Contribution of X-Ray Diffraction in the Identification of Crystalline Phases of the Mineralization Hosted in the Mesozoic Cover of the Tazzeke Hercynian Massif – Maghrawa Region - Morocco

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Abstract Geological Research and prospection, mining exploration, remote sensing, geochemical methods, and geophysical technologies could improve the effectiveness and productivity of mineral exploration and ore identification. The application of these kinds of technologies presents the key factor of the future mining discoveries across the world. In this paper, we present the case study that consists to the use of geological investigation, remote sensing and geochemical studies in order of describing and determining the mineral fraction occurred in the Liasic series of Tazekka that manifests as carbonates cover of the Hercynian basement of the eastern Mesetean domain of Morocco. In fact, the followed procedure assigns the handling of remote sensing maps related to the area study, where we focus the hydrothermal alteration whichever allows the determination of selective and representative sample stations. Note that the collected

samples were subjected for two kind of geochemical analysis, when the first consists to the determination of mineral tenors using Inductive Coupled Plasma (ICP), and the second corresponds to the examination of samples by powder X-Ray Diffraction (XRD) methods in order to provide useful information about sample composition in terms of quantification of crystalline phases and content. In this work, we make in evidence the existence of remarkable mineralization of base and precious metals. These results may present an economic discovery in term of the potentiality of the Liasic cover of Tazekka for the mining exploration.

Keywords Technology, Mineral, Exploration, Remote Sensing, Hercynian, Tazekka, Morocco, ICP, XRD

1. Introduction

The Zone study is located into northeast of the Hercynian basement of Tazekka massif, based in the northeast end of the Middle Atlas of Morocco, and especially in the Mesozoic cover that outcrops SW of Taza (Fig. 1). In the Tazekka, the mineralization occurs in the Hercynian massif, as veins, and stratiform in the Liasic cover [2-4]. The basement, appears as a lower Ordovician epimetamorphic schists, surmounted by volcano sedimentary complex dated Upper Visean–Namurian [5-7].

Note that magmatic rocks as kind of granite and microdiorite, are generally enclosed by an aureole of contact metamorphism [8].

The Mesozoic formations are represented by Triassic and Liassic rocks (Fig. 1), resting in discordance on the

hercynian basement [9]. The Triassic series starts with two formations of red argillites separated by a volcanic formation [3]. The lower and upper Triassic argillites show a huge hydraulic fracturing. The Lower Lias assigns three formations where the lowest consists of fine, massive, and dark dolomites [4].

The middle, presents a series of dolomitic breccias, laminated dolomites and crystalline dolomites, and the upper formation consists of pale grey, fine-grained limestone and dark grey limestone with oolitic and bioclastic intervals [3]. The Middle Lias consists of a series of interbedded limestones and marls, however, the Upper Lias–Aalenian and Lower Bajocian are generally marly [3]. In the Middle Atlas Causse domain, there's an unconformity between the lower Lias and upper formations of the center and upper Lias.

Figure 1. Geographical position of the Zone study situated in the north east of Tazekka, with its geological maps (Geological map of Rif 1/ 500 000, [1]) and stratigraphy

The Liassic platform of the Tazekka contains some Pb–Zn and Fe deposits, whose distribution is controlled by paleogeography and structure. The mineralization is found along the basin margin and it is related to dolomitization [10,11]. It shows a straight paragenesis, essentially based on sphalerite and galena, with small amounts of pyrite and chalcopyrite. Sulfides occur in places and commonly form massive aggregates hosted by both hydrothermal dolomite and saddle dolomite [12,13]. The deposits are globally stratiform (Ain Hallouf, Ben Zerhla, Ain Tarselt, Ain Khebbab and Bou Khalifa) or open-space filling (Sidi Abdellah), and are located along the borders of grabens formed within the Middle Atlas Causse domain during the major Middle Atlas Toarcian–Bathonian tectonic event [9,14,15]. The presence of breccias, layered sediments and fragments confirms the karstic character of the mineralization. In the Lias cover, the mineralization seems to be occurred during two phases: first, the Carixian and so the Toarcian (Auajjar, 1994). Indeed, and based on all these arguments already cited, it appears that the major part of the mineralization detected in the Mesozoic Tazekka cover is stratiform, hosting Pb–Zn ores, that take an MVT form [16,17]. However, because it is clear that the geological and geodynamical contexts of the area is remarkable in term of mining wealth, we notice that the area is yet

unrecognized in terms of mineral exploration and geological prospecting and research.

