Technical report

Modal Analysis of Rock Forming Minerals: Contribution of XRD/Rietveld Analysis Compared to the Classic Point Counting Method

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Abstract

The determination of the mineral composition of aggregates which constitute an important component of concrete is essential to understand and estimate the durability of structures. The modal (quantitative mineralogical) analysis of rocks is generally determined by point-counting method on thin sections or slabs. However, there is a difficulty of mineral identification depending not only on the experience and capability of the operator but also on the size of observable grains. In this study, XRD (X-Ray Diffraction)/Rietveld analysis is proposed as an alternative and a comparison study is performed for eight different rocks. The results show equivalent proportions to those of the point counting method for the major phases (minerals), although discrepancies are observed for the minor minerals. Complementary tests as XRF (X-Ray Fluorescence) and density measurements are also performed to pre-characterize and confirm the obtained modal analysis. For instance, the density calculations based on XRD/Rietveld analysis provide close values to the measured densities. Overall, this method can be an excellent alternative to the point counting method especially in the context of construction materials laboratory.

1. Introduction

After the implementation of restrictions for construction of new nuclear powerplants (NPP) around the world, the aging management of preexisting ones becomes more important. Indeed, the safety of these infrastructures is crucial to reach different national objectives, as meeting the growing energy needs or reducing the greenhouse emissions. As a result, different countries are extending the exploitation lifetime of their NPPs (Rosseel *et al.* 2016). Concrete based structures provide multiple functions for NPPs as foundation, support, shielding and containment (Naus 2012). These structures are generally

not replaceable, and any degradation signifies a direct reduction of the service lifetime. Hence the importance of a better aging management through an accurate evaluation of the concrete behavior.

Radiation damage of concrete is reflected by the reduction of the engineering properties like strength and shielding capacity (Rosseel *et al.* 2016). For instance, under the combined effect of heat and radiation, modifications in concrete are observed for dimensions (generally expansion but shrinkage sometimes like for clay granulates), weight (due to the cement paste dehydration) and mechanical properties (Elleuch *et al.* 1972; Maruyama *et al.* 2017). The first order mechanism behind this reduction was determined as radiation-induced volumetric expansion (RIVE) of aggregates (Field *et al.* 2015; Hilsdorf *et al.* 1978; Maruyama *et al.* 2017). The amorphization (metamictization) of crystalline structures induced by radiations decreases the density of minerals and causes the RIVE. The expansion of aggregates creates a differential strain between cement paste and aggregates (Maruyama *et al.* 2016; Sasano *et al.* 2021). This strain is restrained creating stress and cracks through the concrete. A similar differential behavior exists also at the level of aggregates between the different composing minerals (Denisov *et al.* 2012; Maruyama *et al.* 2017; Le Pape *et al.* 2018). The RIVE is related to many properties of the original rock like its mineral composition, grain size and orientation of minerals (Denisov *et al.* 2012; Maruyama *et al.* 2017; Le Pape *et al.* 2020). For instance, it is well known that silicate-bearing aggregates develop higher RIVE compared to carbonate-bearing aggregates (Maruyama and Muto 2016; Le Pape *et al.* 2018). Therefore, to assess the degradation risk of the biological shield, it is neces-

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sary to have the accurate mineralogy of aggregates and their properties in a such environment (Maruyama *et al.* 2017; Le Pape *et al.* 2020).

Extensive experimental and theoretical studies have been performed for some common minerals under radiation like silica, alumina and zircon (Ewing 1994). This is clearly the example of quartz thanks to its various application as glasses for optical devices, electronic components or as a part of natural aggregates for construction materials. Inside nuclear reactor, quartz alters gradually, and its properties vary consequently by a decrease in density, disappearance of the alpha-beta transition and changes in the absorption spectrum. (Bolse 1999). The irradiated quartz defined mineralogically as metamict (Pabst 1952), is somewhat different from ordinary vitreous silica with slightly higher density (Hobbs and Pascucci 1980) and corresponds to the single structural relaxation product of highly defective matrix (Douillard and Duraud 1996). quartz amorphizes easily at very low fluences due to its exactly constrained structure and its expansion can be explained one part by the structure wakening due to the breaking of bounds, and another part by the new emplacements of the atoms in a tighter part of the structure (Primak *et al.* 1955). There are also different parameters which influences the expansion of the irradiated quartz as temperature (Bykov *et al.* 1981; Luu *et al.* 2020) or the nature of the irradiating particles (Douillard and Duraud 1996). However, similar knowledge is very hard to find for all the minerals composing aggregates used in the NPPs, despite its importance for studying the radiation-damage in order to attenuate radiation or immobilize the radioactive waste (Ewing *et al.* 1987).

To remedy this situation, it is necessary first to develop easy way for identifying the different minerals composing aggregates. This paper aims to compare two methods for modal (quantitative mineralogical) analysis of rocks. The first one is the classic point counting method on thin section and the second one is an approach based on the XRD (X-Ray Diffraction)/Rietveld analysis. Both methods present different advantages and disadvantages that making them suitable in different cases according to the available resources and targeted objectives.

The point counting method is a proven method with recognized accuracy for the identification and quantification of minerals (Poole and Sims 2016). It is a suitable technique for samples without any prior information or pre-characterization. However, it is a time-consuming for the sample preparation and its analysis (this last step can be reduced by using the digital imaging analysis) (Livingood and Cordell 2009). This method is unable to identify accurately the minerals from the same group as plagioclase, alkali-feldspars and clay minerals (Ufer *et al.* 2008). It is also difficult to distinguish minerals with similar optic properties like opaque minerals (magnetite, ilmenite, hematite, pyrite, pyrrhotite, graphite, etc.). The identification is also restricted by the observable size of

grains by microscope. The obtained result presents generally a high standard deviation, and it is directly affected by the human errors committed during the counting process.

The XRD analysis is time saver and simple to use compared to traditional methods (Ovas and Uda 2004; Bish and Post 1993). Also, for a laboratory of cementitious materials, the XRD equipment becomes more and more common with a noticeable growing experience and proficiency of the users. Indeed, many applications of the XRD/Rietveld analysis can be found in literature not only in the geological field but also in the applied engineering field like construction materials. Thus, XRD/Rietveld analysis is a powerful tool to obtain information related to cement hydration (Scrivener *et al.* 2016), to alkali-silica reaction in concrete (Marinoni and Broekmans 2013) or to link the drying shrinkage of concrete to the clay minerals content of aggregates (Igarashi *et al.* 2015). With accurate identification of minerals, a successful quantification based on XRD methods is possible (Omotoso *et al.* 2006). It also provides indicative data about the amorphous content (Philippo *et al.* 1997), but special attention should be given to the powder preparation since an extensive grinding can lead to amorphization (O'Connor and Chang 1986). It can be used to determine the mineral composition (Alves *et al.* 2007; Brinatti *et al.* 2010), but for more complete characterization it is preferable to perform chemical analysis which is complementary to XRD especially in case of high amorphous content (Jercher *et al.* 1998). The Rietveld analysis requires structure model of the composing minerals (Kaufhold *et al.* 2012), but it is generally inappropriate to describe minerals with stacking faults like clays as ideal crystallites (Ufer *et al.* 2008; Omotoso *et al.* 2006). Also, some problems of XRD quantification can be linked for example to the platy habit and cleavability of some minerals with unknown degrees of preferred orientation (Kleeberg *et al.* 2008). The analyst experience is very important for a successful quantification for which the average bias is around 10% to 15% (Omotoso *et al.* 2006).

