace element concentrations varied between 0.02 ppm and 53 ppm (mean: 6 ppm) for Co, 0.2 ppm and 560 ppm (mean: 52 ppm) for Ni, 1 ppm and 654 ppm (mean: 43 ppm) for Cu, 0.01 ppm and 111 ppm (mean: 4 ppm) for Ag, 0.1 ppm and 195 ppm (mean: 37 ppm) for Sb, 0.2 ppm and 6187 ppm (mean: 139 ppm) for Pb, and 0.005 and 9 ppm (mean: 1.2 ppm) for Bi. The ratio of Co/Ni for the margin of Pyrite 4 ranged from 0.02 to 0.8, with an average of 0.16. However, the As/Au ratio for the margin of Pyrite 4 fell between 367 and 294,121 (mean: 7243) and 0.003 and 44.74 (mean: 2.26) for Ag/Au. A network of fractures formed on affected Pyrite 4 during post-pyrite crystallisation and was likely due to deformation or hydrothermal events. Fracture-hosted elements, including Sr, Ba, Rb, Ag, and Zn, were distributed, and a minor concentration of this latter element association

was discovered along the cracked, fractured, and outermost rim of pyrite. However, the deformation process did not affect As, Au, Co, and Ni, which precipitated during the early phase of pyrite formation.

5.2.2. Arsenopyrite Types and Their Composition of Trace Element

From the LA-ICPMS trace element mapping, two types of arsenopyrite have been identified in Pulai: Arsenopyrite 1 (Figure 8A,B) and Arsenopyrite 2 (Figure 9). The element content and zonation pattern of the Pulai arsenopyrite showed significant variances in the core and margin of the grains. Hence, a separate comprehensive evaluation of arsenopyrite was conducted for the core and margin of the grain for a better interpretation and understanding of the mineral, as tabulated in Table 2. As, Au, Sb, Ni, Co, Pb, and Bi were designated as significant trace elements, whereas Ba, Sr, Rb, Mo, Ag, Cu, and Zn were selected as minor trace elements.



Figure 8. Cont.



Figure 8. (**A**) LA-ICPMS element mapping of Arsenopyrite 1 grains in tuffaceous rock: (**a**) tuffaceous metasediments mineralised with sulphide; (**b**,**c**) ore textural and morphological features of the arsenopyrite in reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and margin, based on the trace element distribution. (**B**) LA-ICPMS element mapping of Arsenopyrite 1 grains in tuffaceous rock: (**a**) tuffaceous metasediments mineralised with sulphide; (**b**,**c**) ore textural and morphological features of the arsenopyrite in reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and morphological features of the arsenopyrite in reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and margin, based on the trace element distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and margin, based on the trace element distribution.

Arsenic concentrations in Arsenopyrite 1 varied from 74,012 ppm to 647,746 ppm. The Au and Sb–Mo relationship was the primary indicator to differentiate the elemental and formation phases of Arsenopyrite 1. Zonation of high Sb–Mo was documented at the core of the grain, while Au–Co–Ni was preferentially concentrated at the margin of the arsenopyrite. Au concentration at the core ranged between 0.005 ppm and 8 ppm (average: 0.6 ppm) and was enriched up to 15 ppm (mean: 3.7 ppm) at the margin of the grain. Sb was en-riched in the core, ranging from 62 ppm to 743 ppm (mean: 327 ppm) and dropped to as low as 7 ppm (mean: 150 ppm) at the margin of arsenopyrite. A Mo-barren zone was documented at the region with high Au concentration, while other trace elements were distributed unevenly along the grain. The en-richment of Pb–Bi–Co–Ni–Au–Ag–Ba–Sr–Cu in a non-oriented motion was identified, overprinting the early phase of elemental distribution in the Arse-nopyrite 1 grain, as marked in Figure 8A,B.



Figure 9. LA-ICPMS element mapping of Arsenopyrite 2 grains in a carbonaceous quartz vein: (a) polished block with sulphide, mostly arsenopyrite; (b,c) ore textural and morphological features of the arsenopyrite in reflected-light microscopy; (**d**–**s**) representing the distributions of Fe, S, As, Au, Ni, Co, Sb, Pb, Bi, Rb, Sr, Ba, Mo, Ag, Cu, and Zn. Scales are displayed in parts per million (ppm). The grain is divided into core and margin, based on the trace element distribution.