In this work, we will focus in a first order the lower liassic brecciated dolomitic zones [18] dated hettangian, which may contain some showings of base or precious metal mineralization, and which may give us an idea about the close relation between these mineralization and the buried Hercynian basement, which is granitized, metamorphosed and mineralized (Pb, Zn, Sb, Ag, Au, Sn, W, Fe.....) [19].

2. Methods & Characterization

In this paper, we have based our work on the spatial mapping of hydrothermal alterations in the Maghrawa area via remote sensing [20,21] (Fig. 2). Indeed, it is on the basis of this mapping that we have targeted the potential zones in terms of hydrothermal alteration. We carried out selective sampling of breccia, from which five samples were taken and designed for Geochemical and petrographic analyses.

All the samples were analyzed using inductively coupled plasma analytical techniques for measuring the levels of inorganic elements in the samples (ICP: Inductive Coupled Plasma) [22,23].

Figure 2. Geographical position of the study in Maghrawa region, showing the location of the sample stations, and observation stations

To ensure an optimal characterization, all the samples were analyzed using inductively coupled plasma analytical techniques for measuring the levels of inorganic elements in the samples, while XRD (X-Ray Diffraction) [24] patterns were obtained from X'Pert High Score Report using Cu K α ($\lambda=1.54178$ Å), 2 θ mode was used to scan all the samples in the range of 30° ~ 60° with the step of 0.02° and the stay time is 2~3 s. Finally, to investigate the surface and morphology of the samples, Scanning Electron Microscopy (SEM) analyses were carried out on a FEI Quanta 200 microscope. Each sample is placed on a copper grid covered with a very thin layer of amorphous carbon (20 to 30 nm of thickness).

Note that all the described studies were carried out in the Innovation City of Science of Fes, University of Sidi Mohammed Ben Abdellah University of Fez – Morocco, while the scientific exchanges and interpretation were in collaboration with ATLAS MINING company; Abdus Salam International; Center of Theoretical Physics (Trieste-Italy) and Africa Graphene Center; Nanosciences African Network, University of South Africa Department of Physics, iThemba Labs (South Africa), African Laser Center.

3. Results and Discussions

3.1. ICP Analysis

According to the result of the ICP analysis, we note that no occurrence of (Pb) mineralization were detected in all samples, however the (Zn) (Cu) and (Fe) are present as clues of low concentration (0.018 - 8%), except of SS04 which shows a high tenor of Zn (36%) and Iron ($\approx$ 2%).

We note that this sample is taken from Ain Aouda region located in the north part of the zone study where an old mine of zinc as kind of strata manifested, and for that reason we conclude and suggest that the existence of high tenors of (Zn) and (Fe) is related to some extension of the principal ore body of Ain Aouda.

For the precious metals, we note the existence considerable (Ag) concentration (2-4 ppm) associated to some gold mineralization (1-7ppm). For the (Sb) we note an average of 282 ppm, with 34 ppm of (W) and 164.6 ppm of (Sn).

Based on the geological context/geochemical content, we investigate the crystalline phases and structures of the five samples, by using the techniques of crystallographic analysis by X-ray diffraction.

3.2. Structural Properties

3.2.1. Structural Properties of SS01

X-ray diffraction (XRD) patterns were used to investigate the phases and structures of our five extracted samples. The XRD pattern of the as-prepared sample SS01 (Fig. 3A) revealed the existence of four phases, calcite, manganocolumbite, tetrahedrite and freibergite.

The diffraction peaks of calcite (CaCO₃) could be indexed as the trigonal (hexagonal axes) crystalline phase (Space group R-3c), with the lattice constants of $a = 4.9844$ Å and $c = 17.0376$ Å ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$). This is compatible with the standard value of JCPDS: 96-901-6707 already described in the literature [25].