The quantitative phase analysis can also be performed based on the element composition, but it is difficult in case of complex assemblage of minerals and the uniqueness of the solution is not guaranteed (Herrmann and Berry 2002). Therefore, it is preferable to use the elemental analysis as pre-characterization test (Omotoso *et al.* 2006). An idealized mineral composition can be obtained by the CIPW (Cross, Iddings, Pirsson and Washington) normative calculation (Cross *et al.* 1902).

The density measurements of the studied rocks will be used as a confirmation test. It will allow the comparison between the measured density and the density calculated from the mineral composition obtained by XRD/Rietveld analysis.

In summary, The XRF (X-Ray Fluorescence) and CIPW norm will provide respectively the oxide composition

and an ideal phase composition as pre-characterization step before the XRD/Rietveld analysis. The results obtained by this approach will be compared to those of the point counting method for eight different rocks. The measured density will be used as a confirmation test for the obtained phase quantification.

2. Experiment

In this paper, two methods for the identification and quantification of phases inside rock-forming minerals are presented and compared. The first one is the classic point counting method operated on the thin sections prepared from the studied rocks. The second one is an approach combining the XRF, XRD/Rietveld analysis. The main minerals in the earth's crust are: plagioclase (39%), k-feldspar (12%), quartz (12%), pyroxenes (11%), micas (5%), clays (5%), other silicates (5%) and non-silicates (8%) (Ronov and Yaroshevsky 1966). Knowing that, the XRF provides the oxides in the rock allowing to have an idea about the phases inside the studied rock by calculating the CIPW norm. The crystal structures corresponding to these phases are used for the Rietveld analysis. Thus, the phases inside the rocks can be correctly identified and quantified. To confirm the obtained results, density measurements are performed by the Helium Pycnometer. By using equation (1), the density can be estimated based on the proportions of minerals given by the XRD/Rietveld analysis. The comparison of both values, measured and calculated, can confirm or not the exactitude of our identification/quantification of phases. The details about the different tests are described in the following sections.

$$\rho = \frac{\sum_{i=0}^n m_i}{\sum_{i=0}^n V_i} = 1 / \left(\sum_{i=0}^n \frac{1}{\rho_i} \frac{m_i}{\sum_{j=0}^n m_j} \right) \quad (1)$$

where i and j are dumb variables.

n number of phases in the rock.

ρ density of the rock.

ρ_i density of the phase i .

m_i and m_j masses of the phases i and j .

2.1 Materials

To compare the point counting method with the XRD/Rietveld analysis, eight rocks have been collected. Since feldspars are very common as rock forming minerals, one plagioclase (albitite) and one k-feldspar (pegmatite) have been chosen for this study to be representative of this group. The quartz mineral is also very common in natural aggregates, and to consider this kind of rocks, the metachert will be studied. In the context of nuclear concrete, it is very interesting to study a rock incorporating different minerals which can provide an important insight concerning the internal differential behavior for the same aggregate. Thus, granite which is roughly constituted from quartz, feldspars and mica has been selected. Also, the basalt is a very common rock with different minerals, but since it is a mafic extrusive, it develops smaller crystals. This difference between granite and basalt will allow to observe the effect of the grain size. For this project, it was also requested to work with natural rock with non-negligible fraction of glassy phases. Therefore, andesite rock was a good candidate to satisfy this point. It is also important to consider sedimentary rocks like the chosen sandstone. Finally, the heavy rocks are generally preferred for nuclear infrastructures since they offer a higher coefficient of attenuation for radiation. Peridotite is one of these rocks and will be studied in this perspective. The list of different rocks with their origins are as follows:

1. Albitite from Itoigawa city, Niigata prefecture, Japan.
2. Pegmatite from India.
3. Granite from Takamatsu city, Kagawa prefecture, Japan.
4. Metachert from Kasugai city, Aichi prefecture, Japan.
5. Basalt from Karatsu city, Saga prefecture, Japan.
6. Andesite from Satsumasendai city, Kagoshima prefecture, Japan.
7. Sandstone from Tsuruga city, Fukui prefecture, Japan.
8. Peridotite, from Samani district in Hidaka subprefecture, Hokkaido, Japan.

Pieces of rocks have been extracted from the surface without any observable macro-defects. From these pieces, the samples used for the tests were prepared as follows:

Fig. 1 Extraction of samples and powder from the original rock.

1. Powder for the XRF and XRD measurements.
2. Thin section for the point counting method.
3. For the Helium density measurements, six cylindrical samples were cored. Two from each direction: x, y and z as indicated in **Fig. 1**. Their dimensions are 1 cm of diameter and 1 cm of height.

A small part of the rock (around 20 g) was wet-cut, and it was wiped then conserved in controlled temperature room (20°C) to dry for at least one day. After this it was crushed to make the necessary powder for the XRD and XRF measurements. This piece of the rock was grinded up to 2 min (with cycles of 30 s) and only the powder inferior to 90 μm has been conserved for the tests. In general, the fraction of the particles meeting this condition represents more than 90% of the total obtained powder.

More details concerning the preparation of the samples and the measurements are presented in the following sections.

2.2 Modal analysis

(1) X-ray fluorescence (XRF)/ CIPW norm

The prepared powder was used to measure the composition of oxides by XRF according to the JIS R 5204. Measurements were performed with a glass bead using a wavelength dispersion- type fluorescent X-ray analyzer. The Axios mAX from Malvern Panalytical was used for this characterization. The obtained bulk chemical composition was used to determine the idealized mineralogy by the CIPW norm method (Cross *et al.* 1902). A free access Excel spreadsheet program was used for this calculation (Hollocher 2009) and the same reference provides an extensive explanation for the CIPW method.

(2) Polarized micrograph and point counting method

From the original sample, a small piece of the rock was cut with two parallel surfaces. One surface of this piece was polished before been glued to a rectangular glass. The used thermic glue and glass are designed for the petrographic observation by polarization microscopy. The obtained glued sample in the glass was then cut again to obtain a very thin section. This remaining piece of the glued rock was polished gently until reaching 30 μm of the section thickness (CEN-EN 12407 2019). For this thickness, the minerals can be distinguished and studied by a polarized microscope because the most of them become transparent. The micrograph images were obtained under PPL (plane polarized light) and XPL (cross polarized light) to determine the minerals existing in the studied rocks. Thanks to a mechanical stage, the modal analysis is performed in grid intersection with a constant distance between two successive points. Depending on the different visual properties (like twinning for plagioclase) exhibited under PPL and/or XPL, each selected point is affected to the identified corresponding mineral.