The arsenic levels of Arsenopyrite 2 from the Pulai gold mine varied from 144,137 ppm to 609,335 ppm. Arsenopyrite 2 differed from Arsenopyrite 1 in its elemental content. From the trace element pattern of Arsenopyrite 2, the core and interior of the grain formed a diagonal zonation pattern which was rich in Au–Co–Ni before continuing to deplete towards the margin of the grain. The Au content at the core of the grain ranged from 0.33 ppm to 137 ppm (mean: 32 ppm) and reduced to as low as 24 ppm (mean: 4.3 ppm) towards the grain's margin. The core of Arsenopyrite 2 had a high concentration of Co and Ni that spanned from 0.1 ppm to 2417 ppm (mean: 129 ppm) and 1.1 ppm to 1027 ppm (mean: 66 ppm), respectively, and later depleted to 882 ppm (mean: 41 ppm) for Co and 242 ppm (mean: 11 ppm) for Ni at the margin of the grain. Sb also showed some enrichment at the innermost core but was depleted as it approached the arsenopyrite margin. The association of Rb–Sr–Ba–Pb–Bi created a barren-zone element in the interior of the grain but was then enriched at the outermost margin and formed a thin element outline along the grain boundary.

5.3. Sulphur Isotope

The composition of the sulphur isotope for sulphides (n = 6) from Pulai ranged from -10.23% to 11.65%. From that, δ^{34} S values (n = 2) from the vein-hosted pyrite ranged from 10.08% to 11.62%, while sulphur isotopic composition δ^{34} S values (n = 4) of arsenopyrite in host rock were between -10.23% and -5.96%. The sulphur isotope data indicate that vein-hosted pyrite had more positive values and was heavier than the wall-rock-hosted pyrite. The results of the sulphur isotopic values of sulphides from a few gold mines in the Central Belt of Peninsular Malaysia, including Tersang [84], Selinsing [29,84], and Penjom [85], with other well-known deposits, are compared with Pulai's sulphide isotope signature and presented in Figure 10.



Figure 10. Sulphur isotope composition at Pulai compared with data from Tersang [84], Selinsing [29,84], and Penjom [85] gold deposits in Central Peninsular Malaysia. The diagram also simplifies the sulphur isotope comparison of δ 34S per mil for deposits from Central Peninsular Malaysia and other known deposit types that were studied by previous researchers (modified after [86]). The porphyry (1), mesothermal (3), and Carlin-type (4) Au-deposit-types were investigated by [87], while the epithermal type (2) was researched by [88].

Sulphur isotope analysis in Tersang was conducted for sulphides from quartz veins and host sandstone with δ^{34} S values ranging from -8.3% to 2.5%. The δ^{34} S composition from the vein pyrites varied between -4.5% and 2.5%, while those from pyrite hosted in sandstone ranged from -5.2% to -3.7%. The sulphur isotope value for arsenopyrite varied from -8.3% to -6.0%, and the sulphur isotopic content of one galena sample was -2.6% [84]. However, the sulphur isotopic value of eleven pyrite grains from the

Selinsing gold mine was greater, ranging between 1.2‰ and 9.2‰ [29,84]. The δ^{34} S values of six vein-hosted pyrite grains ranged from 2.8‰ to 9.2‰, while the δ^{34} S content of five wall-rock-hosted pyrite samples varied from 1.2‰ to 6.1‰. In a study conducted by [85], it was found that the sulphur isotopic composition of sulphides in the Penjom deposit was relatively depleted, displaying a range of values between -8.4% and -4.0% The sulphur isotope content of sulphides (pyrite) within the host rock ranged from -4.0% to -6.8%, whereas the δ^{34} S composition of vein-hosted sulphides (arsenopyrite) ranged from -4.9% to -8.4%. From the comparison, Pulai has a wide range of δ^{34} S values that overlap with data from other gold mines.

6. Discussion

6.1. Correlation of Sulphide Trace Elements

The texture, combination, and abundance of trace elements defined the various phases and stages of the ore-bearing sulphides, including their forming mechanisms [89–92]. Several trace elements in the sulphide minerals are dependent on and associated with one or more elements [4,5,17,93]. Hence, the formation of a high-grade ore deposit is not only classified by the volume of gold, types of ore, and sulphide properties but is also linked by its corresponding trace elements [20,23]. A distinctive compositional zoning was observed on the elemental maps for pyrite and arsenopyrite in Pulai. Therefore, the relationship between trace elements in pyrite (Figure 11) and arsenopyrite (Figure 12) from the elemental mapping of LA-ICPMS has been used in this study to interpret the geochemical characteristics of the ore fluid.



