DETERMINATION OF AMORPHOUS MATTER IN INDUSTRIAL MINERALS WITH X-RAY DIFFRACTION USING RIETVELD REFINEMENT.

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Abstract

A great variety of fine grained industrial rocks, which are valued by the industry contain variable amounts of amorphous or poorly crystalline matter, which is not easily detectable by the conventional mineralogical analysis methods based on X-ray diffraction (XRD). The quantification of amorphous matter in industrial rocks is a major task because it provides a thorough characterization of the raw materials and assists to interpret their reactivity. Among the most reliable methods used for quantification of amorphous matter, are those which are based on Rietveld refinement. In this study we prepared 1:1 mixtures of synthetic or natural calcite and quartz with 5-80% glass flour and added corundum (α-Al_2O_3) internal standard and applied the Autoquan2.80 © software based on the BGMN computer code to quantify the amorphous matter content. The mixtures with synthetic minerals yielded results with minimum absolute error due to the similar particle size of the minerals, the internal standard and the glass. By contrast, the mixtures with natural minerals displayed greater relative error due to the particle size difference between the minerals on the one hand and the internal standard and the glass on the other, due to the microabsorption effect. Moreover, preferred orientation was

important in the case of natural calcite, due to perfect $(10\bar{1}1)$ *cleavage plane. Mixtures containing up to 25% amorphous matter did not display the characteristic hump at 20-30 °2θ, suggesting that the lack of the hump is not a safe criterion for the recognition of amorphous matter.*

Keywords: *Amorphous matter, X-ray diffraction, particle size, internal standard, Rietveld refinement*

Περίληψη

Πολλά λεπτόκοκκα βιομηχανικά ορυκτά και πετρώματα περιέχουν ποικίλα ποσοστά άμορφου ή φτωχά κρυσταλλωμένου υλικού, το οποίο δεν ανιχνεύεται εύκολα με τις συμβατικές μεθόδους ορυκτολογικής ανάλυσης που βασίζονται στην περιθλασιμετρία ακτίνων-Χ (XRD). Ο ποσοτικός προσδιορισμός του άμορφου υλικού στα βιομηχανικά ορυκτά και πετρώματα είναι πολύ σημαντικός γιατί παρέχει χαρακτηρισμό σε βάθος των πρώτων υλών και συνεισφέρει στην ερμηνεία της τάσης τους για αντίδραση. Μεταξύ των πιο αξιόπιστων μεθόδων που χρησιμοποιούνται για ποσοτικό προσδιορισμό άμορφου υλικού είναι αυτές που στηρίζονται στην εκλέπτυνση Rietveld. Στα πλαίσια της εργασίας παρασκευάστηκαν μίγματα συνθετικού ή φυσικού ασβεστίτη και χαλαζία σε αναλογία 1:1, με 5-80% λεπτόκοκκο γυαλί (glass flour) και προσθήκη κορουνδίου (α-Al2O3) ως εσωτερικό πρότυπο. Για την ποσοτικοποίηση του άμορφου υλικού, χρησιμοποιήθηκε το λογισμικό Autoquan 2.80©, που βασίζεται στον κώδικα BGMN. Τα μίγματα με τα συνθετικά ορυκτά έδωσαν αποτελέσματα με ελάχιστο απόλυτο σφάλμα, λόγω του παρόμοιου μεγέθους κόκκου των ορυκτών, του γυαλιού και του εσωτερικού προτύπου. Αντίθετα, τα μίγματα με φυσικά ορυκτά έδωσαν αποτελέσματα με μεγαλύτερο σχετικό σφάλμα, λόγω της διαφοράς μεγέθους κόκκου μεταξύ των ορυκτών φάσεων από τη μια, και του γυαλιού και του εσωτερικού προτύπου από την άλλη, που οδηγεί στο φαινόμενο της μικροαπορρόφησης. Επιπλέον, ο φυσικός ασβεστίτης εμφάνισε σημαντική τάση προσανατολισμού των κόκκων εξαιτίας του τέλειου σχισμού κατά $(101\bar{1})$. Μίγματα που περιείχαν μέχρι 25% γυαλί δεν εμφάνισαν χαρακτηριστικό ύβωμα στην περιοχή 20-30°2θ, γεγονός που υποδηλώνει ότι η έλλειψη υβώματος δεν αποτελεί ασφαλές κριτήριο για την αναγνώριση του άμορφου υλικού.