The relative percentage of a given mineral is calcu-

lated as the ratio between the number of points corresponding to this mineral and the total number of points. According to the grain size of phases in the thin section, the total number of studied points should be chosen (Larrea *et al.* n.d.). For this study, 1000 points were chosen for the count in the thin section with a pitch of 0.5 mm which correspond to an area around 2.23 cm^2 . The value of this pitch is chosen to consider the largest possible area of the rock, increasing the number of targeted grains, and enhancing the representativity of the sampling. Similar values can be found in literature for thin section of the rocks (Byers *et al.* 1990).

(3) X-ray diffraction (XRD) / Rietveld analysis

For each studied rock, a part of the obtained powder was mixed with the pure corundum ($\alpha\text{-Al}_2\text{O}_3$) with 90% and 10% of mass ratio, respectively. The D8 Advance XRD instrument (Bruker AXS, Karlsruhe, Germany) was used. The X-ray source was $\text{CuK}\alpha$, with the tube voltage of 40 kV and tube current of 40 mA. The scan field of $5^\circ < 2\theta < 70^\circ$ was used with a step size of 0.02° , and 0.65 s/step. The total time of each test was equal to 37 min. The XRD measurements were done on three samples of 1 g of the mixed powder taken from the same prepared batch. In order to reduce the weighting error, 0.4 g of corundum is mixed with 3.6 g of the rock powder (Kaufhold *et al.* 2012).

The Rietveld analysis was performed with the software application TOPAS ver. 4.2 developed by Bruker AXS. The particle size and lattice parameters were optimized. The preferred crystal orientation was avoided to eliminate its negative effect on the reproducibility of refinement (Snellings *et al.* 2010). The starting point of the pure minerals used for the Rietveld analysis is $2\theta = 2^\circ$. If this low range does not exist in the used file, it is considered null. The results will be presented in this paper as the average and the standard deviation of the three tested samples. As indicators for the quality of the Rietveld analysis three parameters of the calculation will be given: R_{wp} which is the weighted profile R-factor, R_{exp} represents the expected R-factor which corresponds to the best possible R_{wp} . In addition to the GoF (Goodness of fit) defined as the ratio of R_{wp} to R_{exp} (Toby 2006). Concerning the crystal files of minerals, many references can be found like for the most common: albite (Harlow 1982), orthoclase (Vrsweueruanhnowic and Kielhorn 1983), microcline (Bailey 1969), quartz (Levien *et al.* 1980), biotite (Hendricks and Jefferson 1939). For similar information and structural files, the readers can use the American mineralogist crystal structure database (Downs and Hall-Wallace 2003) or to the crystallography open database (Downs *et al.* 2003; Gražulis *et al.* 2009, 2012, 2015; Merkys *et al.* 2016; Quirós *et al.* 2018; Vaitkus *et al.* 2021).

(4) Density by Helium pycnometer

For each studied rock, the density was assessed by Helium pycnometer Ultrapyc 1200e of Quantachrome In-

Table 1 Bulk composition of the studied rocks by X-ray fluorescence (XRF) analysis.

(Wt%)	Albitite	Pegmatite	Granite	Metachert	Basalt	Sandstone	Peridotite	Andesite
Ig.loss	0.42	0.11	0.21	0.52	1.23	1.51	2.61	1.40
Na ₂ O	12.18	1.86	3.94	0.24	3.10	4.58	-	2.94
MgO	0.15	-	0.22	0.46	7.24	1.00	46.14	4.02
Al ₂ O ₃	20.75	20.04	15.18	2.23	14.13	14.41	0.59	15.95
SiO ₂	64.24	65.55	72.20	94.32	41.79	69.84	40.50	58.20
P ₂ O ₅	-	0.02	0.07	0.02	0.41	0.08	-	0.14
SO ₃	0.02	0.02	0.03	-	-	0.25	0.03	0.03
Cl	0.05	-	0.08	-	0.09	-	-	0.14
K ₂ O	0.56	11.84	3.47	0.63	1.09	2.57	-	1.84
CaO	0.97	0.13	2.07	0.27	8.39	1.30	0.24	6.94
TiO ₂	-	-	0.15	0.07	1.73	0.35	-	0.76
Cr ₂ O ₃	0.06	-	0.07	-	0.07	0.14	0.43	-
MnO	-	-	0.05	0.06	0.14	3.20	0.14	0.12
Fe ₂ O ₃	0.32	0.28	2.21	1.09	10.25	-	8.73	7.00
Co ₃ O ₄	-	-	-	-	9.83	-	-	-
CuO	-	-	-	-	-	-	-	-
ZnO	-	-	0.01	-	0.01	0.02	-	-
Rb ₂ O	-	0.04	0.01	-	-	0.01	-	-
NiO	-	-	-	-	-	-	0.36	0.04
SrO	0.08	0.02	0.02	-	0.06	0.04	-	0.05
ZrO ₂	-	-	-	-	0.08	-	-	-
BaO	0.07	-	-	-	-	0.24	-	-
PbO	-	0.03	-	-	-	-	-	-
I	0.14	0.07	-	-	0.35	0.47	0.22	0.41
Total	99.99	100.00	100.00	99.91	100.00	100.00	100.00	100.00

struments. The six cylindrical samples obtained for each rock were used for this test. The volume of the sample is measured up to 10 times until the standard deviation becomes less than 0.05%. By measuring the mass of the sample, the density can be deduced with high accuracy. For a given rock, the result will be presented as the average and standard deviation of the six samples.

3. Experimental results

3.1 XRF

The X-Ray fluorescence (XRF) results for the chosen rocks are presented in the **Table 1**. The oxide composition was implemented in the Excel spreadsheet program to obtain the CIPW norm. The presentation of these results and their discussion will be done for each rock in the following sections.

3.2 Albitite

The chemical composition obtained by XRF is presented in **Table 1**. More than 97% of the rock are formed by SiO₂, Al₂O₃ and Na₂O while K₂O and CaO are under 2%. These proportions are related to the presence of albitite as shown by the CIPW results presented in **Table 2**.

The photomicrographs of albitite under PPL and XPL are presented in **Figs. 2(a)** and **(b)**. The twinning of plagioclase (albite) can be observed in addition to some quartz grains. The grain size of these minerals (phases) is in the order of 1 mm. The estimated mineral composition by the point counting method is presented in **Table 2**. The result of the point counting method shows that this rock is mainly composed of plagioclase with low per-

centage of quartz and calcite with some minor unidentified phases (0.4%).