Figure 11. Binary plots of (**a**) S vs. As; (**b**) Au vs. Sb; (**c**) Pb vs. Sb; (**d**) Sb vs. Bi; (**e**) Sb vs. Cu; (**f**) Sb vs. Ag; (**g**) Co vs. Au; (**h**) Rb vs. Sr; and (**i**) Sr vs. Ba from Pyrite 2, Pyrite 3, and Pyrite 4 of the Pulai gold prospect with the correlation value (r).



Figure 12. Binary plots of (a) Ag vs. Au; (b) Sb vs. Au; (c) Pb vs. Au; (d) Ni vs. Co (e) Pb vs. Bi; (f) Pb vs. Ag; (g) Ba vs. Rb; (h) Mo vs. Au; and (i) Mo vs. Sb from Pyrite 2, Pyrite 3, and Pyrite 4 of the Pulai gold prospect with the correlation value (r).

Pyrite is made up of Fe and S atoms linked in a cubic lattice system with a molar ratio of 1:2, and its simple structure forms two lattice sites for the incorporation of substituent elements by a few possible mechanisms [94,95]. However, for the arsenopyrite crystal lattice, each Fe centre is linked to three As atoms and three S atoms, with each As or S atom attached to another three Fe centres, defined as Fe³⁺ with the diatomic tri-anion of AsS³⁻ [96]. Based on the crystal lattice system, trace metals in pyrite and arsenopyrite can be concentrated in several ways, including (1) forming as an invisible solid solution within the crystal lattice of sulphides, (2) occurring as invisible nanoparticles of sulphides [97], and (3) occurring as visible micron-sized inclusions in sulphides or (4) as visible microscopic-sized inclusions of oxide or silicate minerals [23]. Based on the geochemical results, different types of sulphides indicate several similarities and contrasts in elemental concentration, and this is further discussed below.

6.1.1. Chalcophile Element Concentration with Association of Invisible Gold

Arsenic in arsenopyrite and pyrite plays a significant role in the gold solubility of gold deposits. The Au–As relationship in sulphides is widely used to differentiate between free-gold and refractory gold ores [15,17,23,98,99]. A study on the gold solubility limit and its relationship with arsenic was conducted by [100] and proved that the highest potential amount of Au carried in solid solution is determined by the arsenic content of sulphides. This study demonstrated the solubility limit of epithermal gold and Carlin-type deposits by $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$, and Au occurred in the form of a solid solution (Au⁺) in the pyrite and arsenopyrite. The solubility and saturation outline limit of Au for orogenic gold has been lowered by [101] to $C_{Au} = 0.004 \times C_{As} + 2 \times 10^{-7}$. Au is considered as nanoparticles of native metals (Au⁰) when the ratio of Au/As is above the solubility limit,

which is 1:200. However, Au occurs as Au^+ in solid solution if the Au/As ratio is below the solubility limit [4,100,102].

The plot of Au vs. As in Figure 13a demonstrates that the Au and As contents for arsenopyrite and pyrite in Pulai are distributed in a wedge-shaped pattern below the gold solubility line, which is defined as the feature of an orogenic gold deposit [68,103]. This suggests that Au in pyrite and arsenopyrite occurs as metal nanoparticles, Au⁺, by the cooling of hydrothermal fluid [4,100–102,104]. The coupled geochemistry of Au and As in pyrite from an orogenic deposit displays a wedge-shaped zone dominated mainly by rock-fluid interactions such as wall-rock sulphidation [101]. The low concentration of refractory Au in the pyrite grains of Pulai, which ranges from 0.01 ppm to 11.7 ppm, supports the theory that pyrite originated in orogenic deposits mainly contains less than 100 ppm of Au [101]. A higher value of Au is mainly associated with the occurrence of Au in nanoparticles or inclusion in the sulphides [73,101].



Figure 13. (a) The Au vs. As plot of pyrite and arsenopyrite in Pulai for the gold solubility limit in Carlin-type and orogenic-type gold deposits by [100,101], respectively; (b) the elemental composition of pyrite from Pulai on an As–Fe–S ternary with four different trends shows the substitution of (i) As for S, (ii) As²⁺ for Fe, (iii) As³⁺ for Fe, and (iv) divalent metal Me²⁺ for Fe, after [101]; (c) Ag–Au for the Pulai deposits compared with data from sedimentary pyrite [105,106]; (d) Co vs. Ni binary plot of different varieties of pyrite in Pulai; (e) discriminating diagram of sedimentary and magmatic-hydrothermal pyrite by [106] using the variation of the Ni/Co ratio of pyrite in Pulai.