Diffraction peaks of manganocolumbite (Mn,Fe²⁺)(Nb,Ta)₂O₆ can be indexed to the orthorhombic space group Pbcn with lattice constants of $a = 14.4508$ Å, $b = 5.7741$ Å and $c = 5.1025$ Å ($\alpha = \beta = \gamma = 90^\circ$), in agreement with the standards already described in the literature, i.e. JPCDS 96-901-6707 [26].

Diffraction peaks of tetrahedrite (Cu,Fe)₁₂Sb₄S₁₃ can be indexed to the cubic crystalline phase (space group I-4 3m) were indexed to the space group I-4 3m with calculated lattice constants $a = b = c = 10.4033$ Å and $\alpha = \beta = \gamma = 90^\circ$, compatible with the standard already described in the literature, i.e. JCPDS 96-900-3108 [27].

Furthermore, the diffraction peaks of freibergite (Ag,Cu,Fe)₁₂(Sb,As)₄S₁₃ could be indexed to the cubic crystalline phase (space group I -4 3 m) with the lattice constants $a = b = c = 10.4920$ Å and ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard already described in the literature, i.e. JCPDS 96-901-2611 [28]. Note that no peaks of any other phases or impurities were detected in the spectra, which mean that the sample SS01 is mainly composed of calcite, manganocolumbite, tetrahedrite and freibergite. The diagram in (Fig. 3B) present an estimation of mineral percentage's calculated using the crystal impact software "Match Phase Analysis" which indicates respectively 44,1% of calcite, 27,7% of manganocolumbite, 14,2% of tetrahedrite and 14% of freibergite.

Table 1. Results of ICP analysis

	Pb (%)	Zn (%)	Cu (%)	Fe (%)	Ag (ppm)	Au (ppm)	Sn (ppm)	W (ppm)	Sb (ppm)
SS01	LD	0.032	2	0.7	2	7	34	30	236
SS02	LD	0.018	8	0.62	4	3	156	89	384
SS03	LD	0.3	5	2	3	5	412	20	573
SS04	LD	36	LD	1.9	2	1	11	22	99
SS05	LD	0.3	LD	1	3	4	210	9	120

3.2.2. Structural Properties of SS02

The XRD pattern of the as-prepared sample SS02 (Fig. 4A) revealed the existence of five phases, calcite, freibergite, sylvanite, antimony iodide, and stistaite. The diffraction peaks of calcite (CaCO_3) can be indexed as the trigonal (hexagonal axes) crystalline phase (space group R-3c), with the lattice constants of $a = 4.9766 \text{ \AA}$ and $c = 17.2840 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$) compatible with the standard already described in the literature, i.e. JCPDS: 96-901-5482 [29].

In the case of freibergite $(\text{Ag,Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}$, the diffraction peaks can be indexed to the cubic crystalline phase (space group I-43m) with lattice constants $a = b = c = 10.6100 \text{ \AA}$ and ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard described in the literature, i.e. JCPDS: 96-900-9469 already [30].

The diffraction peaks of sylvanite $(\text{Au,Ag})_2\text{Te}_4$ can be readily indexed to the monoclinic crystalline phase (space group P 12/c1) with calculated lattice constants $a = 8.9600 \text{ \AA}$, $b = 4.4900 \text{ \AA}$ and $c = 14.6200 \text{ \AA}$ and ($\beta = 145.430^\circ$), compatible with the standard described in the literature, i.e.

JCPDS: 96-231-0990 already [31].

Furthermore, the diffraction peaks of native antimony iodide (SbI_3) could be readily indexed to the trigonal (hexagonal axes) crystalline phase (space group R-3m) with the lattice constants $a = 4.2687 \text{ \AA}$ and $c = 10.9244 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard described in the literature, i.e. JCPDS 96-810-0524 already [32].