The experimental XRD curve with the identification of phases are presented in **Fig. 2(c)**. This experimental curve was well reproduced and the parameters showing that are: $R_{\text{exp}}=2.52$, $R_{\text{wp}}=13.41$ and $\text{GoF}=5.31$. In addition to albite and quartz, many other phases have been tested then excluded except calcite for which a small content has been detected. The final composition of this last method is also presented in **Table 2**. Globally, similar result with high plagioclase content is found, especially with CIPW results (on powder obtained from the same batch) for which a similar percentage of albite is obtained. Like the CIPW calculation but unlike the point-counting method, no quartz has been observed by XRD/Rietveld method. Also, the percentage of calcite is lower for the XRD/Rietveld analysis compared to the point-counting method. This difference is due to the natural heterogeneity of the rock reflected in the different sampling. The Rietveld analysis presents non negligible amount of amorphous (17%) which has not been observed by microscopy. This value can be explained by the artefact linked to the approach.

The density estimation based on the identified crystal phases gives approximately the same value as that measured by the Helium pycnometer. The difference is around 0.54% between the calculated density equal to 2.620 and the experimental density equal to 2.606 ± 0.010 . This result presents an additional confirmation for the phase quantification obtained by the XRD/Rietveld analysis.

Table 2 Phase composition of albitite given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Plagioclase: Albite	$\text{NaAlSi}_3\text{O}_8$	2.62	81.59	89.4	2.0	82.91	0.82
Quartz	SiO_2	2.65	-	7.2	2.7	-	-
Calcite	CaCO_3	2.71	-	3.0	1.5	0.26	0.02
Other	-	-	17.59	0.4	0.8	-	-
Amorphous	-	-	-	-	-	16.84	0.82
Total			99.18	100		100	

3.3 Pegmatite

The chemical composition obtained by XRF is presented in **Table 1**. More than 97% of the rock are formed by SiO_2 , Al_2O_3 and K_2O while Na_2O and CaO are under 2%. The CIPW results are presented in **Table 3** and show the dominance of orthoclase/microcline (this method is unable to distinguish polymorphs), in addition to the presence of albite and quartz.

The thin section of the pegmatite rock under the PPL and XPL is presented in **Figs. 3(a)** and **(b)**. The material seems to be composed by uniform dispersed feldspar with some inclusions like quartz and white mica. The order of the size of these inclusions is around 100 μm . The composition of this rock obtained by the point

counting method is shown in **Table 3**. The feldspars identified as microcline and albite constitute most minerals inside this rock.

The crystal structures of common minerals in pegmatite have been implemented for the Rietveld analysis. For this method, no trace of orthoclase was found but a small quantity of albite was detected. The XRD pattern is presented in **Fig. 3(c)** with the assignments of peaks. The reproduction of the experimental XRD pattern by the fitted one was done with the following parameters: $R_{\text{exp}}=2.78$, $R_{\text{wp}}=10.41$ and $\text{GoF}=3.75$. The predominant minerals are detected by the three methods as shown in **Table 3**. The mica as a clay mineral is not included in the CIPW calculation. It was identified as lepidolite by the

Fig. 2 (a) Micrograph under PPL for albitite thin section, (abbreviations: Qz for quartz and Pl for plagioclase), (b) Micrograph under XPL for albitite thin section, (c) Experimental and fitted X-Ray diffraction pattern for the albitite with the dominant phase (abbreviations: Ab for albite).

Table 3 Phase composition of pegmatite given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Microcline	KAlSi_3O_8	2.56	69.97	74.0	3.6	79.36	0.44
Albite	$\text{NaAlSi}_3\text{O}_8$	2.62	16.12	20.2	3.4	8.04	0.54
Quartz	SiO_2	2.65	9.09	4.0	1.9	1.55	0.21
White mica: lepidolite	$\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$	2.84	-	1.8	1.4	0.66	0.13
Other	-	-	4.54	-	-	-	-
Amorphous	-	-	-	-	-	10.39	1.12
Total			99.72	100		100	

XRD/Rietveld analysis which is impossible by both initial methods. As for the previous rock, the amorphous phase (around 10%) was only detected by the XRD method. The thin section gives a higher percentage of albite, quartz, and white mica while microcline is slightly lower by this method.

The measured density for this rock is equal to 2.569 ± 0.100 . The calculated density based on the phase quantification determined by the XRD/Rietveld analysis also gives the same value of 2.569. It can be considered as a complementary confirmation of the obtained mass ratio of minerals obtained by this method.

3.4 Granite

The Oxides content in the granite rock is given by XRF test presented in **Table 1** Bulk composition of the studied rocks by X-ray fluorescence (XRF) analysis. Based on the CIPW results presented in the **Table 4**, the dominant phases are consecutively albite, quartz, and k-feldspar while the hydrated minerals are not considered by this method.

The thin section of granite under PPL and XPL is presented in the **Figs. 4(a)** and **(b)**. The size of quartz grains is in the order of 1 mm. The biotite inclusions are in the order of 500 μm . Some alteration of biotite to chlorite can also be observed. The size order of this

Fig. 3 (a) Micrograph under PPL for pegmatite thin section, (abbreviations: Qz for quartz, Pl for plagioclase and Lpd for lepidolite -white mica-), (b) Micrograph under XPL for pegmatite thin section, (c) Experimental and fitted X-Ray diffraction pattern for the pegmatite with the dominant phase (abbreviations: Mc for microcline and Ab for albite).

Table 4 Phase composition of granite given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Quartz	SiO ₂	2.65	31.02	34.4	6.7	33.43	0.60
Plagioclase: Albite	NaAlSi ₃ O ₈	2.62	41.62	31.0	6.8	31.60	0.86
K-feldspar: Orthoclase Microcline	KAlSi ₃ O ₈	2.56	20.51	23.4	12.6	21.08= 10.73+	2.25= 0.62+
Biotite	K(Mg,Fe) ₃ (OH,F) ₂ (Si ₃ AlO ₁₀)	3.09	-	8.4	3.0	3.21	0.34
Amphibole	{Na} {Ca ₂ } {Mg ₄ Al} (Al ₂ Si ₆ O ₂₂)(OH) ₂	3.12	-	1.3	0.8	0.97	0.03
Fluorite	CaF ₂	3.13	-	0.8	1.0	0.11	0.03
Muscovite and opaque minerals	KAl ₂ (AlSi ₃ O ₁₀)(OH,F) ₂	2.82	-	0.3	0.5	2.06	0.35
Chlorite	(Fe,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	2.95	-	0.2	0.4	0.52	0.07
Zircon	ZrSiO ₄	4.65	-	0.2	0.4	0.13	0.02
Other	-	-	6.24	-	-	-	-
Amorphous	-	-	-	-	-	3.93	2.35
Total			99.39	100		100	

chlorite is under 160 µm. The phase quantification given by the point counting method is presented in **Table 4**. The same predominant phases are also obtained by this test. biotite exists with a non-negligible percentage with

some other minor phases: amphibole, fluorite, muscovite, chlorite, and zircon.