Arsenic is known as one of the most vital and substantial elements in pyrite lattice [16,107]. There are three forms of arsenic that can be identified in pyrite, known as As^{1-} , As^0 , and As^{3+} . As^{1-} and As^{3+} are linked, bound, and incorporated into the pyrite crystal system that forms in a reducing and oxidising environment, respectively [102,108]. Meanwhile, As^0 presents as an amorphous form of Fe–As–S nanoparticles [107]. The ternary plot of Fe–As–S from a study by [101] assisted in defining the matched mechanisms of arsenic incorporation into the pyrite structure. Based on the plot, Pyrite 2, Pyrite 3, and the core of Pyrite 4 fall into a field which parallels the Fe–S axis, implying the Fe substitution trend of divalent metals such as Ni²⁺ and Co²⁺ (Figure 13b) through the direct substitution of the pyrite lattice. However, the margin of Pyrite 4 experienced the direct substitution of arsenic for sulphur, and As was present in the As¹⁻ anionic state in the pyrite bonding system. This is supported by the negative correlation between sulphur and arsenic in the margin of Pyrite 4 (Figure 11a). The negative correlation indicates that the refractory gold, which is in the form of Au⁺, is associated into the margin of Pyrite 4 by the substitution of As⁻¹ for S²⁻ in the sulphide lattice within a reducing environment [1,107–109].

Sedimentary pyrite has a significantly higher ratio of Ag/Au (varies up to 1000), which helps classify the pyrite origin and differentiates between disseminated sedimentary pyrite and disseminated orogenic pyrite [17,105,106]. Ag/Au ratios of pyrite in Pulai range between 0.001 and 10, thus it is clearly classified as orogenic Au pyrite (Figure 13c). The low Ag/Au ratio of pyrite and arsenopyrite combined with microscopic observations in Pulai indicates the lack of electrum detected in the sulphide grains [92].

Antimony (Sb) has a positive correlation with Au, Pb, Bi, Cu, and Ag in Pyrite 2 and Pyrite 4, as it was highly enriched in the arsenopyrite, Pyrite 2, and the margin of Pyrite 4. The enrichment of Sb could indicate a relatively high concentration of Sb in the early generation of ore-bearing fluid for Arsenopyrite 1 and the margin of Pyrite 4. Alternatively, it could also be evidence of the remobilisation and reconcentration of Sb, as well as Au, Pb, and Bi, for pyrite. Sb easily occupied the lattice of the arsenopyrite system, due to the extensive FeAsS–FeSbS solid solution [5].

Aside from Au and Ag, the metallogenetic composition of pyrite and arsenopyrite in Pulai is also dominated by Pb, Bi, Cu, and Zn, which mostly occur as 'invisible' nanoinclusions or nanoparticles. Cu developed into microinclusions of chalcopyrite on pyrite and arsenopyrite grains. No individual mineral with Ag, Pb, and Bi could be identified in the pyrite or arsenopyrite of Pulai under ore microscopy due to their low concentration in the fluids [5]. The nanoparticle dissemination of Pb, Bi, and Ag closely replicates Au [5]. Au association with Bi–Pb is common in gold ores [20,97] and is related to the implications of Au redistribution. These can be seen clearly in Arsenopyrite 1, Pyrite 2, and the margin of Pyrite 4, indicating that these elements were also reconcentrated in the sulphides during the late phase of fluid mobilisation.

6.1.2. Geochemical Proxies on the Origin of Pyrite

The ratio of Co/Ni is related to the pyrite genesis, origin, and geological condition of the gold deposit [20,26,110,111]. The Co vs. Ni plot is useful to distinguish pyrite based on the elemental ratio from volcanic, hydrothermal, sedimentary, or magmatic origins. At the Pulai gold deposit, the plots of Co vs. Ni, as shown in Figure 11d, for Pyrite 2 and Pyrite 3, exhibit similar behaviour, which is scattered between the Co/Ni field ratio of 10 to 0.1, indicating the mixing of both hydrothermal and sedimentary pyrite origins. However, the ratio of Co/Ni for Pyrite 4 is lower, scattered around the region of 1 to 0.1 and attributed to a metamorphic hydrothermal origin, which is related to the sedimentary facies. Both Ni and Co formed as stoichiometric replacements for Fe in the lattice of pyrite and are commonly concentrated in the sedimentary and orogenic pyrite origin [17,99]. As seen in the LA-ICPMS mapping of pyrite in Pulai, the oscillatory zoning of Ni and Co represents typical Ni–Co features developed in hydrothermal-orogenic pyrites, magmatic-origin hydrothermal pyrites in IOCG, and porphyry Cu–Au systems [112].