Λέξεις κλειδιά: *άμορφο υλικό, περιθλασιμετρία ακτίνων-Χ, μέγεθος κόκκου, εσωτερικό πρότυπο, εκλέπτυνση Rietveld*

1. Introduction

Amorphous matter is a common impurity in industrial minerals and rocks, including diatomite, zeolites, bentonites, perlite, pumice and volcanic ash or pumicite (Benito et al., 1998; Barker & Santini, 2007; Breese et al., 2007; Snellings et al., 2010 among others) as well as in synthetic industrial products such as Portland cement, pulverized fly ash, bottom furnace ash and slags (Suherman et al., 2002). It may be a) a primary phase i.e. volcanic glass in perlite pumice or volcanic ash and opal-A in diatomite a) a secondary phase in the form of reaction products during alteration of primary phases including volcanic glass, e.g. amorphous gels in bentonites or zeolites (Christidis, 2001) or c) reaction products during hydration of phases with pozzolanic activity such as Portland cement (Suherman et al., 2002). The latter may not be necessarily amorphous but poorly crystalline phases with very small coherent scattering domains to be detected by X-ray diffraction.

The detection of amorphous or poorly crystalline phases is a major task for complete characterization of these industrial minerals and rocks because they impart pozzolanic activity when mixed with activators such as portlandite ($Ca(OH)_2$), and are used as hydraulic binders (Masazza, 1993; Blanco Valera et al., 2006; Mertens et al., 2009). This activity is particularly important for soil stabilization purposes (Bell, 1996; Guidobaldi et al., 2018). Therefore, except for identification of amorphous matter, a major task is its quantification. The main technique available for quantitative analysis of amorphous or poorly crystalline materials is X-ray diffraction (XRD), although amorphous matter is "invisible" to X-rays.

Identification of amorphous matter is usually feasible by the detection of a hump (bell-shaped increase of the background) between 18 and 35 °2θ for Cu*Kα* radiation. Nevertheless, precise quantification may be difficult if present to small amounts. This results to an overestimation of the remaining crystalline phases, because the quantitative analysis is normalized to 100 % for the crystalline phases (De La Torre et al., 2001; Snellings et al., 2010), thus increasing the error of the determination.

Recent approaches for quantification of the amorphous matter include full pattern fitting approaches by the Rietveld technique (Bish & Ploetze, 2011). These approaches involve the use of a well-crystallized internal standard of known structure, such as corundum (α-Al$_2$O$_3$) or zincite (ZnO) and have the advantage they are not affected by peak overlapping (Post and Bish, 1989). In this work we applied Rietveld refinement to determine and quantify the amorphous matter in a series of synthetic samples. The aims of the work were to determine the accuracy in the determination of the amorphous matter, to evaluate the influence of particle size in the accuracy of the measurements and to identify the amount of glass (cut off limit) at which the presence of the hump at 18-35 °2θ, the criterion to identify amorphous matter, becomes visible.

2. Theoretical background

The Rietveld method (Rietveld, 1969) compares the full experimental profile with the calculated XRD profile. Each data point (2θ step) is an independent observation. Inasmuch as the method uses a pattern-fitting algorithm, all diffraction lines for each phase are explicitly considered, thus minimizing the problem of overlapping diffraction lines of different phases (Post & Bish, 1989; Hill, 1991; Bish and Plötze, 2011). The use of all diffraction lines in the pattern minimizes the uncertainty in the calculated weight fractions of the phases due to possible preferred orientation. Also, during fitting of the complete diffraction pattern, the plot of the difference between calculated and measured pattern allows revealing any additional trace phases present that have not been considered in the refinement.

The main equation of the quantitative analysis with the Rietveld method is the following:

$$w_p = \frac{S_p \rho_p}{\sum_{i=1}^{n} S_i \rho_i} \qquad (1)$$

Where w_p is the weight fraction, S is the scale function to fit the intensity of the observed XRD trace and ρ is the density of each phase. The basic assumption of the approach, similar to other quantitative XRD methods is that the weight fractions are normalized to 1 i.e. to 100%.

