Research Paper

Studies on the Ore Mineralogy and Litho-geochemistry of the Sheba Deposit, Barberton Greenstone Belt, South Africa

Mohammed Alnagashi Hassan Altigani*

Department of Geology of Minerals Wealth, Faculty of Petroleum and Minerals, Alneelain University, 11121, Sudan

*Corresponding author : m.alnagashi@gmail.com

ARTICLE INFORMATION

Manuscript received 8 January 2021

Received in revised form 7 March, 2021

Manuscript accepted 10 March 2021

Available online 28 April 2021

DOI : <http://dx.doi.org/10.9719/EEG.2021.54.2.213>

Research Highlights

- Petrogenesis of the Sheba lithology
- Ore chemistry and genesis of the gold deposits and associated sulphides at Sheba
- Elements distribution on pyrite as indicative criteria for mineralisation stages

ABSTRACT

Ore criteria at the Sheba Deposit indicate orogenic mineralization type. Rocks and mineral assemblages suggest low formation-temperature of green-schist facies. Pyrite found in two generations; Type1 is irregular grains, contains higher arsenic and gold contents, compared to the relatively younger phase Type2 pyrite, which is composed of euhedral grains, found adjacent to late quartz-carbonate veins or at rims of type1 pyrite. Two gold generations were identified; type1 found included in sulphides (mainly pyrite). The second gold type was remobilized (secondary) into free-lodes within silicates (mainly quartz). Gold fineness is high, as gold contains up to 95 wt. % Au, Ag up to 3.5 wt. %, and traces of Cu, Ni, and Fe. Pyrite type2 contains tiny mineral domains (rich in Al, Mn, Hg, Se, Ti, V, and Cr). Zoning, and replacement textures are common, suggesting multiple mineralization stages. The distribution and relationships of trace elements in pyrite type2 indicate three formation patterns: (1) Al, Mn, Hg, Se, Ti, V, Cr, and Sn are homogeneously distributed in pyrite, reflecting a synchronous formation. (2) As, Ni, Co, Zn, and Sb display heterogeneous distribution pattern in pyrite, which may indicate post-formation existence due to other activities. (3) Au and Ag show both distribution patterns within pyrite, suggesting that gold is found both in microscopic phases and as chemically bounded phase.

Keywords : Sheba, pyrite mapping, zoning, LA-ICP-MS, EMP

Citation: Altigani, M.A.H. (2021) Studies on the Ore Mineralogy and Litho-geochemistry of the Sheba Deposit, Barberton Greenstone Belt, South Africa. *Korea Economic and Environmental Geology*, v.54, p.213-232, doi:10.9719/EEG2021.54.2.213.

1. Introduction and Regional Geologic Setting

The Barberton Greenstone Belt (BGB) is surrounded by large areas of granitic gneisses, which range in age from about 3.5-2.7 Ga (Ward, 1995, 1999; Brandl *et al.*, 2006) and 3.6-2.9 Ga (Eglington and Armstrong, 2004; Bumby *et al.*, 2011). The BGB is characterised by a complex and multi-staged deformation events, including shear zones, veining and low- to medium-grade metamorphic alteration of host rocks (Dirks *et al.*, 2009, 2013; Groves *et al.*, 1998). Rocks of the BGB belong stratigraphically to the Swaziland Supergroup (Viljoen and Viljoen, 1969; Anhaeusser, 1975; Kent, 1980; Ward, 1995, 1999; Brandl *et al.*, 2006), which comprises three major lithostratigraphic units (from older to younger):

(1) The Onverwacht Group (ca. 3.49-3.3 Ga) consists of komatiites, komatiitic basalts, basalts and pillow lavas, minor felsic volcanics, and sedimentary rocks (such as chert beds), which are formed in a deep to shallow marine environment (Eriksson *et al.*, 2001; Hofmann, 2005). De Wit *et al.* (2011) suggested that the Onverwacht Formation could be subdivided into seven geological complexes, separated by at least seven major shear zones. These geological units are the Sandspruit Complex, the Theespruit Complex, the Komati Complex, the Hooggenoeg Complex, the Noisy Complex [3432 ±10 Ma. (Grosch *et al.*, 2011), the Mendon Complex, and the Kromberg Complex.

(2) The Fig Tree Group (3.260–3.226 Ga) is a meta-turbiditic succession (Hofmann, 2005), up to 2000 m thick (Eriksson *et al.*, 2001), and mainly consists of greywackes, shale, chert, and dacitic rocks. Five formations have been distinguished north of the Inyoka Fault; namely the Ulundi, Sheba, Belvue Road, Bien Venue, and Schoongezicht Formations (Hofmann, 2005).

(3) The Moodies Group is characterized by arenaceous rocks (Heubeck, and Lowe, 1994; Hofmann, 2005; Van Kranendonk *et al.*, 2007), consisting of conglomerates, sandstones, siltstones, and shale. The Moodies group sequence is approximately 3000 m thick, and consists of conglomerates or pebbly sandstones at the base, a thick sandstone unit in the middle, and siltstones, wackes, shale, and banded iron formation (BIF) at the top (Eriksson *et al.*, 2001; Van Kranendonk *et al.*, 2007).

The Moodies Group (3.2 Ga, Kamo and Davis, 1994) was deposited in a shallow marine to fluvial environment, prior to the emplacement of the Kaap Valley tonalite plutons. Eriksson, *et al.* (1997) and Eriksson *et al.* (2001) suggested braided fluvial, littoral and shelf depositional systems for the Moodies sedimentary rocks.

The Moodies Group, which includes syn-orogenic sediments, may have been deposited during amalgamation of the four terrains just after 3.2 Ga (Heubeck, 1993; Van Kranendonk *et al.*, 2007). Major differences in age relationships, depositional environments, and sediment provenances between rocks to the north and south of the Inyoka fault system suggest that a major suture zone separates the greenstone belt into a northern and southern terrane (De Ronde and De Wit, 1994; Kamo and Davis, 1994; Lowe and Byerly, 1986; Lowe, 1994 and 1999).

Several structural investigations have been carried out at the BGB, e.g., (Robertson *et al.*, 1993; De Ronde and de Wit, 1994; Dirks, *et al.*, 2009, 2013; Kisters, *et al.*, 2010) on the Main Reef Complex (MRC) “one of the main gold sources in the study area” at the western part of the Sheba deposit suggest that gold mineralization was associated with D₂ (second phase of subduction-accretion) and D₃ (terrane assembly, transform boundary tectonics involving transtensional and transpressional events). Dirks *et al.* (2009) show that gold mineralization in the Sheba area occurs along extensional structures that formed after accretion of the BGB. They characterized by three sets of shear zones, which are:

The NE-trending and SE-dipping main shear zones, which are sub-parallel to the bedding planes of the Sheba Formation. (2) The cross-shear zones, which are a set of shallow and southerly dipping structures, (3) the shear zones that truncated the earlier structures.

The structural interpretation model of Robertson *et al.* (1993) represented the principal displacement shears (i) as Y-shears, whereas, the conjugate shear fractures named as R (ii) and P (iii) shears. The cross-shear zones (iii) represent high-angle opposite shears. The geometry shows a WNW–ESE direction of maximum principal stress (i) during shearing which is consistent with the proposed direction of the regional crustal shortening during D₃ (De Ronde and de Wit, 1994; Belcher and Kisters, 2006). Dziggel *et al.*

Fig. 1. Geologic map of the Barberton Greenstone Belt and surrounding granitoid terrane (Kisters, *et al.*, 2010), also shown the locations of the studied gold deposit.

(2007) suggested that the dextral strike slip Sheba Fault is related to the D₃ deformation episode and is consistent with the fracture model proposed by (Robertson *et al.*, 1993).

Archaean greenstone belts, such as the Barberton Greenstone Belt (BGB), represent essential contributor in world gold production. In these belts (Fig. 1), the geological setting of the mineralization source, and host rocks, coupled with high sensitivity of these rocks to metamorphism and hydrothermal alterations, led to a wide range of difficulties and complications, to determine the genesis and characteristics of the enclosed gold bearing-ore deposits. Understanding of the impacts of mineral associations, metamorphism, deformation, and alteration on these lengthily re-worked and deformed rocks (subjected to multiple phases of tectonism and hydrothermal activities) is very important in order to describe gold and associated sulphides deposits.

The main host lithology for gold mineralization of Sheba deposit are quartzites (arkoses), shales, sandstones, meta- mafic and meta-ultramafic, and greywackes, belonging to the Fig Tree and the Moodies Groups (Van Kranendonk *et al.*, 2007; Dziggel *et al.*, 2007, Dirks *et al.*, 2013). A tight to isoclinal fold, referred as Sheba Anticline, occurs within the Onverwacht Group, and consists mainly of talc-carbonate schists and cherts, which are often associated with gold mineralization (Dziggel *et al.*, 2007). The Sheba Fault (Robertson *et al.*, 1993; Dziggel *et al.*, 2007) separates

this northerly-verging fold. Dziggel *et al.* (2010) suggested that the main gold mineralization time in this deposit related to the refolding episode of the Eureka syncline fold (Fig. 1A). Gold mineralization at the BGB was not only related to a single phase of deposition (Agangi, *et al.*, 2014; Altigani *et al.*, 2016). However, Dirks *et al.* (2013) linked the gold mineralization at the Sheba to the late-tectonic shear zones that transect the ductile fold structures. Schouwstra and de Villiers (1988) suggested that gold mineralization is associated with zones plunges at low to moderate angles to the north-east; these zones are situated at the intersections of the main and cross shear zones in the contact between greywackes and shales of the Fig Tree Group, and the cherts of the Onverwacht Group.

The gold-bearing mineralized zones are either hosted in quartz and/or carbonate-rich veins along the shear zones and fractures, also with disseminated sulphides (mainly pyrrhotite, arsenopyrite, and pyrite) within the adjacent wall-rock alteration zones (Altigani *et al.*, 2016). The mineralization in studied area; is associated with intensively hydrothermal alteration processes, which have been noted from the field observations (stock/box works) and from the ore microscopy (presence of hematite at the boundary of oxidised pyrite). Due to intensive alteration processes (e.g., ferrugination), which are very common at the BGB. The existence of iron ores is common in the studied samples, as result of pyrite

Fig. 1A. Geological map around Sheba area, showing the distribution of major mineralised shear zones and associated gold activities. Details of the mineralised shear zones and their envelopes (grey) in the Golden Quarry area (Dirks, *et al.*, 2009).

and other Fe-rich sulphides decomposition (Schouwstra and de Villiers, 1988).