Pyrite in Pulai displayed similar behaviour with a relatively low Co/Ni ratio and a mean ranging from 0.21 to 1.12 (Figure 13d). The cobalt values in pyrite were also very low, less than 403 ppm, indicating a fluid interaction with the low-grade metamorphic host rock. According to [113], the low value of cobalt and the Co/Ni ratio is influenced by the chemical component of the low-grade metamorphic host rocks that usually have low concentrations of cobalt, while no nickel is released during the hydrothermal recrystallisation process. However, nickel is readily bound into the crystal lattice of pyrite as NiS due to its slower water exchange kinetics compared to Fe [89,91,93]. A positive correlation of Co and Ni can be seen on all the pyrite grains of Pulai (Figure 13d), suggesting Co and Ni were incorporated into the crystal lattice of pyrite by Fe isomorphous replacement [26].

Previous findings from [106] on the trace element behaviour of pyrite in magmatichydrothermal deposits indicate that Au-bearing pyrite of orogenic field gold will have a Co/Ni ratio greater than 0.1. Based on the Au vs. Ni/Co plot (Figure 13e), pyrite in Pulai has a ratio greater than 0.1, which groups it into a magmatic-hydrothermal pyrite field. Hydrothermal pyrite with a high temperature of approximately more than 300 °C tends to be Co-rich pyrite but is lower in Au concentration [106]. As indicated in Figure 11g, in Pulai, the negative correlation of Co–Au could be attributed to the temperature effect, in which invisible or refractory gold is more dominant and widely mineralised in low-temperature pyrites rather than in Co-rich high-temperature pyrites. In addition, the surface charge on the gold transport species and crystalline pyrite, as well as its propensity to attract gold from the hydrothermal fluid, could explain this [106]. Based on the Co and Ni composition, pyrite in Pulai has a consistent origin despite the differences in pyrite generations present in a gold prospect.

The inadequacy of utilising the Co/Ni ratio as a trustworthy parameter to determine the origin of pyrite was highlighted by [111]. In analysing the origin of pyrite, the author suggested that the ratios As/Au and Ag/Au are more robust and more reliable when calculated using spot analytical data. Such a conclusion was reached after a comparison with the global sedimentary pyrite dataset from [105]. In this study, pyrite mapping indicates mean values for the ratio Ag/Au mostly above 1, with minimum values < 1 and mean values for the ratio As/Au > 1000. Such variability in Ag/Au and As/Au values indicates a hydrothermal origin of the pyrite as fluid pulses are highlighted by Ni, Co, Au, and As zoning patterns in Pyrite 2, 3, and 4.

6.2. Fluid Origin

In orogenic deposits, gold is mobilised as bisulphide complexes [114,115]. Due to this, the source and origin of sulphur is crucial to understanding the source of gold, the origin of ore-forming fluids related to the gold source, and the genesis of the deposit. The isotopic composition and source of sulphur varies from a metamorphic to magmatic to biogenic origin. The wide range of δ^{34} S values for vein-hosted and wall-rock-hosted Pulai sulphides indicates a variation in the fluid source for the sulphides. The δ^{34} S values of Pulai overlap with other gold deposits in the Central Belt of Peninsular Malaysia and fall in the mesothermal gold deposit range.

At Pulai, the δ^{34} S values are composed of heavier (10.08‰ and 11.65‰) and lighter sulphur (-10.23‰ to -5.96‰). The positive δ^{34} S values of the vein-hosted pyrite in Pulai propose that the sulphur probably originated from a mixing of sedimentary and magmatic sources [29], while the lighter sulphur isotope composition of wall-rock sulphide with negative δ^{34} S values (-10.23‰ to -5.96‰) indicates a biogenic source of the sulphur, possibly indicating that redox reactions were present [84,116]. The significant difference in sulphur isotope composition accounts for sulphides occurring in the quartz veins and host rocks of Pulai. This suggests that the fluids were not equilibrated with the wall rocks, and there was an interaction between the ore fluids and the wall rocks [84].