If we add an internal standard, we will be able to determine the amorphous matter content (w_a) by difference from the following equation (2):

$$w_a = 1 - \sum_i W_{i,c} \qquad (2)$$

where $W_{i,c}$ is the recalculated weight fraction of phase i. Recalculation of the weight fractions is performed, inasmuch as the concentration of all phases including the internal standard is overestimated, because the amorphous matter is not taken into account during the calculations.

The parameters most commonly used to monitor the progress of refinement are the weighted profile index (R_{wp}), the goodness of fit S (the squared ratio of R_{wp} over the R_{exp}) and R_B (measurement of the agreement between the observed and calculated Bragg intensities) (Post and Bish, 1989; Hill, 1991). The R_{exp} index is an estimation of the minimum R_{wp}. Ideally for a perfect refinement $R_{wp} = R_{exp}$, S=1 and R_B <0.1 (10%). Instead of R_B the Autoquan® program used in this study (see Materials and methods section below) calculates the parameter R_{phase}, comparable to R_B.

3. Materials and methods

Both synthetic and natural quartz and calcite were used in this study. The synthetic quartz and calcite were of analytical grade (Merck) with particle size <1 μm. The natural quartz was derived from a quartzite from Crete, whereas the natural calcite was from a Naxos marble. The natural samples were free of impurities, within the accuracy of the analytical method used (see below). The amorphous matter was "glass flour" from a local glass works in Chania town, with particle size < 5 μm. Pure corundum (α-Al_2O_3) < 1μm in size was used as internal standard. The synthetic quartz and calcite had comparable particle size as the internal standard, whereas their natural counterparts were considerably coarser. Consequently, they were ground with an agate pestle and mortar to <15 μm.

The samples were examined on a Bruker D8 Advance Diffractometer equipped with a Lynx Eye strip silicon detector, using Ni-filtered CuKα radiation (35 kV, 35 mA). Data were collected in the range 3–70° 2θ with a step size of 0.02° and counting time 1 s per strip step (total time 63.6 s per step). The XRD traces were

analyzed and interpreted with the Diffract Plus software package from Bruker and the Powder Diffraction File (PDF). The quantitative analysis was performed on random powder samples (side loading mounting) emplaced in Al-holders, by the Rietveld method using the BGMN computer code (Autoquan 2.80© software). The code performs quantitative analysis taking into account the particle size, the crystal microstrain and preferred orientation parameters.

Two series of experiments were performed. The first series included mixtures of synthetic quartz and calcite at 1:1 ratio containing 5, 10, 20, 25, 30, 40, 50 and 80% amorphous material (glass flour). The second series included natural calcite and quartz at the same ratio and the same proportion of glass. In both experimental series corundum internal standard was added. The main difference between the two series of the experiments was particle size which was adjusted by grinding of the natural minerals with an agate pestle and mortar as mentioned before.