Kamo and Davis (1994) suggest that gold deposition occurred in the late tectonic development of the BGB, and has been interpreted to be temporally linked to the intrusion of late potash-granites and syenites of ca. 3.14–3.1 Ga age, and during the D₃ stage. Nevertheless, gold formation could be related to one long-tectonic evolution, which comprises of different stages (Altigani *et al.*, 2016). The age of gold mineralization has been inferred based on a ca. 3,126 ± 21 Ga porphyry dyke that predates the mineralization at the nearby Fairview Deposit, and a ca. 3,084 ± 18 Ga age for hydrothermal rutile from the same deposit (De Ronde *et al.*, 1991).

Gold mineralization at the BGB is structurally controlled by E-W trending and strike-slip shear zones (Dirks *et al.*, 2013), which are situated in or near to the major D₃ structures, which were previously thought to be thrust faults (De Ronde *et al.*, 1992). These shear zones are steeply dipping to the SE and SW (Robertson *et al.*, 1993).

In this study, we applied EMP and LA-ICP-MS techniques in order to determine the elemental relationships in the pyrite Type 2 of Sheba deposit. This guide to better understanding of the formation conditions of the hosted gold in

associated sulphides. The compositional fingerprints of inclusive gold that associated with sulphides should reflect the related genetic processes. Based on this hypothesis, it can be said that the differences or changes in the minerals forming processes/conditions will also be reflected in their trace element contents and distribution patterns.

2. Methodology

Several analytical techniques were utilized to accomplish the purpose of this study, including X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), electron microprobe (EMP), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). For XRD and XRF analyses, the samples were reduced to chips of 4–8 mm by jaw crusher, and were subsequently pulverized in a tungsten carbide disc mill.

2.1. Microscopy

For the microscopic investigations, polished and thin-sections were prepared at the Geology Department - University of Pretoria. These sections were studied using a conventional transmitted and reflected light microscope in order to determine the mineralogical assemblages, textural,

and micro structural characteristics, the degree of mineral alterations, and the metamorphic grade for the rock associations. Representative fresh samples were selected for chemical analyses after microscopic examinations. Finally, the mineral para-geneses, textures, and structures of the ores were also investigated.

2.2. X-Ray diffraction analysis

For the XRD analysis, ten grams from each sample were ground following the standard procedure. They were examined using the X-Ray diffractometer model '*PANalytical X'Pert PRO*'. The measurements were performed at the Department of Geology, University of Pretoria, on a *PANalytical X'Pert PRO* X-ray diffractometer in θ - θ configuration, equipped with a Fe filtered Co-K α radiation (1.789Å) and with an X'Celerator detector and variable divergence- and receiving slits. Samples were prepared according the standardized *PANalytical* back loading system, which provides nearly random distribution of the particles.

The data was collected in the angular range $5^\circ \leq 2\theta \leq 90^\circ$ with a step size $0.008^\circ 2\theta$. The phases were identified using *X'Pert Highscore Plus software*. Errors are on the 3-sigma level, amorphous phases (if present) were not taken into consideration in the quantification

The relative phase amounts (weight %), were estimated by the Rietveld method using Autoquan/BGMN software (GE Inspection Technologies; Kleeberg & Bergamnn) employing Fundamental Parameter Approach. In the Rietveld Method, an observed data pattern is compared to a calculated pattern. By variation of all parameters, the difference between the calculated and observed pattern is then minimized by a least square procedure, until the best possible fit is obtained.

2.3. X-Ray fluorescence analysis

The samples were analysed using the pressed powder technique. Unpublished research in the department of Geology at the University of Pretoria demonstrated that major elements analysis of the same samples using lithium tetra-borate glass and powder briquettes were indistinguishable within standard analytical errors.

Ten to 12 grams (75% <63 μ m) were taken from each sample and mixed with ten drops of polyvinyl alcohol (48-80) saturated solution (as binder) added to each sample powder, then loaded into collapsible aluminium cups (diameter 40 mm) and pressed by a manual oil-hydraulic

press under 15 kPa. The Cr-steel piston (diameter 40 mm) was levelled by polishing. The analyses were performed using the wavelength dispersive X-Ray Fluorescence Spectrometer (PANalytical) model "*ARL 9400XP+*". The analyses were executed using the computer software "*UniQuant*". The quantification of the analyses was obtained by analysing certified standard materials as references. For better understanding of the regional geology in the study area, data from the adjacent Fairview deposit were added.

2.4. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that takes images of the sample surface by passing a high-energy beam of electrons across the surface of the sample (Reed, 2005). The electrons interfere with the atoms of the sample, producing signals that contain information about the samples surface topography and its chemical composition (Goldstein, 2003). The energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterisation of the samples (Goldstein, 2003; Reed, 1983; Reed, 2005).

The polished sections used in this study were coated with carbon with a thickness of approximately 40Å, which allows dispersion of charging during the SEM analyses. A silver strip used for conduction between carbon coating on the sample and the sample holder during the analysis. The scanning microscope instrument, model '*JEOL JSM-5800V*', was used to investigate the samples in this research. This task was done by using an accelerating potential of 20 kV. Semi-quantitative chemical analyses were performed using the Energy Dispersive Spectroscopy (EDS, X-Raytech). Sample photos were taken with the help of the '*Orion 6.60.4*' program, and semi-quantitative analyses were carried out using the '*NSS-X-Ray*' microanalysis software.

2.5. Electron microprobe

Electron microprobe analysis (EMP) is a technique used for chemically analysing small selected areas in solid samples, in which a focused electron beam (Reed, 1983; Reed, 2005) excites X-rays. EMP is suitable for analysing elemental composition down to the level of a few tens of μ g/g (0.010-0.001 % m/m) (Humayun *et al.*, 2010).

In this study, imaging and elemental analysis were performed (using the '*CAMECA VX 100*' electron microprobe) in the gold and sulphide ores from Sheba. The standard

procedures at the University of Pretoria, which depends on (Reed, 2005), were followed. The samples were re-polished on nylon pads with a series of diamond powders to 0.25 μm finish. The spectra were processed by ZAF corrections. Quantification analysis of the samples was performed with an accelerating voltage of 20 kV, a current of 20 nano amperes (nA), and a focused spot (<1 μm diameter). Count times, for all elements, were 10 seconds. Mineral standards were used for calibration.

2.6. Laser ablation inductively coupled plasma mass spectrometry

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is favoured in many geological studies including ore mineral identification, because of its high range of sensitivity, high precision, low detection limits, and relatively a large analysed sample volume compared with EMP, which mainly exadeposits samples surface (Sylvester *et al.*, 2005; Humayun *et al.*, 2010; Shaheen *et al.*, 2012). An LA-ICP-MS technique is also requiring a minimal sample preparation (Pickhardt *et al.*, 2005; Shaheen *et al.*, 2012).

In this research, an Agilent Technologies model 'ICP-MS 7500 Series' instrument was used at the South African Police Forensic Science Laboratory, Pretoria, South Africa. This machine is equipped with a high-performance *NEW WAVE* model UP-213 laser ablation system. This system is presently considered the best type to reduce and minimize the inter-elemental fractionation that could be caused by local temperature changes, ablation time, and variations in the matrix matched elements (Chen, 1999; Gaboardi and Humayun, 2009, Woodhead *et al.*, 2009). The samples were placed in the UP 193FX ablation cell, and the aerosol produced by ablation is swept into the mass spectrometer using a stream of ultra-high purity He gas (800 ml/min). A stream of argon gas with flow rate of ~ 900-1400 ml / min was added downstream to achieve the differential flow needed to obtain a bright, stable signal. A CCD (charge-coupled device) camera allows imaging of the sample during ablation. The operating *MEOLaser 213 software* was used to analyse the trace elements in the sulphides and gold of the Sheba deposit of the BGB. The radio frequency (RF) power was 1200 Watt, and the carrier gas, (optional gas 95%, 0.90-0.95 L/min). The consistent spot size and depth was 25 μm with 10 Hz pulse repetition rate and

100% power output. The spots were each ablated for 45 seconds to reduce the possible inter-elemental fractionation. The electron microprobe results for the same samples spots were used as a reference for the LA-ICP analyses. The machine performance LA-ICP-MS was calibrated with international standards as mentioned in Sylvester (2008). The operational parameters were optimized using blanks and NIST glasses 610 and 612 before starting analysing an individual mineral grain. The selection of these materials instead of pure gold and sulphide standards is because the optimization requires a creation of a steady state signals, and continuous ablation of gold and sulphides may result in coating the core of the laser cell, which contaminates the system for a significant time (Watling and Herbert, 1994). Utility of NIST glasses is applicable and suitable for measuring reproducibility and instrumental optimization (Watling and Herbert, 1994). Sylvester (2008) suggested that NIST 610 glass may be used to measure concentrations of Cu, Zn, Ag, Pt, and Au in sulphides with an accuracy of 10% using Fe as internal standard.

3. Results and discussions

3.1. Rock assemblages

3.1.1. Arkoses

Hessler and Lowe (2006) proposed that the Sheba rocks are composed of meta-psammitic and quartz-rich arkoses. Muscovite is found in the matrix, which formed a weak fabric approximately normal to compositional layering. The XRD results of these arkoses show a high content of quartz and biotite, ranging from 50.1 to 56.4 wt. % and 31.6 to 43.3 wt. % respectively.

3.1.2. Metapelites

These rocks consist of biotite, garnet, and quartz. Biotite is the dominant mineral. Quartz is found as a sub-dominant phase in these rocks. Garnet forms augen micro-textures, zoned, and has developed a new generation of garnet at its boundaries (Fig. 2). Garnet is poikiloblastic and contains abundant inclusions of biotite and quartz. These minerals assemblage is indicative for low to medium-grade metamorphism that could be related to the late granitic intrusions, which implies at least two main metamorphic episodes affected the study area. Dynamic metamorphism is associated with the shearing in the late stages of the two main episodes.

Fig. 2. Photomicrographs of metapelite from the Sheba Deposit, (A) poikiloblastic garnet (cross-polarized light), (B) Biotite occurred after decomposed garnet (plain polarized light).