Finally, the diffraction peaks of stistaite (SbSn) can be indexed as the rhombohedral crystalline phase (space group R-3m) with lattice constants of $a = 6.1240 \text{ \AA}$ and $\alpha = 89.380^\circ$ compatible with the standard already described in the literature, i.e. JCPDS: 96-901-3159 [33]. Mark that no peaks of any other phases or impurities were detected in the spectra, which means that the sample SS02 is mostly composed of calcite, freibergite, sylvanite, antimony and stistaite. The diagram in (Fig. 4B) presents an estimation of these element's percentages, where the software calculations (Match phase analysis) describe 50,8% of calcite, 16,5% of sylvanite, 13,4% of antimony and 8,9% of stistaite.

Figure 3. (A) X-rays diffraction (XRD) patterns of sample SS01 and (B) phase percentage of calcite, manganocolumbite, tetrahedrite and freibergite

Figure 4. (A) X-rays diffraction (XRD) patterns of sample SS02 and (B) Phases percentage of calcite, freibergite, sylvanite, antimony iodide and stistaite

3.2.3. Structural properties of SS03

The XRD pattern of the as-prepared sample SS03 (Fig. 5A) revealed the existence of six phases, calcite, tin (II) halide sulphates, barium iron Selenide, freibergite, tetrahedrite and zinc germanium $\pm$ barite. The diffraction peaks of calcite (CaCO_3) can be indexed as the trigonal (hexagonal axes) crystalline phase (space group R-3c) with the lattice constants $a = 4.9860 \text{ \AA}$ and $c = 17.0592 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard described in the literature, i.e. JCPDS: 96-154-7350 already [34].

Diffraction peaks of tin (II) halide sulphates ($\text{K}_3\text{Sn}_2(\text{SO}_4)_3\text{Cl}$) can be indexed to the hexagonal crystalline phase (space group P 63) with lattice constants $a = 10.1830$ and $c = 7.5400 \text{ \AA}$ and ($\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$), compatible with the standard already described in the literature, i.e. JCPDS: 96-403-1435 [35]. The diffraction peaks of barium iron selenide (BaFe_2Se_3) can be readily indexed to the orthorhombic crystalline phase (space group P nma) with calculated lattice constants $a = 11.9996 \text{ \AA}$, $b = 5.4711 \text{ \AA}$ and $c = 9.2156 \text{ \AA}$ and ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard already described in the literature, i.e. JCPDS: 96-150-4314 [36].

Furthermore, the diffraction peaks of freibergite ($(\text{Ag,Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}$) could be readily indexed to the

cubic crystalline phase (space group I-43m) with lattice constants $a = b = c = 10.4920 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard described in the literature, i.e. JCPDS 96-901-2611 already [28].

Diffraction peaks of tetrahedrite ($(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$) could be readily indexed to the cubic crystalline phase (space group I-43m) with lattice constants $a = b = c = 10.5030 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard already described in the literature, i.e. JCPDS 96-150-9592 [37].

Finally, the diffraction peaks of zinc germanium $\pm$ barite ((Ba,Ge,Sn)) can be indexed as hexagonal crystalline phase (Space group P 63/mmc), with lattice constants $a = 4.4570 \text{ \AA}$ and $c = 9.65500 \text{ \AA}$ and ($\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$), compatible with the standard described in the literature, i.e. JCPDS: 96-152-7802 already [39].

Hence, no peaks of any other phases or impurities were detected in the spectra, which mean that the sample SS03 is composed of calcite, tin (II) halide sulphates, barium iron selenide, tetrahedrite and zinc germanium $\pm$ barite. The diagram in (Fig. 5B) presents an estimation of these element's percentage calculated using the software Match Phase Analysis, where the obtained percentage was found to be respectively (65.4%), (14.9%), (6.2%), (5.1%), (5%) and (3.3%).

Figure 5. (A) X-rays diffraction (XRD) patterns of sample SS03 and (B) Phases percentage of calcite, tin (II) halide sulphate, barium iron selenide, freibergite, tetrahedrite, barium zinc germanium.

3.2.4. Structural Properties of SS04

The XRD pattern of the as-prepared sample SS04 (Fig. 6A) revealed the existence of five phases, calcite, chalcopryrite, krennerite, zinc telluride, antimony iodide and stistaite. The diffraction peaks of calcite (CaCO_3) could be indexed as the trigonal (hexagonal axes) crystalline phase (space group R-3c) with lattice constants $a = 4.9844 \text{ \AA}$ and $c = 17.0376 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard described in the literature, i.e. JCPDS: 96-901-6707 already [40].