4. Results

The XRD traces of the synthetic and natural minerals are shown in Figure 1 and 2 respectively. The area of the hump above the background line determined from the XRD traces increases gradually with increasing glass content, as expected (Table 1). However, the first visual evidence for the presence of an amorphous phase (appearance of hump at 18-35 °2θ in Figures 1 and 2) is observed at 25% glass content in the synthetic minerals and 30% for the natural minerals (shown by the arrows). For lower glass contents there is no visual evidence for the presence of amorphous matter.
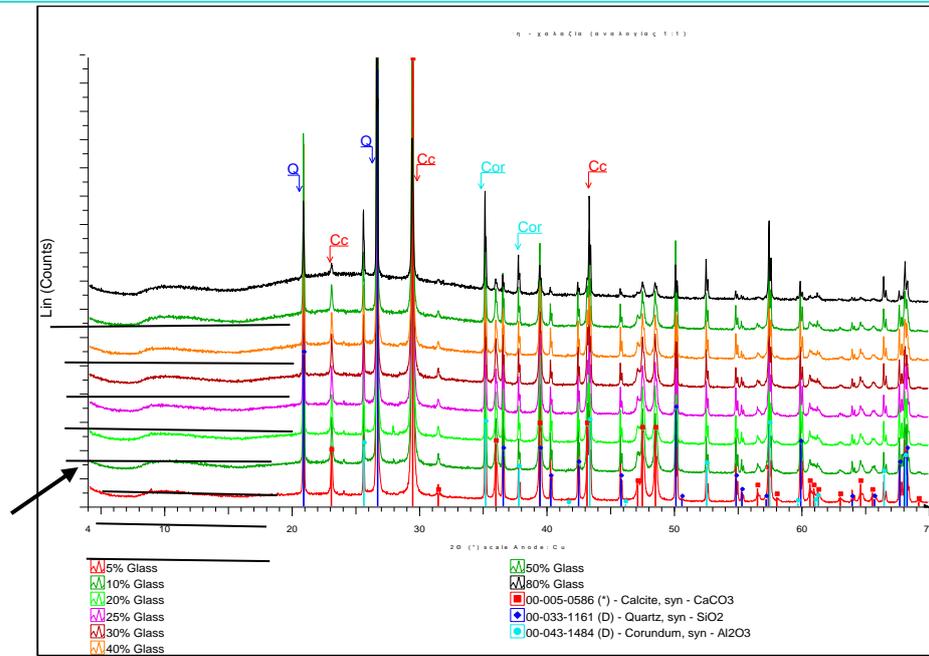
As mentioned before the addition of glass is not evident for glass contents up to 30%. The main evidence for the presence of an additional phase in both the synthetic and the natural samples is the gradual decrease of the intensity of the main diffraction lines for calcite and quartz, with increasing glass content (Fig. 3). This is expected inasmuch as the crystalline phases are diluted with the amorphous phase. However, the observed pattern is different for the different minerals. In calcite the intensity of the synthetic mineral is always higher than that of its natural counterparts, regardless of the amount of glass added, with the

difference in intensity decreasing with increasing amorphous matter content. In quartz a more complex pattern is observed. At lower addition of glass, the intensity of the synthetic quartz is higher than its natural counterpart; the trend is reversed at glass content 25% and till the end of the experiment. In both calcite and quartz, the intensities of the synthetic and natural phases converge at higher glass contents (Fig. 3).

The concentrations of calcite and quartz determined by Rietveld refinement match closely the actual amounts added in the mixtures in both the natural and the synthetic minerals (Fig. 4). In both the calcite and quartz, the deviation from the 1:1 line is small for the synthetic minerals. In general, the natural phases display greater scattering. Indeed, the average absolute relative error (Table 2) in the mixtures with natural minerals is 5.7% for both quartz and calcite, whereas in the mixtures with synthetic minerals, the average absolute relative error is 1.1% for calcite 1.6% for quartz.

Table 1: Area of the hump in the 2θ range 18-35 °2θ, determined from the XRD traces, attributed to the amorphous matter (glass) in the experiments with natural and synthetic samples.

| Glass content (wt. %)	Area of the hump at 18-35 °2θ in synthetic samples (arbitrary units)	Area of the hump at 18-35 °2θ in natural samples (arbitrary units)
5	20.1	22.4
10	27.8	29.6
20	33.8	35.5
25	40.3	47.5
30	58.1	57.9
40	65.4	71.6
50	77	88.5
80	122.6	131.9