The measured XRD pattern the assignments of the minerals is shown in **Fig. 4(c)**. The Rietveld analysis was

Fig. 4 (a) Micrograph under PPL for granite thin section, (b) Micrograph under XPL for granite thin section, (abbreviations: Qtz for quartz, Pl for plagioclase, Afs for alkali-feldspars, Bt for biotite and Chl for chlorite), (c) Experimental and fitted X-Ray diffraction pattern for the granite with the dominant phase (abbreviations: Qtz for quartz, Ab for albite, Or for orthoclase, Mc for microcline, Amp for amphibole and Bt for biotite).

performed with the following parameters $R_{\text{exp}}=2.47$, $R_{\text{wp}}=11.66$ and $\text{GoF}=4.72$. The feldspars were identified as albite, microcline, and orthoclase. In addition, the presence of quartz was confirmed as well as that of biotite. Some other minor minerals were detected and are presented in **Table 4**. The composition of minerals is similar for dominant phases between the three methods (quartz, plagioclase, and alkali-feldspars). The biotite detected by the point counting method is higher compared to the XRD method. The remaining minor phases are in similar range for both methods if the standard deviation is considered. The XRD amorphous phase for this rock is very low which is comparable to its no detection by the point counting method.

The measured density of granite is equal to 2.655 ± 0.003 and that calculated based on the XRD/Rietveld analysis is equal to 2.643. The difference between both values is very low: 0.45%, which can be considered as a complementary confirmation of the obtained phases identification and quantification.

3.5 Metachert

The XRF gives a very high percentage of SiO_2 94% as shown in **Table 1**. This is the highest percentage of this oxide among the studied rocks which is a very strong indicator of the high percentage of quartz in this metachert. The CIPW norm confirms quartz as the major phase, in addition to some other minerals.

The thin section of the metachert under the PPL and XPL is presented in **Figs. 5(a)** and **(b)**. To measure the very small size of the grains in this rock, the x10 objective is used. The size of the grains is around 20-30 μm . The quantification of the phases by the point counting method is gathered in **Table 5**. The quartz is the major mineral with approximately 84% of the counted points. 8% of mica is observed with 4% of chlorite and 4% of muscovite.

The XRD curve of the metachert is presented in **Fig. 5(c)**, it is like that of pure quartz as observed with the identified peaks. The experimental chart was reproduced by the Rietveld method with the following parameters: $R_{\text{exp}}=2.57$, $R_{\text{wp}}=8.98$ and $\text{GoF}=3.50$. The Rietveld analysis results are presented in **Table 5**, confirming the high quartz content (97.55%), the remaining content is mainly identified as amorphous.

The measured density is equal to 2.648 ± 0.007 and the calculated one is equal to 2.637. This difference of 0.42% is an additional indicator of the purity of this metachert with a very high percentage of crystal quartz.

3.6 Basalt

The oxides measured by XRF method contained in the basalt is presented in **Table 1**. The percentage of SiO_2 is around 42% which is very low compared to the previous rocks. It can be a sign of quartz absence in this rock. The CIPW norm for this rock is presented in **Table 6**, with high percentage for plagioclase which is a combination of albite and anorthite in this method. The next important

phase detected is the olivine and then pyroxene considered as diopside.

The thin section for the basalt under PPL and XPL is presented in the **Figs. 6(a)** and **(b)**. With x4 objective some big inclusions can be observed with an order of the grain size of 1 mm. However, the major grains of this rock have dimensions inferior to this value which were determined by more accurate objective x10. Some pyroxenes with small dimensions (between 60 μm and 140 μm) have been observed as well as olivine (around 80 μm). The mineral composition of basalt obtained by point counting method is given in **Table 6**.

Many crystal structures have been tested to fit the experimental XRD pattern and the identified phases are presented in **Fig. 6(c)**. The parameters of fitting in this case are: $R_{\text{exp}}=2.27$, $R_{\text{wp}}=7.79$ and $\text{GoF}=3.44$. The found minerals with their weight percentages are presented in **Table 6**. A low percentage of amorphous has been detected by this way and the major phases (plagioclase and pyroxene) have the same order by these last two methods. However, higher content of opaque minerals and olivine was detected by the point counting method. The plagioclase has been identified as a mixture of andesine and labradorite, the pyroxene as a combination of augite and diopside. The olivine corresponds to forsterite and the smectite to hectorite. The opaque minerals observed in thin section were assigned to magnetite and ilmenite.

The final confirmation test is the density calculation based on the XRD/Rietveld analysis results. The obtained density in this case was equal to 2.910 which is lower by 0.10% than the measured density equal to 2.913 ± 0.008 . This result represents an additional confirmation for the presented identification and quantification of minerals inside the studied basalt.

3.7 Andesite

The oxides composition given by the XRF method is given in **Table 1**. The SiO_2 percentage equal to 58% which is very low compared to the rocks containing quartz that can be an indicator of its absence. The CIPW norm is presented in **Table 7**. The plagioclase is found as a combination of albite and anorthite. The identified pyroxene is a mixture of hypersthene and diopside. The remaining content is composed from quartz, orthoclase, and some minor phases.

The thin section of andesite under PPL and XPL is given in the **Figs. 7(a)** and **(b)**. Big inclusions are observed in these images like the plagioclase with grain size greater than 1.60 mm, pyroxene grains superior in size 0.80 mm are detected. Big glassy content can also be seen in the pictures. The phase quantification obtained by the point counting method is presented in **Table 7**. Based on this method, three phases are determined as predominant: plagioclase (37%), pyroxene (35%) and amorphous phase (26%). Other phases (smectite and opaque mineral) are detected but their contents are very low.

The identified peaks of the experimental XRD charts are presented in **Fig. 7(c)**. The quality of the

Table 5 Phase composition of metachert given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Quartz	SiO ₂	2.65	88.55	84.0	2.1	97.55	2.09
Mica: biotite	K(Mg,Fe) ₃ (OH,F) ₂ (Si ₃ AlO ₁₀)	3.09	-	8.0	1.7	0.33	0.03
Staurolite	Fe ²⁺ 2Al ₉ O ₆ (SiO ₄) ₄ (O,OH)	3.75	-	-	-	0.03	0.00
Chlorite	(Fe,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	2.95	-	4.0	1.7	-	-
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH,F) ₂	2.82	-	2.0	0.8	-	-
Opaque minerals	-	-	-	2.0	0.9	-	-
Other	-	-	10.73	-	-	-	-
Amorphous	-	-	-	-	-	2.09	2.08
Total			99.28	100		100	

XRD/Rietveld analysis can be reflected in the following parameters: $R_{exp}=2.36$, $R_{wp}=6.30$ and $GoF=2.67$. The major phases detected by this method are like that detected by the thin section microscopy but with different proportions. The plagioclase content is lower and pyroxene fraction higher by the point counting method. The minor phases detected by this method are opaque minerals and Smectite while those given by the XRD/Rietveld analysis are magnetite and zircon as shown in **Table 7**. The plagioclase is identified as labradorite (44%) and albite (3%). The pyroxene corresponds to augite (10%) and pigeonite (2%). Zircon is also detected as a minor phase by the XRD analysis. Contrary

to the CIPW norm, for both last methods, neither quartz nor orthoclase are found. Finally, despite the amorphous is detected by the point counting method (26%), its value still way far from the percentage obtained by the XRD method (41%).