3.1.3. Greywackes

These rocks are composed of 53.3-56.4 wt. % quartz, 25.9-31.6 wt. % muscovite, 12.6-16.3 wt. % dolomite, 11.5-12.6 wt. %, pyrite 2.7-11.5 wt. %, and 2.5-4.4 wt. % chlorite. The rocks display alternating bands of quartz and dolomite, intercalated with sub-parallel sulphides veins. Two types of pyrite are distinguished: the first one is well-developed porphyroblast, which are spatially situated close to the quartz-carbonate veins (Altigani, *et al.*, 2016).

The other pyrite type has anhedral shape. Minor amounts of muscovite, chlorite, and quartz polygons are commonly associated with these sulphides. Carbonate-rich rocks of the Sheba deposit consist of a fine-grained quartz matrix, which is crosscut by sub-parallel veins of calcite and muscovite. The groundmass contains disseminated sulphide porphyroblasts.

The majority of the studied samples from Sheba deposit are dominated by quartz, calcite, biotite, muscovite, garnet, and chlorite. This mineral assemblage indicates low greenschist metamorphic facies (Miyashiro, 1973; Stiegler *et al.*, 2010). Generally, local high amphibolite facies (indicated by hornblende from the lithology of nearby New Consort and Fairview deposits) that might be due to later granitic intrusions. Generally, rocks of the Sheba Deposit can be subdivided into arkoses, greywackes, and metapelites.

Hessler and Lowe (2006) suggested that the basal conglomerates of the Moodies Group (which the Sheba Deposit represents part of it), were derived from volcanic and sedimentary rocks of the Swaziland Supergroup. They indicated that felsic volcanic rocks, cherts, silicified ultramafic fragments, and quartz veins dominate the sedimentary clasts

of the Moodies Group.

The dissolution and re-crystallization of the quartz during the prograde metamorphism formed a new generation of small (120° triple-junction) quartz polygons. This texture indicates textural equilibrium during the re-crystallization at higher temperatures coupled with lack of deformation (Barrie *et al.*, 2010). The quartz contents in the Sheba greywackes indicate a major granitic component (McLennan, 1984). Stringers of graphite characterize the arkoses and metapelites, reflecting an early existence of organic materials (early life??) across these sediments.

Quartz and carbonate veins are common in the majority of the Sheba rocks. Most of these veins were deposited concordantly with either relicts of primary bedding, or the foliation planes, while some of these veins filled the shearing planes. The shape, symmetry, and the interaction of these veins with the country rocks suggest late injection. These quartz veins may have formed due to a recent magmatic hydrothermal activity (De Vries and Touret, 2007) or due to dehydration that was caused by prograde metamorphism (Dziggel *et al.*, 2002).

The mineralogical relationships in the Sheba rocks indicate multi-metamorphism episodes affected the lithologies of the BGB. The first, is regional type affected the mafic and ultrabasic units, and associated with early tectonism, and; producing greenschist metamorphic facies. The second is a prograde thermal and/or regional type that delivers higher-grade metamorphic facies (high greenschist, low amphibolite facies), which found occasionally close to the granitic intrusions. The third is dynamic metamorphic event was associated with shearing, which caused brecciating,

fracturing and recrystallization of these rocks and associated ores, forming structural porosity and pathways for the syn- to late orogenic mineralized fluids. These metamorphic events produced changes to the mineralogy and morphology of the ore-minerals of Sheba deposit, reflected in heterogeneity, zoning, alteration processes, and trace elements (Au) remobilization (Altigani *et al.*, 2016).

3.2. Rocks Chemistry

Several geochemical investigations were carried out on the pelites of the Sheba Formation (e.g., Danchin, 1967; Condie *et al.*, 1970; McLennan, *et al.*, 1983; Toulkeridis *et al.*, 1999; Hofmann, 2005, etc.). Rocks of the Sheba display a range of various compositions in terms of their major element composition (Hofmann, 2005). The geochemical characteristics of the Sheba rocks indicate a mixture of calc-alkaline tholeiitic affinities. SiO_2 contents have a range of 37.4 and 75.3 wt. % (average 59.3 wt. %). Al_2O_3 values are relatively low (average 14.8 wt. %).

The XRF whole rock analyses indicate that most of the studied arkoses of the Sheba Formation display a felsic rock composition. SiO_2 values explain the relatively high quartz contents for the majority of the samples. The relatively low values of Al_2O_3 suggest low clay contents, which indicate chemical weathering and short transporting distance from the original material of the Sheba rocks (Hofmann, 2005).

The metapelites of the Sheba are rich in MgO and Fe_2O_3 rather than Na_2O , K_2O , and CaO . The Mg content ranges between 1.4–7.8 wt. % (average 3.7 wt. %). Fe_2O_3 values are higher than 10 wt. %, which is consistent with values from other Archaean greywackes terrains (McLennan, 1984). The CaO values in most of these samples are very low, with an average of 2 wt. %. However, two of the samples from the Sheba Deposit have relatively high values of CaO (6.1 and 3.3 wt. %). The positive correlation between K_2O and TiO_2 suggests that these elements are located within the micas of the Sheba pelites (Hofmann, 2005).

Greywackes at Sheba show a dacitic to rhyodacitic composition in the major-element chemical composition (Toulkeridis *et al.*, 1999). Most of the high field strength elements (HFSE) such as Zr, Hf, Ta, Nb, and Y are low in the Sheba greywackes compared to other Archaean greywackes and to post-Archaean greywackes and implies a source with low (HFSE) tenor for these sediments, i.e.,

Fig. 3. Ternary diagram of molecular Al_2O_3 ($\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) ($\text{FeO} + \text{MgO}$), showing-weathering trends of granitic source (A) and basaltic source (B). C= diagenetic and/or metasomatic transformation of kaolinite (Ka) into illite (Ill) with fluids characterized by high K^+/H^+ ratios. D= diagenetic and/or metasomatic transformation of kaolinite into chlorite (Chl) with fluids characterized by high $\text{Mg}^{+2}/\text{H}^+$ ratios. Bt= biotite; Kfs= feldspar; Hb= hornblende; Ms= muscovite; Sm= smectite, (Toulkeridis *et al.*, 1999).

mafic rocks (Condie, 1993). The greywackes plot of the Sheba Deposit is located close to the igneous trend, between the weathering trends of the basaltic and granitic rocks (Fig. 3), the samples trend toward Al_2O_3 in this diagram, probably reflects physical rather than chemical alteration processes. Based on (Fig. 3), the shift of the samples towards higher CaO contents reflects late carbonatization processes and/or saussuritization process that affected plagioclases of the parental rocks. Evidences for these processes were observed in the Sheba rocks thin-sections, by the presence of carbonate mineral such as dolomite, ankerite and calcite. Rouchon *et al.* (2009) proposed that the reasons for the relatively high values of FeO and CaO are due to the reaction of old mafic volcanics with seawater (alteration products), as well as due to the enrichment of carbonate fillings of inter-pillow pore-spaces with these elements, which were remobilized during the metasomatism and alteration processes.

The Na_2O values are less than 1%. Fe_2O_3 and MgO show high values (Table 1). High Mg and relatively high iron contents suggest a significant mafic to ultramafic component in the source of the Sheba greywackes (Hofmann, 2005), and intermediate to basic rock fragments (McLennan, 1984). Thus, the chemical compositions and chemical affinities

Table 1. Selected whole rock analyses using XRF powder pellets of fresh Sheba Deposit rock samples

Sample	125208 (metapelites)	125490 (metapelites)	125941 (metapelites)	FSC-307917 (greywacke)	FSC-307919 (metapelites)	FSC-307929 (muscovite arkoses)
SiO ₂	63.89	60.51	67.04	37.40	56.29	75.34
Al ₂ O ₃	19.4	12.3	19.4	15.8	19.5	14.8
Na ₂ O	0.15	0.16	0.80	0.23	0.18	0.15
MgO	0.99	1.48	5.11	1.39	7.78	2.93
P ₂ O ₅	0.03	0.02	0.02	0.02	0.06	0.01
K ₂ O	5.09	4.56	1.52	7.18	2.98	1.78
CaO	0.10	0.24	0.36	0.08	6.06	3.32
Fe ₂ O ₃	4.26	6.65	9.19	10.60	9.60	3.18
Cr ₂ O ₃	0.14	0.14	0.26	0.23	0.30	0.12
TiO ₂	0.64	0.61	0.23	0.97	0.50	0.19
V	0.04	0.04	0.02	0.06	0.05	0.02
Mn	0.01	0.04	0.05	0.01	0.28	0.15
Co	0.02	0.01	0.04	0.02	0.03	0.03
Ni	0.04	0.04	0.08	0.06	0.08	0.04
Cu	0.01	0.02	0.02	0.03	0.01	0.58
Zn	0.01	0.02	0.01	0.04	0.01	0.11
Ga	0.00	0.00	0.00	0.00	0.00	0.00
As	2.02	4.30	4.47	6.95	0.00	1.30
Br	0.00	0.00	0.00	0.00	0.41	0.00
Rb	0.02	0.00	0.01	0.01	0.00	0.00
Sr	0.00	0.02	0.01	0.02	0.01	0.01
Y	0.01	0.00	0.00	0.00	0.02	0.01
Zr	0.02	0.01	0.00	0.01	0.01	0.00

(calc-alkaline - tholeiitic) for the Sheba Formation implies mixed mafic–felsic (volcano-sedimentary) sources of different proportions (Toulkeridis *et al.*, 1999).

3.3. Ore mineralogy

3.3.1. Arkoses

In these rocks, the main sulphides are pyrite (2.7–11.5 wt. %, XRD analyses), and arsenopyrite (3.5–7.7 wt. %, XRD analyses). Pyrite forms poikiloblast large grains, which are consistent with the host rocks general foliation. Small amounts of gold electrum are enclosed within the pyrite. Based on the textural evidence obtained from the reflected microscope, subhedral to euhedral crystals of arsenopyrite were formed after the pyrite.

3.3.2. Greywacke

Pyrite represents the dominant sulphide phase in these rocks (up to 11.5 wt. %, XRD analyses). Two phases of pyrite exist in the studied deposit (Figs. 4 A and B); the early pyrite type 1 (core) phase is porous, irregular shape,

and includes arsenopyrite, pyrrhotite, chalcopyrite, and rare gold inclusions. The later pyrite phase type 2 (rims) occurs as large idiomorphic, seems to be clear, very compact, and concentrates close to the late quartz-carbonate veins. In some samples pyrite type 2 (rim) overgrowing pyrite type 1 (core).