Fig. 1: XRD traces of the 1:1 mixtures of synthetic minerals. Q= quartz, Cc= calcite, Cor= corundum. The arrow indicates the first visible indication for the presence of amorphous matter observed as hump in the range 18-35 °2θ. *[please note that a corrected version of this figure appears on the supplementary section as FIG.1]*
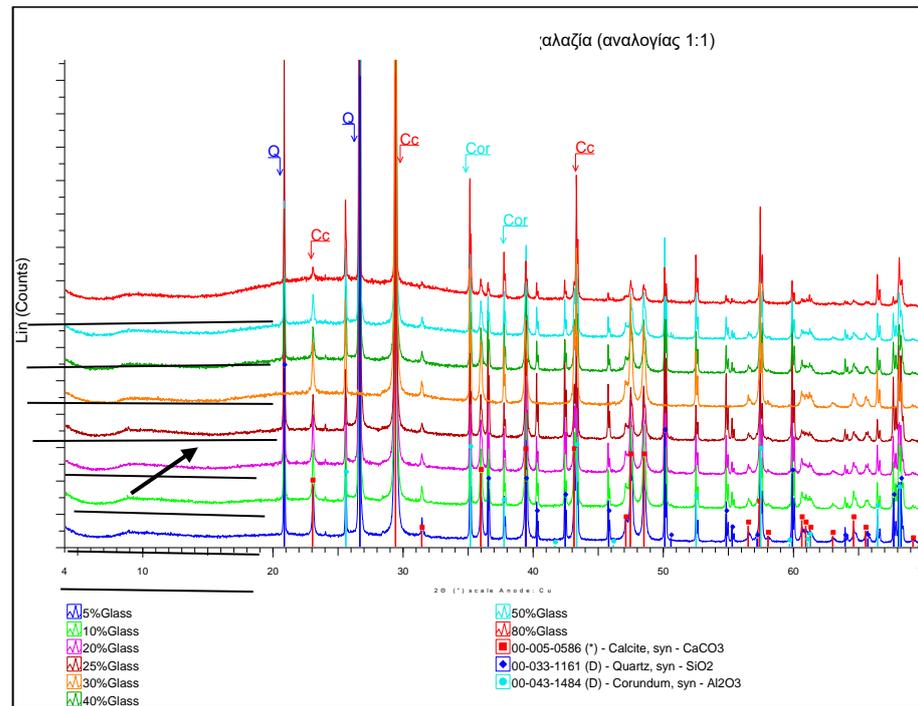
Fig. 2: XRD traces of the of the 1:1 mixtures of natural minerals. Q= quartz, Cc= calcite, Cor= corundum. The arrow indicates the first visible indication for the presence of amorphous matter observed as hump in the range 18-35 °2θ. *[please note that a corrected version of this figure appears on the supplementary section as FIG.2]*
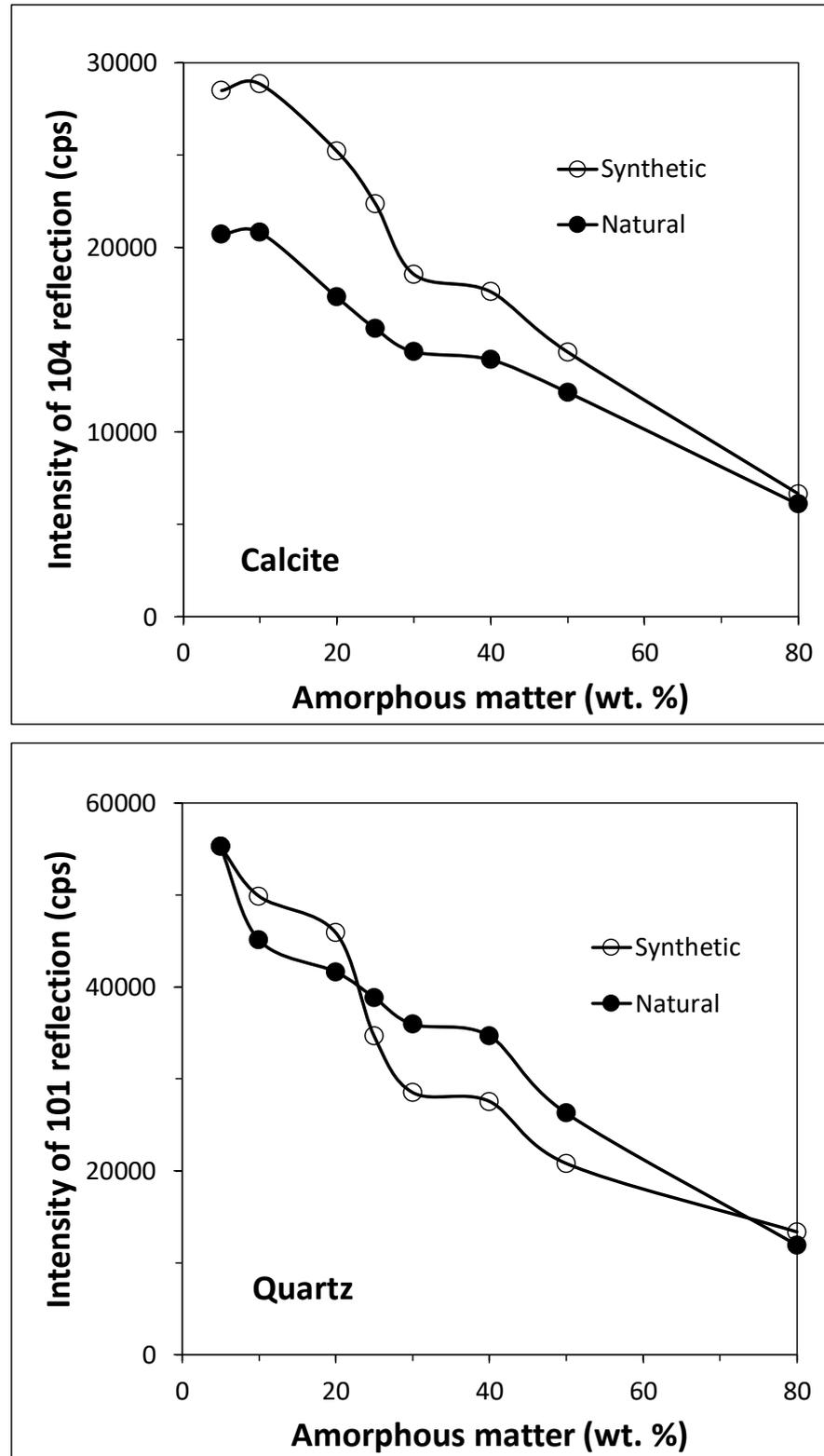
Fig. 3: Evolution of the major diffraction lines of calcite (top) and quartz (bottom) with increasing amorphous matter content.