6.3. Pyrite and Arsenopyrite Genesis Related to the Gold Mineralisation Phase

The multistage formation of sulphide and genesis are common for orogenic gold deposits [81]. Different mineralisation stages are identifiable in multiple pyrite generations, as documented in previous studies [15,17,29,112,117]. The LA-ICPMS mapping revealed a systematic trace element evolution in the arsenopyrite and pyrite genesis in Pulai. The solubility of gold in arsenopyrite and pyrite indicates that gold occurrences are preferred in the ionic Au+ form as refractory gold [100,101]. Arsenopyrite in Pulai contained more refractory gold than pyrite, showing that arsenic carried out a vital role in the transport of ionic gold [5,73,92].

The mineralogy and mapping of the trace elements of pyrite and arsenopyrite grains in Pulai revealed that early-phase sulphide mineralisation began with assemblages Pyrite 2, Pyrite 3, and Arsenopyrite 1, which were hosted in tuffaceous volcaniclastic and metasedimentary rock. A remarkably enriched zone of refractory gold at the margin of the arsenopyrite-pyrite assemblage probably crystallised towards the ending of the Au-forming event, suggesting Au remobilisation in the sulphide grains. This is primarily due to the initial scavenging and remobilisation phase of Au, where gold was excreted from the sulphide crystal lattice during the remobilisation event and reconcentrated around the margins of the same grain [5]. This redistribution and remobilisation activity at the margin of the grain resulted in a low-to-barren zone of Au and other metal element content in the core of sulphides. The distribution and association of other metal elements at the margin of Pyrite 2, including Pb, Bi, Ag, and Sb, closely resemble and replicate Au, showing that these elements were also reconcentrated. The remobilisation of metal elements also resulted in the formation of sulphide inclusions such as chalcopyrite and pyrrhotite at the edge of Pyrite 2. The mineralisation of Pyrite 3 continued, producing intergrowth at the edge of Pyrite 2, but was completed with very little Au concentration, with a maximum concentration of only 1.1 ppm.

Co and Ni accompanied the redistribution and concentration of Au at the margin of Arsenopyrite 1. Additionally, the high concentration of Sb at the core of the grain may result from the ability of Sb to enter the arsenopyrite lattice via the extensive FeAsS–FeSbS solid solution. Another late series of fluid enrichment in Arsenopyrite 1 was recognised in most of the trace element concentrations, including Pb–Bi–Co–Ni–Au–Ag–Ba–Sr–Cu, and was observed spreading in a non-oriented pattern and cutting through the early mineral fluid phase. These multiple stages of sulphide formation and enrichment indicate multiple pulses of fluid ingress or the reactivation of these late-phase elements, leading to post-crystallisation elemental mobilisation.

Low concentrations of Au were detected in the host rock with early-phase sulphide assemblages. The refractory gold content of Pyrite 2, Pyrite 3, and Arsenopyrite 1 was only up to 5.6 ppm, 1.1 ppm, and 8.8 ppm, respectively. Thus, the hydrothermal fluid responsible for the assemblages of early-phase pyrite and arsenopyrite in the host rock cannot be considered the major gold mineralisation phase in Pulai. However, the latephase fluid derived from a metamorphic-hydrothermal origin for the mineralisation of vein-hosted sulphides (Pyrite 4 and Arsenopyrite 2) is favourable for gold concentration and is suggested as the main Au mineralisation stage in the sulphide generations in the Pulai gold deposit.

Two phases of Au enrichment localised at the core and margin of Pyrite 4 were detected, with the highest Au content reaching 11.7 ppm at the core of the grain, marked with the Au–As ore zoning pattern. The ore-bearing fluid of Arsenopyrite 2 represented the highest refractory gold content in the sulphides, which reached up to 137 ppm. The Au concentration decreased towards the margin of Arsenopyrite 2, while a pulse of Au enrichment was observed in Pyrite 4 as the grain continued to form. These pulses might be related to fold-lock-up and fault-enhanced fluid flows towards the end of the deformation [118,119]. The second phase of Au enrichment was observed at the margin of Pyrite 4, together with other metal elements, including Ni, Co, Sb, Pb, Bi, Ag, and Cu. Those elements closely resembled the distribution of Au, with a positive correlation to one another (Figure 11b–f). The Au enrichment towards the end phase of pyrite crystallisation could be related to the remobilisation and reconcentrated processes of Au and other metal elements at the edge of Pyrite 4. Au and other trace elements have been excreted out from the core and precipitated in the same grain. Brittle deformation, as shown on deformed Pyrite 4, led to the reactivation of the late fluid system enriched with Sr, Ba, Rb, Ag, and Zn. The enrichment was also concentrated along the fracture and outermost rim of Pyrite 4. The late enrichment of Rb–Sr–Ba–Pb–Bi at the outermost grain of Arsenopyrite 2 has also been identified as the late reactivation of fluid injection. The variation and fluctuation of Au with other trace elements in the sulphide assemblages indicate temporal and chemical variations during the crystallisation of ore-forming fluids. This may occur by a variably intense metamorphic-hydrothermal fluid reaction of the wall rock with sulphur derived from the mixing of sedimentary and magmatic sources.