3.3.3. Metapelites

In these rocks, the dominant ore mineral is arsenopyrite (up to 7.7 wt. %, XRD analyses). Gold in these rocks is found as small grains located between arsenopyrite and pyrrhotite, intergrowth textures are very common between different sulphide phases such as arsenopyrite-pyrite, pyrite-pyrrhotite, arsenopyrite-pyrrhotite, and chalcopyrite-pyrrhotite.

Arsenopyrite is found close to the pyrite and is restricted to parallel bands concordant with the general foliation. Minor sphalerite is found located close to pyrite. Chalcopyrite is found enclosed by the early pyrite phases.

3.4. Ore phase relationships

Spot analyses (131 points - Table 2) were performed on

Fig. 4. A: Pyrite Type 1 in metapelite, sample 125941, section B, Sheba Mine. Shows rotation in the pyrite grains. B: Pyrite Type 2 in arenaceous rocks, FSC-307917, Sheba. The pyrite grains are located close to a carbonate vein. Fibrous quartz is located in the pressure shadows (Altigani, *et al.*, 2016).

the sulphides of the Sheba Deposit, using the electron microprobe (EMP). The principal sulphide phases in the Sheba ores are pyrite, pyrrhotite, arsenopyrite, and rare chalcopyrite and sphalerite.

The EMP results show that there are differences in the elemental contents of the analysed pyrite grains, coupled

with the textural variations gives an indication that there are two types of pyrite within the Sheba ores (Table 2). These are:

A) Pyrite type 1 (core), which is considered as the older type. This type of pyrite varies in its S + Fe contents due to the substitution of Fe and S by both Ni, Co, and As

Table 2. Representative Electron Microprobe analyses for the Sheba Deposit ore in wt. %

Mineral	S	Fe	As	Co	Ni	Cu	Zn	Pd	Ag	Cd	Sb	Au	Hg	Pb	Bi	Mn	Total
pyrite-core	51.91	45.22	2.06	0.01	0.8	0	0	0.13	0	0.03	0	0.02	0.07	0	0.01	0	100.27
pyrite-core	52.92	46.4	0.37	0	0.19	0	0.03	0	0.01	0.01	0	0	0.06	0	0	0.01	99.99
pyrite-core	52.83	46.21	1.18	0.01	0.35	0.02	0.03	0	0	0	0	0.03	0	0	0	0	100.66
pyrite-core	52.73	46.25	0.81	0.16	0.3	0.02	0	0.04	0	0.02	0	0	0.09	0	0	0	100.4
pyrite-core	52.64	46.33	0	0	0	0	0.01	0.04	0.01	0.01	0	0	0.08	0	0	0	99.11
pyrite-rim	52.16	46.46	0.86	0	0.04	0.01	0	0	0.01	0	0	0	0	0	0	0	99.54
pyrite-rim	53.25	46.91	0	0	0.03	0.03	0	0	0.01	0.03	0	0.11	0.09	0	0	0	100.47
pyrite-rim	53.12	46.61	0.24	0	0.08	0	0.01	0	0	0	0	0	0.07	0	0.06	0	100.2
pyrite-rim	53.03	46.77	0.04	0	0.09	0	0	0.01	0	0	0	0	0.14	0	0	0	100.09
pyrite-rim	53.15	46.95	0.12	0	0.05	0	0.03	0	0	0.01	0	0	0.02	0	0.22	0.01	100.55
arsenopyrite	19.91	32.76	46.21	0	0.1	0	0	0	0	0.03	0	0.42	0	0.01	0.23	0	99.67
arsenopyrite	19.66	34.84	45.94	0	0.11	0	0	0	0	0	0	0	0	0	0.2	0.01	100.76
arsenopyrite	19.99	35.04	45.24	0	0.1	0.02	0	0.07	0.01	0	0	0.04	0	0.03	0.07	0	100.62
arsenopyrite	20.42	34.95	44.75	0	0.06	0.02	0.02	0.01	0	0.09	0	0.15	0.12	0.03	0.36	0.01	101.01
arsenopyrite	19.46	34.26	46.58	0	0.24	0.01	0	0	0	0	0	0.09	0.13	0	0.41	0.02	101.2
pyrrhotite	38.08	58.78	1.39	0	0.17	0	0	0.01	0	0	0	0.06	0.08	0	0.03	0	98.62
pyrrhotite	38.34	58.69	1.82	0	0.15	0	0	0.04	0.03	0	0	0	0.01	0	0.14	0.03	99.25
pyrrhotite	38.71	59.01	2.26	0	0.21	0.02	0.01	0	0	0.04	0	0	0	0	0.09	0	100.36
pyrrhotite	38.51	60.29	0.75	0	0.42	0	0	0	0	0.01	0	0.11	0.27	0	0.03	0.01	100.41
pyrrhotite	33.97	54.73	5.22	0	0.35	0.05	0.01	0.02	0	0	0	0.03	0.02	0	0.17	0.02	94.59
gold	0.05	0.37	0	0	0	0.07	0	0	3.91	0	0	96.24	0	0	0	0	100.64
gold	0.01	0.24	0	0	0.01	0.09	0	0	3.89	0.06	0	95.53	0	0.29	0	0	100.13

Fig. 5. Compositional variation in the different types of pyrite from the Sheba Deposit using EMP data, showing different major and trace elements relationships.

respectively, to form small domains of arsenian pyrite, and arsenopyrite. The EMP results show that gold content in pyrite type 1 increases with increasing iron and sulphur rather than arsenic. However, nickel content increases with arsenic concentration in the pyrite composition. Bismuth content is higher in this type compared to pyrite type 2. However, nickel content increase with arsenic concentration and replaced iron (Fig. 5). This also seen in LA-ICP-MS results, in which Ni is positively correlated with As, but has no systematic relationship with Co (Fig. 6).

B) Pyrite type 2 (rim) is relatively younger and is found overgrowing pyrite type 1. It forms well-developed cubes and eight-sided crystals. This pyrite type is homogenous and not showing any zoning or inclusions when using microscopy or back-scattered electron imaging. Nevertheless, the use of LA-ICP-MS mapping technique (Table 3) revealed that this type contains micro-zoning and very minute inclusions.

The iron content of pyrite is slightly variable; indicating the replacement of Fe by Ni, As and Co. The substitution and possible metasomatism, which occur due hydrothermal activities causes a development, occasionally, of new generations of Ni and Co rich pyrite and Ni-arsenides.

Both types of pyrite in this deposit commonly contains invisible gold (up to 1 wt. %), which was thought by many authors (e.g., Vaughan and Kyin, 2004) to be related to the arsenic content in the pyrite itself. Analysed gold in pyrite grains does not illustrate any systematic relationships between Au and Fe, S, As, Ag, Ni, Bi, and Hg (Fig. 5).

Sphalerite of the Sheba Deposit contains considerable amounts of Co, Ni, Bi, and Cd. The chemical composition of sphalerite is variable, indicating a chain of mineral, which may form between sphalerite to Fe-rich member, which might be due to the effects of associated chalcopyrite and arsenopyrite. Chalcopyrite and pyrrhotite are usually form intergrowth textures, suggesting corresponding formation.

Fig. 6. LA-ICP-MS results from pyrite type 2 of the Sheba Deposit illustrating the relationship between Ni and As, Co.

Table 3. Selected LA-ICP-MS qualitative analyses for the Sheba Deposit ores, in count per second (cps)

Mineral	S	Fe	Mn	Co	Ni	Cu	Zn	As	Ag	Sb	Au	Hg	Pb	Bi
Pyrite-rim	225381.34	231599352	840.57	680.05	15196.15	130.02	490.19	195668.6	0	146.68	6.67	0	116.67	0
Pyrite-rim	159633.49	169724678	0	0	15582.88	446.73	0	77841.82	0	0	26.67	0	0	0
Pyrite-rim	482341.33	122922928	0	890.15	2944.24	956.94	0	0	0	41054.28	24336.11	0	1874.75	80.01
Pyrite-rim	465099.66	115471260	0	184179	370886.1	0	0	0	0	63629.63	20	0	43.33	10
Pyrite-rim	676483.22	95567132.8	840.57	680.05	15196.15	130.02	490.19	195668.6	0	146.68	6.67	0	116.67	0
Pyrite-core	255598.74	264074752	1550.69	403.36	22555.15	483.92	193.4	249102.88	20	0	23.34	6589	33.33	0
Pyrite-core	237884.24	235613652	480.56	7705.23	23939.58	18330.13	413.46	703464.78	0	880.12	964.42	2900.3	686.77	13.34
Pyrite-core	209421.14	228641152	937.05	86228.64	18426.58	90.02	553.52	225692.18	0	13.34	50	0	20	0
Pyrite-core	179210.39	169634078	0	43622.18	37235.91	0	0	135835.2	0	0	0	0	0	0
Pyrite-core	165636.49	150386478	0	0	36200.68	0	0	99918.21	0	0	0	0	0	0
Pyrite-core	184889.79	169017978	0	0	27463.14	8755.71	0	422058.21	0	0	486.7	0	0	0
Pyrite-core	182040.79	169491578	0	0	118627	2981.62	0	336172.51	0	0	203.34	0	0	0
Pyrite-core	1498761.75	270500947	86.71	1086.89	2073.96	730.15	273.41	0	0	33777.11	12228.5	0	836.86	60.01
Pyrite-core	1200742.94	241436571	0	0	15582.88	446.73	0	77841.82	0	0	26.67	0	0	0
Pyrrhotite	66251.87	102739690	0	200.01	20690.85	496.95	433.62	2504.75	0	76.67	13.33	0	1600.42	183.35
Pyrrhotite	64029.48	104781190	0	360.03	20000.75	170.01	0	67388.22	0	173.35	16.66	0	363.36	230.02
Pyrrhotite	28883.58	23781338	0	0	0	15863290	0	2358.35	0	0	0	0	0	0
Sphalerite	20361.36	3224898	0	0	0	2736820	324029.14	12724	342661.2	8908022.67	0	0	0	0
Sphalerite	24059.33	3852101.7	0	0	0	21193197	383165.04	39966.13	697027.7	10950330.67	0	0	0	0
Sphalerite	26703.28	4123606.7	0	0	0	19985491	340788.94	44460.01	350643.5	10356800.67	0	0	0	0
Arsenopyrite	69033.05	119907152	0	890.15	2944.24	956.94	0	21514550	0	41054.28	24336.11	0	1874.75	80.01
Arsenopyrite	66307.07	93026362.8	86.71	1086.89	2073.96	730.15	273.41	19547570	0	33777.11	12228.5	0	836.86	60.01
Arsenopyrite	66541.96	112879490	0	184179	370886.16	0	0	29801965	0	63629.63	20	0	43.33	10
Gold	0	0	0	0	0	6972.93	0	586.69	3059111.6	0	24383633.28	0	0	0
Gold	0	0	0	0	0	0	0	0	2989561	0	28967353	0	0	0
Gold	0	0	0	0	0	0	0	0	3234967	0	24813073	0	0	0

Arsenopyrite of the Sheba Deposit contains up to 0.26 wt. % Ni, 0.15 wt. % Au, 0.24 wt. % Hg and 0.41 wt. % B (Table 2). Found in rhombic domains, long laths, and irregular shaped with oscillatory growth zones.