In the case of copper iron sulphide, the diffraction peaks of chalcopryrite (CuFeS_2) can be indexed to the tetragonal crystalline phase (space group P-42m) with lattice constants $a = 5.2700 \text{ \AA}$ and $c = 5.1940 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard outlined in the literature, i.e. JCPDS: 96-101-0319 already [41].

Indeed, the diffraction peaks of krennerite (AuTe_2) can be catalogued to the orthorhombic crystalline phase (space group P ma2) with calculated lattice constants $a = 16.5800 \text{ \AA}$, $b = 8.8490 \text{ \AA}$ and $c = 4.4640 \text{ \AA}$ and ($\alpha = \beta = \gamma = 90^\circ$), accordant with the standard described in the literature, i.e. JCPDS: 96-900-9619 already [42].

Furthermore, the diffraction peaks of zinc telluride (Zn_2Te) can be readily indexed to the cubic crystalline

phase (space group F m-3m) with lattice constants $a = b = c = 6.0700 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard already described in the literature, i.e. JCPDS 96-101-0536 [43].

Diffraction peaks of antimony Iodide (SbI_3) can be indexed as the trigonal (hexagonal axes) crystalline phase (space group R-3m), with lattice constants $a = 4.2687 \text{ \AA}$ and $c = 10.9244 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard already described in the literature, i.e. JCPDS: 96-810-0524 [32].

Finally, the diffraction peaks of the stistaite (SbSn), could be indexed as the rhombohedral crystalline phase (space group R-3m), with lattice constants $a = 6.1240 \text{ \AA}$ and ($\alpha = 89.380^\circ$), compatible with the standard assigned in the literature, i.e. JCPDS: 96-901-3159 already [33].

Note that no peaks of any other phases or impurities were detected in the spectra, which mean that the sample SS03 is mainly composed of calcite, copper iron sulphide, krennerite, zinc telluride, antimony and stistaite. The diagram in (Fig. 6B) shows an estimation of these element's percentage calculated using the software Match Phase Analysis, where the obtained percentage was found to be respectively (46.2%), (16.3%), (10.9%), (9.6%), (9.2%) and (7.9%).

Figure 6. (A) X-rays diffraction (XRD) patterns of sample SS04 and (B) Phases percentage of calcite, copper iron sulphide, krennerite, zinc telluride, antimony iodide and stistaite

3.2.5. Structural Properties of SS05

Theoparacelsite, iron (II) iodide, niobium sulphate, calcite, silver telluride, germanium antimony telluride, dicesium potassium manganese and sodium nitrate. The diffraction peaks of theoparacelsite ($\text{Cu}_3(\text{OH})_2(\text{As}_2\text{O}_7)$) could be indexed as the orthorhombic crystalline phase (Space group $P mma$) with calculated lattice constants $a = 8.3212 \text{ \AA}$, $b = 2.9377 \text{ \AA}$ and $c = 4.6644 \text{ \AA}$ and ($\alpha = \beta = \gamma = 90^\circ$), compatible with the standard described in the literature, i.e. of JCPDS: 96-900-9987 already [44].

The diffraction peaks of iron (II) iodide (FeI_2) could be indexed as the trigonal (hexagonal axes) crystalline phase (space group $P-3m1$), with lattice constants $a = 4.0400 \text{ \AA}$ and $c = 6.7500 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with

the standard noticed in the literature, i.e. JCPDS: 96-900-9104 already [46]. Moreover, the diffraction peaks of niobium sulphate (NbO_4S) can be readily indexed to the orthorhombic crystalline phase (space group $P na21$) with calculated lattice constants $a = 5.5140 \text{ \AA}$, $b = 4.8761 \text{ \AA}$ and $c = 11.7961 \text{ \AA}$ and ($\alpha = \beta = \gamma = 90^\circ$) corresponding to the standard described in the literature, i.e. JCPDS: 96-152-6181 already [45].