The calculated density is equal to 2.812 which is 4.73% higher than the measured density equal to 2.685 ± 0.011 . This overestimation of the density is due to the high amorphous content in the rock which is not considered in the calculation. Indeed, the amorphous phases have generally a lower density which explains the lower value of the measured density.

Fig. 5 (a) Micrograph under PPL for metachert thin section, (abbreviations: Qz for quartz and Bt for biotite), (b) Micrograph under XPL for metachert thin section, (c) Experimental and fitted X-Ray diffraction pattern for the metachert with the dominant phase (abbreviations: Qz for quartz).

Table 6 Phase composition of basalt given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Plagioclase: Andesine Labradorite	$(Ca,Na)(Al,Si)_4O_8$ $(Na,Ca)(Al,Si)_4O_8$	2.67 2.69	40.74	48.6	4.2	57.33= 17.67+ 39.67	1.72= 0.47+ 1.25
Pyroxene: Augite Diopside	$((Si,Al)_2O_6)(Ca,Mg,Fe,Ti,Al)_2$ $MgCaSi_2O_6$	3.40 3.278	13.77	23.2	3.1	24.43= 17.17+ 7.27	1.40= 0.95+ 0.45
Olivine (forsterite)	Mg_2SiO_4	3.27	17.81	12.8	1.7	6.5	0.08
Opaque Mineral: Magnetite Ilmenite	Fe_3O_4 $FeTiO_3$	5.15 4.789	0.74	11.9	1.6	2.92= 1.52+ 1.4	0.24= 0.08+ 0.16
Smectite (Hectorite)	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$	2.5	3.29	3.5	1.3	2.3	0.16
Other	-	-	10.96	-	-	-	-
Amorphous	-	-	-	-	-	6.52	2.94
Total			87.31	100		100	

3.8 Sandstone

The oxides composition of the sandstone is presented in the **Table 1**. High percentage of SiO_2 corresponding to a probable existence of quartz inside the rock. Despite the sandstone is a sedimentary rock and the classic CIPW norm is not suitable for this category of rocks, the modal analysis is done by this method (**Table 8**) and can be

considered as an indicative calculation. The rock is found to be composed from three major phases: plagioclase (albite 37.12% and anorthite 5.93%), quartz (27.95%) and alkali-feldspar (15.25%) which is taken as orthoclase for this method.

The thin section of sandstone under PPL and XPL is shown in **Figs. 8(a)** and **(b)**. The rock has clearly a

Fig. 6 (a) Micrograph under PPL for basalt thin section, (b) Micrograph under XPL for basalt thin section, (abbreviations: Pl for plagioclase, Ol for olivine and Opq for opaque minerals), (c) Experimental and fitted X-Ray diffraction pattern for the basalt with the dominant phase (abbreviations: Lb for labradorite, An for andesine, Aug for augite and Fo for forsterite).

Table 7 Phase composition of andesite given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Plagioclase: Albite+ Labradorite	$\text{NaAlSi}_3\text{O}_8$ $(\text{Na,Ca})(\text{Al,Si})_4\text{O}_8$	2.62 2.69	48.67	37.0	2.4	47.03= 2.97+ 44.06	0.92= 0.28+ 0.65
Pyroxene: Augite+ Pigeonite	$((\text{Si,Al})_2\text{O}_6)(\text{Ca,Mg,Fe,Ti,Al})_2$ $(\text{Ca,Mg,Fe})(\text{Mg,Fe})\text{Si}_2\text{O}_6$	3.4 3.38	22.85	34.8	2.3	11.77= 10.11+ 1.67	0.39= 0.30+ 0.09
Opaque mineral (magnetite)	Fe_3O_4	5.15	0.51	1.3	0.8	0.29	0.06
Smectite	-	2.35	-	0.4	0.5	-	-
Zircon	ZrSiO_4	4.65	-	-	-	0.13	0.02
Other	-	-	25.30	-	-	-	-
Amorphous	-	-	-	26.5	3.3	40.77	0.61
Total			97.33	100		100	

granular nature. To measure the size of these grains, the 10x objective was also used. The plagioclase and quartz order of their grains' size is under 100 μm . The phase quantification estimated by the point counting method is presented in the **Table 8**. The major phase is quartz with 53% of weight fraction. High content of clay minerals was also observed (17%) as well as of alkali-feldspar (9%). The minor phases detected in this thin section are opaque minerals (4%) and calcite (4%). No glass phase

was observed in this sandstone.

The experimental XRD curve with the identified phases is presented in **Fig. 8(c)**. The parameters related to the quality of the fitting are $R_{\text{exp}}=2.47$, $R_{\text{wp}}=9.26$ and $\text{GoF}=3.75$. As described in **Table 8**, this rock contains oligoclase (44%), quartz (32%), orthoclase (14%), chlorite (7%) with small percentage of microcline and biotite. Higher percentage of quartz, clay minerals and lower content of feldspar were detected in the thin section. Also,

Fig. 7 (a) Micrograph under PPL for andesite thin section, (abbreviations: Px for pyroxene, Pl for plagioclase and Gls for glassy phases), (b) Micrograph under XPL for andesite thin section, (c) Experimental and fitted X-Ray diffraction pattern for the andesite with the dominant phase (abbreviations: Lb for labradorite and Aug for augite).

Table 8 Phase composition of sandstone given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Quartz	SiO ₂	2.65	27.95	52.6	2.9	31.65	1.12
Clay minerals: Chlorite	(Fe,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	2.95	-	17.5	3.8	7.33	0.18
Plagioclase Oligoclase	(Na,Ca)[Al(Si,Al)Si] ₂ O ₈	2.65	43.04	12.4	3.7	43.69	1.30
Alkali-feldspar: Microcline Ortho- clase	KAlSi ₃ O ₈	2.56	15.25	9.4	2.4	15.22= 1.12+ 14.10	0.29= 0.12+ 0.17
Opaque mineral	-	-	-	4.3	1.8	-	-
Calcite	CaCO ₃	2.71	-	3.8	1.8	-	-
Biotite	K(Mg,Fe) ₃ (OH,F) ₂ (Si ₃ AlO ₁₀)	3.09	-	-	-	0.69	0.01
Other	-	-	11.39	-	-	-	-
Amorphous	-	-	-	-	-	1.42	2.35
Total			97.63	100		100	

the minor phases of opaque minerals and calcite were found in thin section but not in the XRD results. Biotite in contrary, was only detected in small portion by the XRD method. The biggest difference in the result between both last methods has been registered for this rock. As explained before, this difference can be related to the heterogeneity of rocks reflected in the sampling. The

CIPW method provides in this case a reasonable result but without considering the clay minerals which can be problematic in case of high proportion.