Gold in pyrite and arsenopyrite and with large, pyrrhotite grains of the Sheba Deposit occurs in two chemical forms: invisible and elemental (Cabri *et al.*, 2000). Tiny gold inclusions are usually occurred as fillings at the growth boundaries and fractures of these sulphides. The width of the fractures might be separated by the later crystallization of gold nano-particles (Cook *et al.*, 2009a; Bi *et al.*, 2011). Gold also occurs as free-subhedral-small to medium-grained lodes, associated with the silicates of the host rocks (usually quartz). These free gold lodes are composed of about (95 wt. % Au and 3.9 wt. % Ag and traces of Cu, Pb, Fe, and Ni (Table 2).

4. Discussions

4.1. Ore Criteria

The ore microscopic investigations demonstrated that the dominant sulphides in Sheba are pyrite, arsenopyrite, pyrrhotite, chalcopyrite, and, to a lesser degree, sphalerite. Nevertheless, the primary ore-forming process is difficult to distinguish in such assemblages, because they were subjected to long period of metasomatism and deformation. Ores and host rocks were intensively tectonically reworked. Native gold occurs in many of these samples as inclusions associated with haematite. This reflects hydrothermal (orogenic) origin rather than magmatic for these sulphides (Hutchinson, 1993). The origin of hydrothermal solutions plays a major distinguished role appeared in textures and trace elements distributions among the ores (Altigani *et al.*, 2016; Altigani, 2021), reflecting multiple processes of hydrothermal activities. Nickel is found in most of the lithologies of the Sheba deposit, it reflects possible contribution of mafic/ultramafic sources. The elemental substitutions and replacements in the pyrite type 2 of Sheba are collective evidences to support syn-to- late, and different-source hydrothermal solutions (Altigani *et al.*, 2016; Altigani, 2021). In some samples, pyrrhotite and chalcopyrite display fine intergrowth textures suggesting co-precipitation. Alternatively, it may indicate the early existence of solid solutions between the two phases, which were deposited at a high temperature.

In most of the Sheba samples, two (generations) types of pyrite were identified based on textural and chemical variations. However, Agangi *et al.* (2014) identified three stages of pyrite from Sheba deposit (poikilotic, arsenian, and inclusive pyrite). In this study pyrite type 1 has an irregular shape and in some cases, follows the general foliation and fractures of the rocks, utilizing low-temperature metamorphism micro-textures (Barrie *et al.*, 2007). In some other samples, it forms augen textures, which reflect the syn-orogenic formation of this type. This pyrite type is possibly compared to the first pyrite stage described by (Agangi *et al.*, 2014). This type of pyrite was partially decomposed to the lower sulphur content mineral pyrrhotite (Hu *et al.*, 2006). This might have happened due to increase of the temperatures resulted from the post-orogenic granitic intrusions and their associated hydrothermal solutions, coupling with lowering in the sulphur fugacity. The morphology, trace-elements distribution, relationships, and association of this pyrite type indicate long and complicated deformational history, and multi-depositional events (Altigani *et al.*, 2016; Altigani, 2021). The majority of the early type pyrite grains are dominated by lot of pores in their cores, which reflect deformational events coupled with the elongation in the pyrite (Barrie *et al.*, 2007). The textural features of pyrite and occurring of intensive pores allow both gold nano-particles and inclusions to deposit in the pyrite (Ciobanu *et al.*, 2011).

The early pyrite type 1 is partially decomposed to pyrrhotite, which may possibly have happened as result of increasing the temperature, and lowering of the sulphur fugacity (Hu *et al.*, 2006). Alterations of this pyrite type occurred close to the contact zones with late granitic intrusions, or close to the relatively late quartz-carbonate hydrothermal veins (Hu *et al.*, 2006). The mineral chemistry of this pyrite type indicates that As and Ni substitute S and Fe respectively. This explains the limited variations in both S and Fe contents of pyrite type 1. Pyrite type 1 is As-Ni-rich compared to type 2. No systematic relationship was observed between Au and As, which confirmed by EMP, suggesting that gold is not directly linked to arsenic contents in the pyrite. The second pyrite type formed later; it displays euhedral shapes. The recrystallization of this type is an indication of high formation temperatures that might cause by thermal effects of late granitic intrusions and associated volatiles, which subsequently caused an

elimination and dislocation of the grain boundary of most ancient pyrite grains (Barrie *et al.*, 2007).

This type 2 is found adjacent to quartz-carbonate veins, reflecting the fundamental effects of these late hydrothermal veins in remobilizing and reforming pyrite and other sulphides of the Sheba Deposit (Cook *et al.*, 2009a). The euhedral shape and the absence of pores in this type of pyrite suggest a high-temperature metamorphism-related hydrothermal origin, or post-sedimentation formation (Hofmann, *et al.*, 2009).

The contacts between pyrite type 2 and pyrrhotite suggest relatively later formation of pyrite type 2. In some samples, arsenopyrite is found close to sphalerite, but is more commonly inter-grown with pyrite than with pyrrhotite. Arsenopyrite commonly forms oscillatory zones, which reflect different timing of arsenopyrite formation, fluctuation of trace elements, or reactions. The effects of the late hydrothermal solutions are obvious in the Sheba Deposit ores. It contributes by a wide range of textural variations and chemical reactions between the solutions and the pre-existent gold-bearing sulphides, which obviously inherited in their element's distribution, forming elemental zoning or heterogeneities (Hammond and Tabata, 1997; Hammond, *et al.*, 2007; Cook, *et al.*, 2009a; Ciobanu, *et al.*, 2011; Winderbaum, *et al.*, 2012).

These solutions are responsible of the formation of many textures, such as, atoll texture in the pyrite type 1. The rounded pyrite, found in these ores, seems to be a detrital, which may have been derived from different sources including: (1) sulphides of magmatic-hydrothermal or metamorphism-related hydrothermal origin, hosted in granitoid-greenstone regions of sedimentary basins, (2) Older sedimentary rock successions, or (3) syn-depositional to a diagenetic intra-formational sulphides signifying primary chemical precipitates, early diagenetic products or secondary replacements (Hofmann *et al.*, 2009). Simpson *et al.* (2012) gave some evidence for aeolian formations in the Archaean Moodies Group. This Archaean wind might possibly have carried some of the pyrite (probably other sulphides and tiny gold) grains with it and deposited as rounded (poorly sorted) pyrite at the BGB basins.

The differences in the gold size and shapes represented in the Sheba Deposit indicate the variation in the geological processes (Cook *et al.*, 2009a; Ciobanu *et al.*, 2011; Bi *et al.*, 2011; Winderbaum *et al.*, 2012), which have been

responsible for, and affected the ore body formation in this deposit. It also implies different depositional environments for gold mineralization.

Pyrite can incorporate Au through different processes, which include solid solution, or containing very small inclusions of gold or gold bearing mineral (Simon *et al.*, 1999). Gold association with pyrite and arsenopyrite could reflect co-precipitation (Hammond and Tabata, 1997). In this study, the EMP results show that gold is positively correlated to Fe more than As, which reflects the affinity towards iron. Nevertheless, this relationship might be due to the presence of tiny gold grains inside the pyrite (suggested by LA-ICP-MS). LA-ICP-MS profiles on pyrite revealed that gold, silver, and other elements occur in tiny grains within the pyrite type 1, which contribute to the high variability when these elements are compared to each other (Cook, *et al.*, 2009a; Sung, *et al.*, 2009; Bi, *et al.*, 2011).

4.2. Elements mapping on pyrite

LA-ICP-MS mapping results of three pyrite grains disclosed that the pyrite type 2 from the Sheba Deposit is compositionally zoned, and heterogeneous (Fig. 7). These zones are due to differences in elemental distributions in the pyrite grains (Dixon, *et al.*, 2013). The results also indicate an existence of very minute gangue mineral inclusions inside this pyrite type. These gangue inclusions are rich in Al, Ti, V, Ge, and Cr, which are distributed homogeneously within the pyrite, indicating an existing of very tiny inclusions of silicates or oxides inside the pyrite type 2 of the Sheba Deposit. The existence of these elements in the pyrite might be due empty pores, which exposed the groundmass materials (silicates). Ni distribution suggest replacement with iron rather than an existence of Ni-rich phases in the pyrite, this indicated by non-systematic relationship between Fe and Ni.

Trace elements, such as Sn, Mn, Cu, Hg are displaying homogenous distributions in the structure of the pyrite type 2 of the Sheba Deposit, which implies synchronous incorporation of these elements with the pyrite. In contrast, other trace elements, such as As, Zn, Ni, Co, and Sb show positively skewed distributions in the pyrite, suggesting that these elements were hosted by the pyrite due to exchanges with late hydrothermal solutions. These elements are rather concentrated in certain zones.

Gold and silver show both distribution styles, which

Fig. 7. Ni distribution around pyrite from Sheba. Concentration in the low ppm range, showing several generations of crystal growth of this composite grain. Concentration shown as counts per second.

indicates two generations (episodes) of gold mineralization s, or could be due to existence of silver as solid solution or micro-inclusions in the pyrite (Cook *et al.*, 2009b). The fist was deposited simultaneously with the pyrite, and the second was delivered later by the hydrothermal solutions to form very tiny electrum. LA-ICP-MS profiles indicate that Au and Ag may be present as nanoparticles of native gold, electrum, or Au-Ag-tellurides in pyrite, supported by the observations of (Bi *et al.*, 2011).