The two orders of magnitude difference in Au between Pyrite 4 and Arsenopyrite 2 supports the empirical evidence for the incorporation of higher Au content in arsenopyrite compared to pyrite [1,100,109], suggesting a potential undefined partitioning of gold (Au) between the two minerals under equilibrium condition. This suggests that the two sulphides in Pulai were crystallised at the same time and from the same fluid phase. The redistribution process of gold by remobilisation from the sulphide crystal lattice and precipitation within the parent mineral, or close to the parent material, is recognised as a crucial phase in an orogenic gold ore deposit. These mobilisations have started during a series of fluid inputs and persistent fluid infiltration at temperatures consistent with greenschist facies metamorphism or higher, mostly under oriented strain [5,120]. The mineralisation of pyrite and arsenopyrite in Pulai is simplified in Table 3 and illustrated in Figure 14.



Figure 14. The simplified evolution of mineralisation and morphological changes for Pyrite 2, Pyrite 3, Pyrite 4, Arsenopyrite 1, and Arsenopyrite 2 in the Pulai gold prospect: R = remobilisation, E = enrichment. Au mineralisation shows a distinctive pattern with an elevated concentration in the Arsenopyrite 1 rim and a lesser concentration in the Arsenopyrite 2 core.

Pyrite Type	Mineral Formation	Mineral Morphology	Gold Content	Trace Element Association	Significant	Mineralisation Phase	
Pyrite 2 Intergrowth with Pyrite 3 in silicified tuffaceous rock		Corroded, porous, anhedral grain with irregular shape; replaced or rimed by Pyrite 3 or pyrrhotite	0.01 < Au < 5.6 ppm; Average: 0.6 ppm	Au barren at the core. High concentration of Au–As and Pb–Bi–Sb–Ag at margin of the grain	Remobilisation and precipitation of element at	Middle phase of ore mineralisation	
Pyrite 3	Intergrowth with Pyrite 2 in silicified tuffaceous rock	Euhedral and clean grain; not associated with gold mineralisation	0.01 < Au < 1.1 ppm; Average: 0.1 ppm	Barren of Au concentration. No significant enrichment of other trace element	margin of Pyrite 2		
Pyrite 4	Hosted in quartz vein, within	Coarse, euhedral to	Core: 0.2 < Au < 11.7 ppm; Average: 1.4 ppm	Core: High in Au and As.	Early phase of Au precipitation Fluid enrichment by metamorphic-hydrothermal reaction from wall rock alteration	Late phase of ore mineralisation	
	metasedimentary rock	spotted at some grain	Margin: 0.3 < Au < 8.8 ppm; Average: 1.0 ppm	Margin: High in Au–As and Ni–Co–Sb–Pb–Bi–Ag–Cu concentration Late enrichment of Sr–Ba–Rb–Ag–Zn along fracture and rim of the grain	Remobilisation and precipitation of elements Post deformation and fluid reactivation	Main phase of Au mineralisation within pyrite	
Arsenopyrite 1			Core: 0.004 < Au < 8.1 ppm, Average: 0.6 ppm	Core: High in Sb and Mo; low in Au–Co–Ni			
	Hosted in tuffaceous or volcaniclastic rock, associated with pyrrhotite and Pyrite 2	Euhedral to subhedral grain, rhombohedral; coarse to fine aggregates with inclussion rich	Margin: 0.1 < Au < 15.0 ppm; Average: 3.6 ppm	Margin: High in Au-Co-Ni; depleted in Sb-Mo. Late enrichment of Pb-Bi-Co-Ni-Au-Ag-Ba-Sr in non oriented pattern	Remobilisation and precipitation of Au at the end of the Au-forming event	Middle phase of ore mineralisation	
Arsenopyrite 2	TT - 1 - 1	Euhedral grain,	Core: 0.3 < Au < 137.1 ppm; Average: 31.9 ppm	Core: High in Au–Co–Ni; barren in Rb–Sr–Ba	Fluid enrichment by	Late phase of ore mineralisation	
	vein, within tuffaceous rock	fine disseminated aggregates	Margin: 0.3 < Au < 23.7 ppm; Average: 4.3 ppm	Margin: Depleted in Au-Co-Ni Enrichment of Rb-Sr-Ba-Pb-Bi at the outermost rim of the grain	reaction from wall rock alteration	Main phase of Au mineralisation within arsenopyrite	

Table 3. Simplified pyrite and arsenopyrite characteristics in the Pulai gold prospect, based on their mineralogical and geochemical study.