For the calcite (CaCO_3), the diffraction peaks can be indexed as the trigonal (hexagonal axes) crystalline phase (space group $R-3c$) with lattice constants $a = 4.9761 \text{ \AA}$ and $c = 17.4163 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard value of JCPDS: 96-901-4345 already described in the literature [29].

Figure 7. (A) X-rays diffraction (XRD) patterns of sample SS05 and (B) Phases percentage of theoparacelsite, iron (II) iodide, niobium sulphate, calcite, silver telluride, dicesium potassium manganese, sodium nitrate

In the case of silver Telluride (Ag_2Te), the diffraction peaks can be indexed as the trigonal (hexagonal axes) crystalline phase (space group $P\bar{3}m1$) with lattice constants $a = 4.2820 \text{ \AA}$ and $c = 28.6360 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard value of JCPDS: 96-700-0756 already described in the literature [46].

Furthermore, the diffraction peaks of germanium antimony telluride ($\text{Ge}_2\text{Sb}_2\text{Te}_3$) could be indexed as the trigonal (hexagonal axes) crystalline phase (space group $R\bar{3}m$) with lattice constants $a = 4.2495 \text{ \AA}$ and $c = 41.2990 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$), compatible with the standard described in the literature, i.e. JCPDS: 96-703-1376 already [47].

In addition, the diffraction peaks of dicesium potassium manganese ($\text{Cs}_2\text{F}_6\text{KMn}$) can be readily indexed to the tetragonal crystalline phase (Space group $I4/mmm$) with lattice constants $a = 6.1260 \text{ \AA}$ and $c = 8.9810 \text{ \AA}$ ($\alpha = \beta = \gamma = 90^\circ$), this is compatible with the standard value of JCPDS: 96-152-2261 already described in the literature [48].

Finally, the diffraction peaks of sodium nitrate (NaNO_3), can be indexed as the trigonal (hexagonal axes) crystalline phase (Space group $R\bar{3}m$) with the lattice constants $a = 5.0889 \text{ \AA}$ and $c = 8.8680 \text{ \AA}$ ($\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$),

compatible with the standard already described in the literature, i.e. JCPDS: 96-810-3617 [49].

Hence, no peaks of any other phases or impurities were detected in the spectra, which mean that the sample SS05 is mainly composed of Calcite, Iron (II) Iodide, Niobium Sulphate, Theoparacelsite, Silver antimony telluride, Germanium Antimony Telluride, Dicesium Potassium Manganese and Sodium Nitrate.

The diagram in (Fig. 7B) presents an estimation of these element's percentage calculated using the software Match Phase Analysis where the obtained percentage was found to be respectively (32.8%), (15.2%), (14.8%), (12.5%), (8.9%), (6.6%), (4.7%), (3.2%), and (1.4%).

3.2.6. Structural Interpretation

Note that the average crystallite size of the five extracted samples was calculated by using Scherrer's formula [50]:

$$d = K\lambda / \beta \cos(\theta) \quad (1)$$

Where (d) is the average crystallite size, K is a dimensionless shape factor, with a value close to unity, called the Scherrer constant. The shape factor has a typical value of about 0.89, but varies with the actual shape of the

crystallite, λ is the wavelength of X-ray source used in XRD ($\lambda = 0.15418$ nm), β is the full width at half the maximum intensity (FWHM) and θ is the diffraction angle in degrees.

The average crystallite size values calculated from XRD (using the most intense peak) patterns of SS01, SS02, SS03, SS04 and SS05 have been found to be 72.55, 65.53, 52.41, 38.62 and 78.63 nm respectively (Fig. 8).

In addition, the typical panoramic SEM images presented in (Fig. 8) Obviously shows smaller microparticles in all samples with a non-uniform size distribution confirming the existence of numerous phases in each sample. Furthermore, the overall products, compositions, crystalline phases, space groups, lattice parameters, densities and cristallite sizes are summarized in the Table 2.