(a) Distribution of elements in the inclusions enclosed by the pyrite grains

the distribution pattern, obtained from some elements like Al and Ti reflects appearance of micro to nano-scale particles of Al and Ti-rich mineral (rutile, sphene!). Discrete chromite and rutile grains were also found inside the pyrite of the adjacent Fairview Deposit, which obtained by using high quality SEM (Fig. 8). Gold and other sulphides could also be found as nano-particles within the pyrite structure (Chenery *et al.*, 1995; Reich *et al.*, 2005; Deditius *et al.*, 2011). The origin of these nano-particles could be direct

precipitation from hydrothermal solution, and/or due to exsolution processes (Palenik *et al.*, 2004; Deditius *et al.*, 2011).

The elements distribution patterns of S and Fe reflect variations in the ablation rate rather than substitution. Sulphur and iron distributions in pyrite show zigzagging pattern (Fig. 9A), which reflects zonation. Nickel and cobalt utilize increasing at the pyrite boundaries (Figs. 9B&C) that could be related to later hydrothermal activities. The elements (Al, Ti, V, Ge and Cr) have homogenous distribution inside the pyrite, while others are showing heterogenous distribution pattern (As, Ni, Co).

LA-ICP-MS mapping reveals those very minute inclusions rich in such trace elements (Sn, Mn, Cu, and Hg) display homogenous distributions (Fig. 10A) in the structure of the pyrite type 2 of the Sheba Deposit, which implies synchronous incorporation of these elements with the pyrite. In contrast, other rich-inclusions in (As, Zn, Ni, Co, and Sb) show positively skewed distributions in the pyrite (Fig. 10B), suggesting these elements were hosted by the pyrite due

Fig. 8. Back-scattered electron images for pyrite grain from the adjacent Fairview Deposit, indicating micro-nuggets of chromite and rutile (zoned!) occur within the pyrite. The appearance of chromite micro-grains is indicating mafic to ultramafic provenance (Altigani, 2021).

Fig. 9. a, b, c distribution of trace elements on Sheba pyrite grains.

to exchanges by late hydrothermal solutions. These elements are rather concentrated in certain zones.

(b) The zonation of trace-elements in the pyrite grains

The pyrite type 2 of the Sheba Deposit is zoned, this revealed by the distribution patterns of the trace elements

in the pyrite.

(c) The distribution of the trace-elements in structure of the pyrite grains

Some of these elements show normal distributions (Sn, Mn, Cu, Hg), however; others are displaying heterogeneous distribution patterns in the structure of the pyrite itself (As, Zn, Ni, Co, Sb). gold and silver show the both distribution types.

(d) The relationships of trace-elements in the pyrite grains

The data set was cleaned from the zones results to examine the elemental relationships only in the pyrite. No systematic relationship was found between gold and arsenic in the structure of the pyrite. Nickel has a positive correlation with arsenic. While cobalt does not indicate any clear relationship with nickel. the decreasing of As and Ni in single pyrite grains from core to rim, indicating these ores formed in reduction conditions (Hammond and Tabata, 1997).

5. Conclusions

The dominant rock types at the Sheba deposit are arkoses, metapelites, and greywackes. Most of these rocks have the same lithology with minor variations in the quartz and mica contents (up to 56 and 31 wt. %) respectively. At least two generations of quartz, muscovite, and sulphides are distinguished in this deposit. This suggests two episodes of metamorphism and/or remobilization affected these

Fig. 10. (A) Homogeneous distributions of some trace elements throughout three pyrite grains of type 2 from the Sheba Deposit in the, suggesting synchronous formation of these elements with pyrite, could possibly be due to background effects as well; indicating the presence of very small mineral inclusion. (B): The skewed distributions of some elements in the three pyrite grains of type 2 from the Sheba Deposit, indicating later accumulation of these elements in the pyrite by later hydrothermal solutions. These distributions reflect heterogeneity in the pyrite type 2, which is not observed by microscopy, EMPA, or LA-ICP-MS single shots.

rocks. The lithology of this deposit reflects sequence of immature, and impure sandstones beds (which intercalated with shale and carbonate seams), and intermediate to basic metamorphosed rocks that intercalated with the sedimentary sequence. All of the Sheba rock assemblage is metamorphosed generally under green schist facies conditions, however, some metapelite shows medium to high metamorphic assemblages, which localized adjacent to the granitic intrusions, there are also indications for retrograde metamorphism that could be seen in the formation of secondary biotite after the garnet porphyroblast.

The two main types of metamorphism in this deposit caused very faint effects on the primary sedimentary structures. The second episode of metamorphism led to a retrogression for the micas and feldspars in the Sheba rocks, creating new generations of carbonates, chlorites, and epidote-mineral group. Graphite (organic materials) is very common in the arkoses and metapelite of this deposit; it may suggest an existence of an Archaean life within these sediments. The chemistry of the Sheba rocks indicates an intermediate to acidic provenance of sediments. The high values of SiO_2 and Al_2O_3 (up to 75-19 % respectively), represent the dominance of quartz and mica in this deposit lithology. Low values of Fe_2O_3 and MgO indicate the low contents of mafic mineral in these rocks. Ores of this deposit are greatly affected by the metasomatism, shearing, and hydrothermal alterations caused by repeated metamorphism episodes and solutions pulses, which are very clear in the ores textures (oscillatory) and trace-elements content. Remobilization of gold under green schist metamorphic facies is very significant in the Sheba ores, where the two types of gold were observed: a) associated and enclosed by sulphides, especially pyrite, which represents the principal sulphide mineral in this deposit. b) Found as free-lode grains within the silicates (mainly quartz).

Pyrite, pyrrhotite, arsenopyrite, and chalcopyrite are the main sulphides in the Sheba Deposit. There are significant variations in the chemistry of the different generations of these minerals. Pyrite was found in two generations: Pyrite 1 contains more minor and trace elements compared to pyrite 2. The substitution of Fe and S by (Ni, Co) and arsenic respectively is common in this type. Au (2 wt. %), Bi, Ni, Mn, Co, Au, Ag, As, and Pb show a significant increase in content in this type. These replacements cause the development of new generations of Ni-sulphides and

Ni-arsenides in some parts inside this pyrite type. Pyrite 2 is relatively younger, found overgrowing pyrite 1, and consists of well-developed cubic and eight-side crystals.

Textural and trace element data may not be able to identify stage margins or sharp sequential boundaries of genetic evolution of the deposits in Sheba; however, they provide clear evidences for the different tectonic and metamorphism events, hydrothermal pulses, and their impact on Au distribution.

LA-ICP-MS mapping technique applied on three pyrite grains from this deposit, revealed an existence of very tiny mineral in nano scale within the pyrite type 2. It also shows an elemental zoning within these pyrite grains. The distribution and relationships of the trace elements in these pyrite grains indicate three genetic behaviours: 1) Al, Mn, Hg, Se, Ti, V, Cr, and Sn distributed equally within pyrite, reflecting a synchronous formation of these domains with pyrite. 2) As, Ni, Co, Zn, and Sb distributed heterogeneous in the pyrite, indicating post-interference due to late solutions. Moreover 3) Au and Ag show both homogenous and heterogenous distribution within pyrite, which suggests the possibility of (1) and (2) formations.

Acknowledgment

This work was part of author's PhD thesis that sponsored by Alneelain University and conducted at University of Pretoria. The author declared no conflict-of-interest present in this study. Deep thanks to Alneelain University- Sudan, and the Geology department at the University of Pretoria for facilitating their laboratories and instruments to achieve the purposes of this research. Special thanks extended to Late Dr. RD Dixon and the South African Police Forensic Laboratory in Pretoria for allowing us to use their LA-ICP-MS instrument.

References

- Agangi, A., Hofmann, A. and Przybyłowicz, W. (2014) Trace element zoning of sulfides and quartz at Sheba and Fairview gold deposits: Clues to Mesoarchean mineralization in the Barberton Greenstone Belt, South Africa. *Ore Geol. Rev.*, v.56, p.94-114. doi: 10.1016/j.oregeorev.2013.08.016
- Altigani, M.A.H. (2021) Insights on Mineralogy and Chemistry of Fairview Gold Mine, Barberton Greenstone Belt, South Africa. *Indonesian Journal on Geoscience*, v.8(1), p.73-99. doi: 10.17014/ijog.8.1.73-99