7. Conclusions

The Pulai gold deposit is one of the promising gold prospects in the Central Belt of Peninsular Malaysia. The orebodies of the Pulai prospect are hosted in a structurally controlled NE-SW major fault of Permian-Triassic Gua Musang metasediment and metavolcanic sequence. From the textural differences, four types of pyrite and two types of arsenopyrite were discovered in the mineralised quartz veins and host rocks in Pulai. From the paragenesis sequence, Pyrite 1 was first recognised as a discrete equigranular microcrystalline in the carbonaceous slate. Arsenopyrite 1 later formed coevally with inclusion-rich Pyrite 2, the intergrowth of Pyrite 3 and pyrrhotite crystallisation. Chalcopyrite, sphalerite, and galena also crystallised as disseminated, intergrowth, or inclusion elements with other sulphide minerals during the middle crystallisation phase. The late phase crystallisation of sulphides was identified by massive grains of euhedral to subhedral Pyrite 4, precipitated in a limonitic quartz vein and Arsenopyrite 2 in carbonaceous quartz veinlets. Overall, no visible or gold inclusions were observed in the sulphides.

LA-ICPMS imaging analysis of different types of sulphides in Pulai indicates that

- Gold occurrences are preferred in the form of Au⁺, as refractory gold in pyrites and arsenopyrites, and its concentration is significantly varied within sulphides. The main Au-bearing sulphides are represented in the late-phase mineralisation of Pulai, within vein-hosted Pyrite 4 and Arsenopyrite 2, while Pyrite 3 records the lowest Au concentration. Two phases of Au enrichment were recorded in Pyrite 4, mainly at the core (2–11.7 ppm; average: 1.4 ppm) and margin of the grain (0.3–8.8 ppm; average: 1.2 ppm), while the highest Au content was detected at the core of Arsenopyrite 2 (0.3–137.1 ppm; average: 31.9 ppm).
- 2. Au mineralisation is highly associated with As, thus forming an elemental oscillatory zoning pattern on the trace element map. Other trace elements, including Co, Ni, Sb, Pb, Bi, Cu, and Zn, show systematic variation and composition between the different types of pyrite and arsenopyrite. For early-phase sulphides, the enrichment of Au localised at the margin of Pyrite 2 and Arsenopyrite 1, together with Co–Ni and P–Bi–Sb and Ag in the same oriented pattern, indicates the remobilisation and redistribution phase of Au in sulphides.
- 3. The late crystallisation phase of vein-hosted sulphides forms a rich Au–As ore zoning pattern in the core of Arsenopyrite 2 and Pyrite 4. The second phase of gold enrichment continued at the margin of Pyrite 4 through remobilisation and precipitation of Au together with Ni, Co, Sb, Pb, Bi, Ag, and Cu. The late deformation phase reactivated the late fluid system with the enrichment of Sr, Ba, Rb, Ag, and Zn along the fracture and outermost rim of Pyrite 4 and Rb–Sr–Ba–Pb–Bi for the rim of Arsenopyrite 2.
- 4. Pyrite 4's margin underwent the direct substitution of As¹⁻ for S²⁻ in the pyrite lattice, while other types of pyrite experienced the direct substitution of divalent metals such as Ni²⁺ and Co²⁺ for Fe in the crystal system. The microsize inclusion of pyrrhotite, sphalerite, chalcopyrite, and galena in sulphide grains resulted in a high Pb, Bi, Cu, Ag, and Zn content.
- 5. Low Co/Ni ratios indicate that the sulphides in Pulai are originated from lowmetamorphic host rocks. Still, the significant difference in sulphur isotope composition between sulphides in the quartz vein and host rock in Pulai suggests the possible interaction between the wall rocks and ore fluids.
- 6. The Pulai gold deposit is regarded as an orogenic-style gold mineralisation in Malaysia, supported by the Au/Ag and Ni/Co ratios, and arsenic can be used as an indicator for proximity to its ore mineralisation and exploration purposes.

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