Figure 8. The crystallite size of our four samples calculated by using Scherrer's formula

Table 2. Compositions, crystalline phases, space groups, lattice parameters, densities and crystalline sizes of our five extracted samples

SS01							
Product	(%)	Crystalline phase	Space group	Mesh Parameters		Density (g/cm ³)	Ref
				Lattice parameter (Å)	Angles		
calcite	44.1	Trigonal (hexagonal axes)	R-3c	a = b = 4.98, c = 17.03	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	2.720	[25]
manganocolumbite	27.7	Orthorhombic	Pbcn	a = 14.45, b = 5.77, c = 5.10	$\alpha = \beta = \gamma = 90^\circ$	5.438	[26]
tetrahedrite	14.2	Cubic	I -4 3 m	a = b = c = 10.40	$\alpha = \beta = \gamma = 90^\circ$	5.235	[27]
freibergite	14	Cubic	I -4 3 m	a = b = c = 10.49	$\alpha = \beta = \gamma = 90^\circ$	5.442	[28]
SS02							
calcite	50.8	Trigonal (hexagonal axes)	R-3c	a = b = 4.97, c = 17.28	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	2.690	[29]
freibergite	16.5	Cubic	I -4 3 m	a = b = c = 10.61	$\alpha = \beta = \gamma = 90^\circ$	5.104	[30]
sylvanite	14.3	Monoclinic	P 12/c1	a = 8.96, b = 4.49, c = 14.62	$\beta = 145.43^\circ$	8.112	[31]
Antimony iodide	10.4	Trigonal (hexagonal axes)	R-3m	a = b = 4.26, c = 10.92	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	7.035	[32]
stistaite	8.9	Rhombohedral	R-3m	a = 6.12	$\alpha = 89.380^\circ$	6.955	[33]
SS03							
calcite	61.3	Trigonal (hexagonal axes)	R-3c	a = b = 4.98, c = 17.05	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	11.079	[34]
tin (II) halide sulphates	14.9	Hexagonal	P 63	a = b = 10.18, c = 7.54	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	3.331	[35]
barium Iron Selenide	6.2	Orthorhombic	P nma	a = 11.99, b = 5.47, c = 9.21	$\alpha = \beta = \gamma = 90^\circ$	5.335	[36]
freibergite	5.1	Cubic	I -4 3 m	a = b = c = 10.49	$\alpha = \beta = \gamma = 90^\circ$	5.442	[28]
tetrahedrite	5.0	Cubic	I -4 3 m	a = b = c = 10.50	$\alpha = \beta = \gamma = 90^\circ$	4.959	[37]
barium zinc germanium	3.3	Hexagonal	P 63/mmc	a = b = 4.45, c = 9.65	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	5.505	[39]
SS04							
calcite	46.2	Trigonal (hexagonal axes)	R-3c	a = b = 4.98, c = 17.03	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	2.720	[47]
chalcopryrite	16.3	Tetragonal	P-42m	a = b = 5.27, c = 5.19	$\alpha = \beta = \gamma = 90^\circ$	4.225	[40]
krennerite	10.9	Orthorhombic	P ma2	a = 16.58, b = 8.84, c = 4.46	$\alpha = \beta = \gamma = 90^\circ$	8.833	[41]
zinc telluride	9.6	Cubic	F m-3m	a = b = c = 6.07	$\alpha = \beta = \gamma = 90^\circ$	5.731	[42]
antimony	9.2	Trigonal (hexagonal axes)	R-3m	a = b = 4.26, c = 10.92	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	7.035	[32]
stistaite	7.9	Rhombohedral	R-3m	a = 6.12	$\alpha = 89.380^\circ$	6.955	[33]
SS05							
Theoparacelsite	32.8	Orthorhombic	P mma	a = 8.32, b = 2.93, c = 4.66	$\alpha = \beta = \gamma = 90^\circ$	4.703	[43]
Iron (II) Iodide	14.8	Trigonal (hexagonal axes)	P-3m1	a = b = 4.04, c = 6.75	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	5.389	[44]
Niobium Sulfate	12.5	Orthorhombic	P na21	a = 5.51, b = 4.87, c = 11.79	$\alpha = \beta = \gamma = 90^\circ$	6.137	[46]
Calcite	8.9	Trigonal (hexagonal axes)	R-3c	a = b = 4.97, c = 17.41	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	2.670	[29]
Silver telluride	6.6	Trigonal (hexagonal axes)	P-3m1	a = b = 4.28, c = 28.63	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	6.742	[45]
Germanium antimony telluride	4.7	Trigonal (hexagonal axes)	R-3m	a = b = 4.24, c = 41.29	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	6.465	[46]
Dicesium Potassium Manganese	3.2	Tetragonal	I 4/mmm	a = b = 6.12, c = 8.98	$\alpha = \beta = \gamma = 90^\circ$	4.669	[47]
Sodium Nitrate	1.4	Trigonal (hexagonal axes)	R-3m	a = b = 5.08, c = 8.86	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	2.128	[48]