- Altigani, M.A.H., Merkle, R.K.W. and Dixon R.D. (2016) Geochemical identification of episodes of gold mineralisation in the Barberton Greenstone Belt, South Africa, *Ore Geol. Rev.*, v.75, p.186-205. doi: 10.1016/j.oregeorev.2015.12.016
- Anhaeusser, C.R. (1975) Precambrian Tectonic Environments. *Annu. Rev. Earth Planet Sci.*, v.3, p.31-53. doi: 10.1146/annurev.ea.03.050175.000335
- Barrie, C.D., Boyle, A.P. and Prior, D.J. (2007) An analysis of the micro-textures developed in experimentally deformed polycrystalline pyrite and minor sulphide phases using electron backscatter diffraction. *J. Struct. Geol.*, v.29, p.1494-1511. doi: 10.1016/j.jsg.2007.05.005
- Barrie, C.D., Boyle, A., Cook, N.J. and Prior, D.J. (2010) Pyrite deformation textures in the massive sulfide ore deposits of the Norwegian Caledonides. *Tectonophysics*, v.483, p.269-286. doi: 10.1016/j.tecto.2009.10.024
- Belcher, R.W. and Kisters, A.F.M. (2006) Syntectonic emplacement and deformation of the Heerenveen batholith: Conjectures on the structural setting of the 3.1 Ga granite magmatism in the Barberton granite greenstone terrain, South Africa. In: Reimold, WU, Gibson, RL (Eds.), *Processes on the Early Earth*. *Geol. Soc. Am. Bull., Special Publication*, v.405, p.211-231. doi: 10.1130/2006.2405(12)
- Bi, S., Li, J., Zhou, M. and Li, Z. (2011) Gold distribution in As-deficient pyrite and telluride mineralogy of the Yangzhaiyu gold deposit, Xiaoqinling district, southern North China craton, *Miner. Deposita*, v.46, p.925-941. doi: 10.1007/s00126-011-0359-2
- Brandl, G., Cloete, M. and Anhaeusser, C.R. (2006) Archaean greenstone belts. In: Johnson, MR, Anhaeusser, C.R. and Thomas, R.J. (Eds.) (2006). *Geology of South Africa*, Geological Society of South Africa, Johannesburg/ Council for Geosciences, Pretoria, p.9-56.
- Bumby, A.J., Eriksson, P.G., Catuneanu, O., Nelson, D.R. and Rigby, M.J. (2011) Meso-Archaean And Palaeo-Proterozoic Sedimentary Sequence Stratigraphy of The Kaapvaal Craton, *Mar. Pet. Geol.*, v.33, p.92-116. doi: 10.1016/j.marpetgeo.2011.09.010.
- Cabri, L.J., Newville, M., Gordon, R.A., Crozier, E.D., Sutton, S.R., McMahon, G. and Jiang, D.T. (2000) Chemical speciation of gold in arsenopyrite. *Canad. Mineral*, v.38, p.1265-1281. doi: 10.2113/gscanmin.38.5.1265
- Chen, Z. (1999) Inter-element fractionation and correction in laser ablation inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.*, v.14, p.1823-1828. doi: 10.1039/a903272j
- Chenery, S., Cook, J.M., Styles, S. and Cameron, E.M. (1995) Determination of the three-dimensional distributions of precious metals in sulphide mineral by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAEMP-ICP-MS). *Chem. Geol.*, v.124, p.55-65. doi: 10.1016/0009-2541(95)00024-g
- Ciobanu, C.L., Cook, N.J., Utsunomiya, S., Pring, A. and Green, L. (2011) Focussed ion beam transmission electron microscopy applications in ore mineralogy: Bridging micro- and nanoscale observations. *Ore Geol. Rev.*, v.42, p.6-31. doi: 10.1016/j.oregeorev.2011.06.012
- Cook, N.J., Ciobanu, C.L. and Mao, J. (2009a) Textural control on gold distribution in As-free pyrite from the Dongping, huangtuliang and Hougou gold deposits, North China Craton. *Chem. Geol.*, v.264, p.101-121. doi: 10.1016/j.chemgeo.2009.02.020
- Cook, N.J., Ciobanu, C.L., Pring, A., Skinner, W., Shimizu, M., Danyushevsky, L., Saini-Eidukat, B. and Melcher, F. (2009b) Trace and minor elements in sphalerite: A LA-ICP-MS study, *Geochim. Cosmochim. Acta*, v.73, p.4761-4791. doi: 10.1016/j.gca.2009.05.045
- Condie, K.C. (1993) Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. *Chem. Geol.*, v.104, p.1-37. doi: 10.1016/0009-2541(93)90140-e
- Condie, K.C., Macke, J.E. and Reimer, T.O. (1970) Petrology and geochemistry of early Precambrian greywackes from the Fig Tree Group South Africa. *Geol. Soc. Am. Bull.*, v.81, p.2759-2776. doi: 10.1130/0016-7606(1970)81[2759:pageop]2.0.co;2
- Danchin, R.V. (1967) Chromium and nickel in the Fig Tree Shale from South Africa. *Science*, v.158, p.261-262. doi: 10.1126/science.158.3798.261
- Deditius, A.P., Utsunomiya, S., Reich, M., Kesler S.E., Ewing R.C., Hough, R. and Walshe J. (2011) Trace metal nanoparticles in pyrite. *Ore Geol. Rev.*, v.42, p.32-46. doi: 10.1016/j.oregeorev.2011.03.003
- Dirks, P.H.G.M., Charlesworth, E.G. and Munyai, M.R. (2009) Cratonic extension and Archaean gold mineralisation in the Sheba-Fairview mine, Barberton Greenstone Belt, South Africa. *S. Afr. J. Geol.*, v.112, p.291-316. doi: 10.2113/gssajg.112.3-4.291
- Dirks, P.H.G.M., Charlesworth, E.G., Munyai, M.R. and Wormald, R. (2013) Stress analysis, post-orogenic extension and 3.01 Ga gold mineralisation in the Barberton Greenstone Belt, South Africa. *Precambrian Res.*, v.226, p.157-184. doi: 10.1016/j.precamres.2012.12.007
- Dziggel, A., Otto, A., Kisters, A.F.M. and Meyer, F.M. (2007) Tectono metamorphic controls on Archaean gold mineralization in the Barberton greenstone belt, South Africa: an example from the New Consort gold mine. In: Van Kranendonk, M., Smithies, R.H., Bennett, V. (Eds.), *Earth's Oldest Rocks*. *Developments in Precambrian Geology*, v.15, p.699-727. doi: 10.1016/s0166-2635(07)15058-1
- Dziggel, A., Poujol, M., Otto, A., Kisters, A.F.M., Trierloff, M., Schwarzd, W.H. and Meyer, F.M. (2010) New U-Pb and ⁴⁰Ar/³⁹Ar ages from the northern margin of the Barberton greenstone belt, South Africa: Implications for the formation of Mesoarchaean gold deposits. *Precambrian Res.*, v.179, p.206-220. doi: 10.1016/j.precamres.2010.03.006
- De Ronde, C.E.J., Kamo, S., Davis, D.W., De Wit, M.J. and Spooner, E.T.C. (1991) Field, geochemical and UPb isotopic constraints from hypabyssal felsic intrusions within the Barberton Greenstone Belt, South Africa: implications for tectonics and the timing of gold mineralization. *Precambrian Res.*, v.49, p.261-280. doi: 10.1016/0301-9268(91)90037-b
- De Ronde, C.E.J., Spooner, E.T.C., De Wit, M.J. and Bray, C.J. (1992) Shear zone-related, Au quartz vein deposits in the Barberton greenstone belt, South Africa; field and petrographic characteristics, fluid properties, and light stable isotope geochemistry. *Economic Geology*, v.87, p.366-402. doi: 10.2113/gsecongeo.87.2.366

- De Ronde, C.E.J. and De Wit, M.J. (1994) The tectonic history of the Barberton greenstone belt, South Africa: ~ 490 million years of the Archaean crustal evolution. *Tectonics*, v.13, p.983-1005. doi: 10.1029/94TC00353
- De Vries, S.T. and Touret, J.L.R. (2007) Early Archaean hydrothermal fluids; a study of inclusions from the ~3.4 Ga Buck Ridge Chert, Barberton Greenstone belt, South Africa. *Chem. Geol.*, v.237, p.289-302. doi: 10.1016/j.chemgeo.2006.06.027
- De Wit, M.J., Furnes, H. and Robins, B. (2011) Geology and tectono-stratigraphy of the Onverwacht Suite, Barberton Greenstone Belt, South Africa. *Prec. Res.*, v.186, p.1-27. doi:10.1016/j.precamres.2010.12.007.
- Dixon, R.D., Merkle, R.K.W., Kurta, C. and Altigani, M.A.H. (2013) LA-ICP-MS ELEMENTAL MAPPING: AN EXAMPLE FOR PYRITE FROM SHEBA MINE, BARBERTON. *Igneous and Metamorphic Studies Group*. v.2013. Conference paper. Department of Geology, University of Free State, South Africa.
- Eglington, B.M. and Armstrong, R.A. (2004) The Kaapvaal Craton and adjacent orogens, southern Africa: a geochronological database and overview of the geological development of the craton. *South African Journal of Geology*, v.107, p.13-32. doi: 10.2113/107.1-2.13
- Eriksson, K.A., Krapez, B. and Fralik, P.W. (1997) Sedimentological aspects. In: De Wit, M.J., Ashwal, LD (Eds.), *Greenstone Belts*. Clarendon Press, Oxford, p.33-54.
- Eriksson, P.G., Martins-Neto, M.A., Nelson, D.R., Aspler, L.B., Chiarenzelli, J.R., Catuneanu, O., Sarkar, S., Altermann, W. and Rautenbach, W. (2001) An introduction to Precambrian basins: their characteristics and genesis. *Sedimentary Geology*, v.141-142, p.1-35. doi: 10.1016/S0037-0738(01)00066-5
- Gaboardi, M. and Humayun, M. (2009) Elemental fractionation during LA-ICP-MS analysis of silicate glasses: implications for matrix-independent standardization. *Journal of Analytical Atomic Spectrometry*, v.24, p.1188-1197. doi: 10.1039/B900876D
- Goldstein, J., Newbury, D. E., Michael, J. R. and Ritchie, M. W. M. (2003) Scanning electron microscopy and x-ray microanalysis, Springer, doi: 10.1007/978-1-4939-6676-9
- Grosch, E.G., Kosler, J., McLoughlin, N., Drost, K., Slama, J. and Pedersen, R.B. (2011) Paleoarchean detrital zircon ages from the earliest tectonic basin in the Barberton Greenstone Belt, Kaapvaal craton, South Africa. *Precambrian Res.*, v.191, p.85-99. doi: 10.1016/j.precamres.2011.09.003
- Groves, D.I., Goldfarb, R.J., Gebre-Mariam, M., Hagemann, S.G. and Robert, F. (1998) Orogenic gold deposits: a proposed classification in the context of their crustal distribution and relationship to other gold deposit types. *Ore Geol. Rev.*, v.13, p.7-27. doi: 10.1016/S0169-1368(97)00012-7
- Hammond, N.Q. and Tabata, H. (1997) Characteristics of ore mineral associated with gold at the Prestea mine, Ghana. *Mineralogical Magazine*, v.61, p.879-894.
- Hammond, N.Q., Moore, J.M. and Sheets, R.W. (2007) Physico-chemical conditions of ore-forming fluids associated with genesis of the Kalahari Goldridge deposit, Kraaipan Greenstone Belt, South Africa. *Ore Geol. Rev.*, v.30, p.106-134. doi: 10.1016/j.oregeorev.2005.11.003
- Hessler, A.M. and Lowe, D.R. (2006) Weathering and sediment generation in the Archaean: An integrated study of the evolution of siliciclastic sedimentary rocks of the 3.2 Ga Moodies Group, Barberton Greenstone Belt. South Africa. *Precambrian Res.*, v.151, p.185-210. doi: 10.1016/j.precamres.2006.08.008
- Heubeck, C.E. and Lowe, D.R. (1994) Depositional and tectonic setting of the Archaean Moodies Group, Barberton greenstone belt, South Africa. *Precambrian Res.*, v.68, p.257-290. doi: 10.1016/0301-9268(94)90033-7
- Heubeck, C.E. (1993) Geology of the Archaean Moodies Group, central Barberton greenstone belt, south Africa. PhD thesis (unpubl.), Stanford Univ., California, 413p.
- Hofmann, A., Bekker, A., Rouxel, O., Rumble, D. and Master, S. (2009) Multiple sulphur and iron isotope composition of detrital pyrite in Archaean sedimentary rocks: A new tool for provenance analysis. *Earth and Planetary Science letters*, v.286, p.436-445. doi: 10.1016/j.epsl.2009.07.008
- Hofmann, A. (2005) The geochemistry of sedimentary rocks from the Fig Tree Group, Barberton greenstone belt: Implications for tectonic, hydrothermal and surface processes during mid-Archaean times. *Precambrian Res.*, v.143, p.23-49. doi: 10.1016/j.precamres.2005.09.005
- Humayun, M., Davis, F.A. and Hirschmann, M.M. (2010) Major element analysis of natural silicates by laser ablation ICP-MS. *Journal of analytical Atomic Spectrometry*, v.25, p.998-1005. doi: 10.1039/C001391A
- Hutchinson, R.W. (1993) A multi-stage, multi-process genetic hypothesis for greenstone hosted gold. *Ore Geol. Rev.*, v.8, p.349-382. doi: 10.1016/0169-1368(93)90022-Q
- Kamo, S.L. and Davis, D.W. (1994) Reassessment of Archean crust development in the Barberton Mountain Land, South Africa, based on U-Pb dating. *Tectonics*, v.13, p.167-192. doi: 10.1029/93TC02254
- Kent, L.E. (1980) Stratigraphy of South Africa. South African Committee for Stratigraphy, Geological Survey of South Africa, Handbook v.8, 960p.
- Kisters, A.F.M., Belcher, R.W., Poujol, M. and Dziggel, A. (2010). Continental growth and convergence-related arc plutonism in the Mesoarchaeon: Evidence from the Barberton granitoid-greenstone terrain, South Africa. *Precambrian Res.*, v.178, p.15-26. doi: 10.1016/j.precamres.2010.01.002
- Lowe, D.R. (1994) Accretionary history of the Archean Barberton greenstone belt (3.55– 3.22 Ga). *Southern Africa, Geology*, v.22, p.1099-1102. doi: 10.1130/0091-7613(1994)022%3C1099:ahotab%3E2.3.co;2
- Lowe, D.R. (1999) Shallow-water sedimentation of accretionary lapilli-bearing strata of the Msauli Chert: Evidence of explosive hydromagmatic komatiitic volcanism. In: Lowe, D.R., Byerly, G.R. (Eds.), *Geologic Evolution of the Barberton Greenstone Belt, South Africa*. *Geol. Soc. Am. Bull., Special Paper*, v.329, p.213-232. doi: 10.1130/0-8137-2329-9.213
- Lowe, D.R. and Byerly, G.R. (1986) Archaean flow-top alteration zones formed initially in a low temperature sulphate-rich environment. *Nature*, v.324, p.245-248. doi: 10.1038/324245a0
- McLennan, S.M., Taylor, S.R. and Kroner, A. (1983) Geochemical