The density calculated based on the XRD/Rietveld analysis results is equal to 2.658 that is only lower by 0.11% than the measured density 2.661 ± 0.003 . This value can be considered as an additional confirmation of

Fig. 8 (a) Micrograph under PPL for sandstone thin section, (abbreviations: Qz for quartz, Pl for plagioclase and Opq for opaque minerals), (b) Micrograph under XPL for sandstone thin section, (c) Experimental and fitted X-Ray diffraction pattern for the sandstone with the dominant phase (abbreviations: Qz for quartz, Chl for chlorite and Olg for oligoclase).

Table 9 Phase composition of peridotite given by point-counting on thin section and XRD/Rietveld analysis.

Phase	Chemical formula	Density	CIPW	Thin section		XRD/Rietveld	
			Wt (%)	Count (%)	SD (%)	Wt (%)	SD (%)
Olivine (forsterite)	Mg_2SiO_4	3.27	84.88	85	7.7	80.67	2.62
Carbonate mineral:				9.9	3.7	1.88=	0.29=
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	3.83	-			0.68+	0.10+
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$	3.8	-			0.31+	0.02+
Hydrozincite	$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$	3.37	-			0.87	0.17
Serpentinite (lizardite)	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$	2.58	-	1.9	2.9	2.73	0.25
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	2.75	-	1.7	3.0	3.7	0.67
Opaque mineral:				1.0	0.9	2.15=	0.55=
Hematite	Fe_2O_3	5.3				0.18+	0.05+
Ilmenite	FeTiO_3	4.789				0.87+	0.21+
Magnetite	Fe_3O_4	5.2	0.64			1.10	0.29
Spinel	MgAl_2O_4	3.65	-	0.5	1.2	0.07	0.01
Other	-	-	10.04	-	-	-	-
Amorphous	-	-	-	-	-	8.81	1.86
Total			95.56	100		100	

the obtained results.

3.9 Peridotite

The peridotite is the only studied rock for which SiO_2 is not the highest oxide content. The highest percentage is for MgO equal to 46% which is included in the olivine

atomic composition. The SiO_2 oxide content is the lowest among all the studied rocks which can be linked to the absence of quartz. The CIPW norm given in **Table 9** presents composition of this rock with 85% of olivine in addition to hypersthene pyroxene (8.7%) and some other minor phases as magnetite (0.64%).

Fig. 9 (a) Micrograph under PPL for peridotite thin section, (abbreviations: Ol for olivine), (b) Micrograph under XPL for peridotite thin section, (c) Experimental and fitted X-Ray diffraction pattern for the peridotite with the dominant phase (abbreviations: Fo for forsterite, Tlc for talc and Lz for lizardite).

The thin section of peridotite under PPL and XPL is presented in **Figs. 9(a) and (b)**. The observed grains in this rock have different sizes. The big observed grains of olivine are in the order of 1 mm while the small grains are in the range of 10 to 100 μm . The mineral compositions given by point counting method is presented in **Table 9**. The major phase in this rock is olivine 85% and the minor phases are carbonate mineral (10%), serpentine (2%), talc (2%), opaque mineral (1%) and spinel (0.5%).

The XRD Rietveld analysis was performed based on the XRF description. The experimental curve with the assigned peaks is presented in **Fig. 9(c)**. The parameters related to the quality of fitting are: $R_{\text{exp}}=2.50$, $R_{\text{wp}}=7.03$ and $\text{GoF}=2.81$. Olivine is identified as forsterite with 81% of content. The carbonate minerals are detected in low percentage as three different minerals: azurite, malachite and hydrozincite. The serpentine is under the lizardite form. Also, three phases are identified as opaque minerals: hematite, ilmenite, and magnetite. The Phases quantification by the XRD/Rietveld analysis is presented in **Table 9**. For all methods, high amount of olivine was observed. The carbonate minerals content given by the thin section is higher than that obtained by XRD. Other percentage of minor phases stay in the standard deviation ranges. As for major studied rocks, no glass phases have been observed by the microscopy contrary to the Rietveld result.

The peridotite has the highest measured density value among the studied rocks with a value of 3.272 ± 0.013 . The estimation of this density based on the phase identification and quantification provides a value of 3.252 which is a slightly lower (0.61%) than the measured density. Here also, this value can be considered as an additional confirmation of the obtained results.

4. Discussion

For the eight studied rocks, the results obtained by the

Fig. 10 Counts in thin section versus mass fraction given by XRD/Rietveld analysis.

XRD/Rietveld analysis are comparable to the those of the point counting method (**Fig. 10**). Concerning the phase identification, the dominant phases obtained by both methods are equivalent, especially in granite. However, in some rocks, some differences in the identification of minor phases (under 10%) can be observed. It is the case of four rocks among eight: albitite, metachert, andesite and sandstone. For the albitite rock, quartz is only observed in the thin section (7.2%). Concerning the metachert, very negligible amount of staurolite (0.03%) is only shown with the Rietveld analysis while chlorite (4%) and muscovite (4%) are only shown by the point counting method. The andesite contains smectite (0.4%) according to the thin section and zircon (0.13%) by XRD. The last rock is sandstone which contains opaque mineral (4.0%) and calcite (3.8%) by point counting method while biotite (0.69%) is detected by the XRD. For all studied rocks, the cumulative difference for the phases undetected separately by both methods is under 10% and can be as low as 0.53% in the andesite case. These small differences between both methods are not systematic and can be explained by the heterogeneity of rocks and the small size of samples used in both methods.