4. Conclusion

In this paper, we realized a series of field and laboratory studies in order of determining, sampling and analyzing five sample rocks that were taken from the carbonates liassic cover of Tazekka paleozoic inlier, located in the north eastern part of Middle Atlas domain of Morocco.

According to the result of ICP analysis of these five samples, we note that no occurrences of (Pb) mineralization were detected, however the (Zn) (Cu) and (Fe) are present as clues of low concentration (0.018 - 8%), except of SS04 which shows a high tenor of Zn (36%) and Iron ($\approx 2\%$). We mark that this sample is taken from Ain Aouda where an old mine of zinc as kind of strata is manifested, and for that reason we conclude and purpose that the existence of high tenors of (Zn) and (Fe) may be related to some extension of the principal ore body of Ain Aouda. For the precious metals, we note the existence considerable (Ag) concentration (2-4 ppm) associated to some gold mineralization (1-7ppm). For the (Sb) we note an average of 282 ppm, with 34 ppm of (W) and 164.6 ppm of (Sn).

Elsewhere in terms of XRD analysis, we confirmed that the sample SS01 contains mainly calcite, manganocolumbite, tetrahedrite and freibergite. The percentages of these products are calculated by software and show respectively (44.1%), (27.7%), (14.2%) and (14%). The second sample SS02 assigns the existence of calcite, freibergite, sylvanite, antimony iodide, and stibite, where the phase percentages manifest as (50.8%), (16.5%), (13.4%), (10.4%) and (8.9%). The results of SS03 indicates that the product is mainly formed by calcite, tin (II) halide sulphates, barium iron selenide, tetrahedrite and zinc germanium $\pm$ barite. In this sample, the phase estimation is conjointly (61.3%), (14.9%), (6.2%), (5.1%), (5%), (4.1%) and (3.3%).

For the sample SS04, we note the presence of five phases as kind of calcite, copper iron sulphide, krennerite, zinc telluride, antimony iodide and stibite, and the related percentages are respectively (46.2%), (16.3%), (10.9%), (9.6%), (9.2%) and (7.9%). Finally, the sample SS05 displays a set of calcite, iron (II) iodide, niobium sulphate, theoparacelsite, silver antimony telluride, germanium antimony telluride, dicesium potassium manganese and sodium nitrate. However, the related estimation phases of sample SS05 is reciprocally (32.8%), (15.2%), (14.8%), (12.5%), (8.9%), (6.6%), (4.7%), (3.2%), and (1.4%).

Taking into account the results of the ICP and XRD analysis, in this work, we highlight the presence of metalliferous concentrations in the five samples taken from the dolomitic breccias of the lower Lias in the MAGHRAWA region. These concentrations concern base metals whose (Fe), (Pb) and (Zn) manifest as sulphate form, associated with supergeneous copper. On the other hand, we note that the precious metal including (Ag), (Au), and (Sb) are well developed and depends to the surface

condition chemistry. It should be noted that other elements such as (Sn) have been detected in trace amounts.

In fact, the setting up of these metalliferous occurrences in the Mesozoic Liassic cover presents in a first-hand a concrete case of the evolution of the mineralization which is rich in Fe-Pb-Zn-Cu-Ag-Sb-Sn-W..., from the deep Hercynian basement up to its Liassic platform cover, and present in a second hand a new opportunity to conduct deep studies in terms of petrography, metallogeny, geophysics, and all disciplines of geology allowing the understanding of the distribution of these mineralization, and more precisely those of (Ag), (Au), (Sb), (Sn) which present new potential prospects for precious metals in the Tazekka Liassic cover.

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