- evolution of Archean shales from South Africa. The Swaziland and Pongola Supergroups. *Precambrian Res.*, v.22, p.93-124. doi: 10.1016/0301-9268(83)90060-8
- McLennan, S.M. (1984) Petrological characteristics of Archean greywackes. *J. Sediment. Res.*, v.54(3), p.889-898. doi: 10.1306/212f852b-2b24-11d7-8648000102c1865d
- Miyashiro, A. (1973) *Metamorphism and Metamorphic belts*. George Allen and Unwin., London, 492p. doi: 10.1007/978-94-011-6836-6
- Palenik, C.S., Ustunomiya, S., Reich, M., Kesler, S.E., Wang, L. and Ewing, R.C. (2004) "Invisible" gold revealed: direct imaging of gold nanoparticles in a Carlin-type deposit. *Am. Mineral.*, v.89, p.1359-1366. doi: 10.2138/am-2004-1002
- Pickhardt, C., Dietze, H. and Becker, J.S. (2005) Laser ablation inductively coupled plasma mass spectrometry for direct isotope ratio measurements on solid samples. *Int. J. Mass Spectrom.*, v.242, p.273-280. doi: 10.1016/j.ijms.2004.12.014
- Reed, S.J.B. (1983) *Electron Microprobe Analysis*, Applied Science Publishers Ltd., Analysis of High Temperature Materials, p.91-127.
- Reed, S.J.B. (2005) *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*, Cambridge Univ. Press, New York, 189 p. doi: 10.1017/cbo9780511610561
- Reich, M., Kesler, S.E., Ustunomiya, S., Palenik, C.S., Chrysosoulis, S.L. and Ewing, R.C. (2005) Solubility of gold in arsenian pyrite. *Geochim. Cosmochim. Acta*, v.69, p.2781-2796. doi: 10.1016/j.gca.2005.01.011
- Rouchon, V., Orberger, B., Hofmann, A. and Pinti, D.L. (2009) Diagenetic Fe-carbonates in Paleoproterozoic felsic sedimentary rocks (Hooggenoeg Formation, Barberton greenstone belt, South Africa): Implications for CO₂ sequestration and the chemical budget of seawater. *Precambrian Res.*, v.172, p.255-278. doi: 10.1016/j.precamres.2009.04.010
- Robertson, M.J., Charlesworth, E.G. and Phillips, G.N. (1993) Gold mineralization during progressive deformation at the Main Reef Complex, Sheba Gold Deposit, Barberton Greenstone-Belt, South-Africa. *Information Circular, Economic Geology Research Unit, University of the Witwatersrand, Johannesburg*, v.267, 26p.
- Schouwstra, R.P. and De Villiers, J.P.R. (1988) Gold mineralization and associated wall rock alteration in Main Reef Complex at Sheba deposit, South Africa. *Transactions Institute Mining Metallurgy*, v.97B, p.158-170.
- Shaheen, M.E., Gagnon, J.E. and Fryer, B.J. (2012) Femtosecond (fs) lasers coupled with modern ICPMS instruments provide new and improved potential for in situ elemental and isotopic analyses in the geosciences. *Chem. Geol.*, v.330-331, p.260-273. doi: 10.1016/j.chemgeo.2012.09.016
- Simon, G., Huang, H., Penner-Hahn, E., Kesler, S.E. and Kao, L.S. (1999) Oxidation state of gold and arsenic in gold-bearing arsenian pyrite. *Am. Mineral.*, v.84, p.1071-1079. doi: 10.2138/am-1999-7-809
- Simpson, E.L., Erikson, K.A. and Mueller, W.U. (2012) 3.2 Ga aeolian deposits from the Moodies Group, Barberton Greenstone Belt, South Africa: Implications for the origin of first-cycle quartz sandstones. *Precambrian Res.*, v.214-215, p.185-191. doi: 10.1016/j.precamres.2012.01.019
- Stiegler, M.T., Lowe, D.R. and Byerly, G.R. (2010) The Petrogenesis of Volcaniclastic Komatiites in the Barberton Greenstone Belt, South Africa: a textural and Geochemical Study. *J. Petrol.*, v.51, p.947-972. doi: 10.1093/petrology/egq008
- Sung, Y.H., Brugger, J., Ciobanu, L., Pring, A., Skinner, W. and Nugus, M. (2009) Invisible gold in arsenian pyrite and arsenopyrite from a multistage Archean gold deposit: Sunrise Dam, Eastern Goldfields Province, Western Australia, *Mineral Deposits*, v.44, p.765-791. doi: 10.1007/s00126-009-0244-4
- Sylvester, P.J., Cabri, L.J., Tubrett, M.N., McMahon, G., Laflamme, J.H.G. and Peregoedova, A. (2005) Synthesis and evaluation of a fused pyrrhotite standard reference material for platinum group element and gold analysis by laser ablation-ICPMS, in Törmänen, T.O., and Alapieti, T.T., eds., 10th International Platinum Symposium: Oulu, Geological Survey of Finland, Extended Abstracts, p.16-20.
- Sylvester, P.J. (2008) Laser ablation-ICP-MS in the earth sciences: Current practices and outstanding issues. *Mineralogical Association of Canada*, 348p.
- Toulkeridis, T., Clauer, N., Kroner, A., Reimer, T. and Todt, W. (1999) Characterization, provenance, and tectonic setting of the Fig Tree greywackes from the Archean Barberton Greenstone Belt, South Africa. *Sediment. Geol.*, v.124, p.113-129. doi: 10.1016/S0037-0738(98)00123-7
- Van Kranendonk, M.J., Smithers, R.H. and Bennet, V.C. (2007) Earth's Oldest Rocks, *Developments in Precambrian Geology*, v.15, 1331p.
- Vaughan, J.P. and Kyin, A. (2004) Refractory gold ores in Archean greenstones, Western Australia: mineralogy, gold paragenesis, metallurgical characterization and classification. *Mineral. Mag.*, v.68, p.255-277. doi: 10.1180/0026461046820186
- Viljoen, M.J. and Viljoen, R.P. (1969) An introduction to the geology of the Barberton granite-greenstone terrain. Upper Mantle Project. Special Publication Geological Society of South Africa, v.2, p.9-28.
- Ward, J.H.W. (1995) Geology and metallogeny of the Barberton greenstone belt: a survey. *J. Afr. Earth. Sci.*, v.21, p.213-240. doi: 10.1016/0899-5362(95)00067-4
- Ward, J.H.W. (1999) The metallogeny of the Barberton Greenstone Belt, South Africa and Swaziland. *Geological Survey of South Africa, Memoir*, v.86, 116p.
- Watling, R.J., Herbert, H.K., Delev, D. and Abell, J. D. (1994) Gold fingerprinting by laser ablation inductively coupled plasma mass spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy*, v.499, p.205-219. doi: 10.1016/0584-8547(94)80019-7
- Winderbaum, L., Ciobanu, C.L., Cook, N.J., Paul, M., Metcalfe, A. and Gilbert, S. (2012) Multivariate Analysis of an LA-ICP-MS Trace Element Dataset for Pyrite. *Mathematical Geosciences*, v.44, p.823-842. doi: 10.1007/s11004-012-9418-1.
- Woodhead, J., Hergt, J., Meffre, S., Large, R.R., Danyushevsky, L. and Gilbert, S. (2009) In situ Pb-isotope analysis of pyrite by laser ablation (multi-collector and quadrupole) ICP-MS. *Chem. Geol.*, v.262, p.344-354. doi: 10.1016/j.chemgeo.2009.02.003