For the quantification of phases, the first remark concerns the high amorphous content given by the XRD/Rietveld analysis. This tendency can be related essentially to the fitting errors of calculation and partially to the reduction of the crystallinity according to the duration of the grinding process. In previous studies (Takahashi 1957; Kim *et al.* 2019; Hlavay *et al.* 1978), it has been confirmed that, the intensity of peaks as well as their broadening are decreasing with the grinding time. It is explained by the creation of an amorphous layer (~ 30 nm) during the powdering process known as Beilby-Bowden layer (Bowden and Hughes 1937; Castro *et al.* 2012). To reduce this error, it is important to enhance the procedure experimentally and numerically. Experimentally, the created amorphous phase should be reduced by a slower grinding time and using a wet grinding approach for instance. For the soft rocks in this study, a lapse of 30 seconds is at least required to obtain the powder with particle size distribution under 90 μm . For harder rocks, the powder obtained after one cycle is generally insufficient and up to four cycles can be necessary. To reduce the drop in crystallinity, the users are encouraged to add cycles of 30 seconds one by one until grinding completely the rock. Also, the time of data acquisition can be increased to have more accurate experimental XRD chart, but the quality vs acquisition time is an asymptotic curve and the gain in the quality of the curves will be limited compared to the longest time. Numerically, the minerals exist in natural rocks under solid solution form. The use of multiple raw files corresponding to different solutions can allow the selection of the most appropriate one for the analysis. In this case, the error will be reduced automatically, and the amorphous content will be minimized. Thus, compared to the thin sections, the analyzed powders taken from the same

rocks have a higher amorphous content. In addition, for rocks with small amorphous content, the uncertainties given by the XRD/Rietveld analysis for the amorphous fraction becomes larger (Snellings *et al.* 2010). A higher amorphous content is equivalent to lower contents of crystalline material which can partially explain the underestimation by XRD method of some phases when high amorphous difference is detected between both methods. It is the case of pyroxene in andesite and all phases in albitite. Other examples are albite, quartz and white mica in pegmatite rock, olivine, and carbonate minerals in peridotite rock. Therefore, the most important factor behind this overestimation of the amorphous phase is the artefact linked to the Rietveld analysis for such well crystalized materials. The second remark concerns the calculation of the standard deviation which is based on 10 series of 100 points for the point counting method. The obtained values remain very high compared to that of the XRD/Rietveld analysis. Statistically, a higher accuracy can be obtained with more points, but the method is already time consuming and expensive. For the third remark, it should also be noticed that the quantification given by the XRD/Rietveld analysis corresponds to the mass fraction of minerals while that given by the point counting method is more related to their volume fraction. Thus, the thin section values should be higher (lower) than the values obtained by the XRD/Rietveld analysis for phases with a lower (higher) density compared to the rock density.

The major phases obtained by both methods are almost similar for all rocks except for sandstone. For this rock, the major mineral detected by the thin section observation is the quartz (52.6%) while it is oligoclase (43.69%) based on the XRD method. For intermediate phases, some discrepancies are noted between both tests.

The density measurements are used to confirm the results obtained by both methods. the obtained value is compared to the density calculated from the composition given by the XRD/Rietveld analysis. If the identification and the quantification are well done, the difference between both values should be low. For seven rocks with low amorphous phase, this difference is lower than 1% supporting the composition result. In the case of andesite, the difference is very high (4.73%) which can be explained by the high amorphous content. Indeed, the density calculation is only based on the crystal phases because the minerals composing the amorphous part with their densities are generally unknown. Thus, the density is generally overestimated making the density confirmation test inappropriate in this case.

In the context of civil engineering laboratory, the approach based on the XRD/Rietveld analysis can certainly offer quick, accurate and accessible method for modal analysis of rock-forming minerals, although more accuracy is necessary for petrological studies. The results will be very useful for modelling concrete behavior especially when aggregates play a central role. It is the case when aggregates swell due to alkali silica reaction or irradiation.

The modal analysis will allow to implement the properties of each mineral during modeling. For instance, the composing minerals can be associated with their corresponding tensors of elastic stiffness, elastic compliance, and coefficient of thermal expansion. To be the most representative of the aggregate's behavior, the content of the amorphous phase is also an important data to consider as input for the modeling. Generally, the amorphous phases are less sensitive to the environment conditions (temperature, radiation) compared to the crystal phases. The presented methods do not provide the composition of the amorphous phases, however the obtained percentage combined with the assumption of low sensitivity can be used as the best available input data for this modeling. Under different kind of external solicitations, the stress inside aggregates or concrete as well as the corresponding damage can be estimated properly. A such predictive calculation will certainly allow a better aging management of preexisting NPP and provide an interesting tool to discriminate aggregates according to their performances under different conditions for future infrastructures.

5. Conclusion

The point counting method for the identification and quantification of minerals inside rocks was compared in this paper to an approach based on the XRD/Rietveld analysis combined with XRF and CIPW norm as a pre-characterization test with a confirmation test: density measurement. This approach presents the advantage of being faster and less expensive allowing it to be more representative of the studied rocks by multiplying the number of tested samples. In addition, more detailed description of the composing minerals is given by this approach which is required in some advanced studies. This comparison was performed on eight rocks and the following conclusions can be shown:

- 1) The atomic composition obtained by XRF is a useful pre-characterization test. It allows combining with the knowledge about the geological nature of the rock to have a general idea of the composing minerals. In the case of a rock with a high quartz content, the identification can immediately be related to the high percentage of SiO_2 . The presence of feldspar requires a non-negligible percentage of Al_2O_3 . In this case, a good indication of the composing feldspar minerals is deduced based on the proportion of Na_2O , K_2O and CaO . If high amount of some other oxides like Magnesium or iron are detected, the choice of minerals can be oriented to olivine, pyroxene, clay minerals or biotite for example. For more detailed description, the CIPW norm can be calculated and an optimized mineral composition can be obtained which should be used carefully.
- 2) The amorphous content obtained by the point counting method is systematically inferior to that given by the Rietveld analysis. In many cases, the glassy phase

is not even observed by the microscope. This difference is mostly related to the cumulated errors during the fitting process. The powder preparation by grinding can also be partially accountable for the crystallinity reduction of the material. In the case that non negligible fraction of glassy phases exists in the rock, a mismatching between the measured density and the calculated one (based on the XRD/Rietveld analysis) should be observable.

- 3) The dominant phases obtained by both methods are generally similar with some differences in the obtained fractions. Some discrepancies are observed for the intermediate phases and more of them are registered for the minor phases. However, the standard deviation of the point counting method is very high compared to that of the XRD/Rietveld analysis, making an overlap between the values obtained by these methods especially for the minority minerals.
- 4) The comparison of the calculated density based on the results of XRD/Rietveld analysis with the measured density represents an efficient verification criterion. However, this method cannot be considered if the rock contains a high amount of amorphous. This result confirms that the detected amorphous phases provided by the XRD/Rietveld analysis is mostly related to the calculation artefact than other thing.

Finally, it can be concluded that the XRD/Rietveld analysis can represent a good alternative for the point counting method. Especially in the context of construction materials laboratory for which the XRD equipment and the analysis tools are already available. The experience of the users in the characterization of cementitious materials can be helpful for the case of rock forming minerals. This method becomes also more efficient for rocks with small grains undetectable by the microscope. It should also be noted that the complementary test like XRF and density measurements can be performed but are not necessary to obtain good modal analysis by XRD/Rietveld analysis.

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