Also the absolute relative error in the mixtures with natural minerals tends to decrease with increasing glass content, but it is maximized at highest glass content (14% for calcite and 18% for quartz at 80% glass content) due to the increasing uncertainty. A similar but more concise trend is observed in mixtures with synthetic minerals, whereby the absolute relative error is minimized at high glass contents (Table 2). Similar trends were observed in the quantitative determination of amorphous matter in the mixtures with natural and synthetic minerals (Fig. 5). Again, in the mixtures with synthetic minerals the deviation from the 1:1 line was smaller compared to the mixtures with natural minerals (Fig. 5a). The relative error in natural samples was higher for amorphous matter contents lower than 20% (Fig. 5b). In both cases deviations from the actual values were greater for smaller glass contents. In general, the mixtures with natural minerals displayed greater errors than their counterparts with synthetic minerals. As expected, for higher amorphous matter contents the relative error decreased, due to the decreased uncertainty and it was comparable in the two sets of experiments (Fig. 5b)

Table 2: Quantitative analysis of calcite and quartz by Rietveld refinement and absolute relative error of the quantitative determinations.

Natural minerals									
Actual content (wt. %)	**47.5**	**45**	**40**	**37.5**	**35**	**30**	**25**	**10**	**Average error (%)**
Calcite calculated content (wt. %)	45.7	42.5	38.5	33.7	32.5	29.9	25.3	8.6	
Quartz calculated content (wt. %)	46	42.7	38	39.2	33.3	29.6	24.2	8.2	
Calcite absolute relative error (%)	3.8	5.6	3.7	10.1	7.1	0.3	1.2	14.0	**5.7**
Quartz absolute relative error (%)	3.2	5.1	5.0	4.5	4.9	1.3	3.2	18.0	**5.7**
Synthetic minerals									
Actual content (wt. %)	**47.5**	**45**	**40**	**37.5**	**35**	**30**	**25**	**10**	
Calcite calculated content (wt. %)	45.4	44	40.1	37.6	35	30.6	25	10	
Quartz calculated content (wt. %)	49.3	45.8	40.4	37.3	34.5	29.6	25.4	10.1	
Calcite absolute relative error (%)	4.4	2.2	0.3	0.3	0.0	2.0	0.0	0.0	**1.1**
Quartz absolute relative error (%)	3.8	1.8	1.0	0.5	1.4	1.3	1.6	1.0	**1.6**
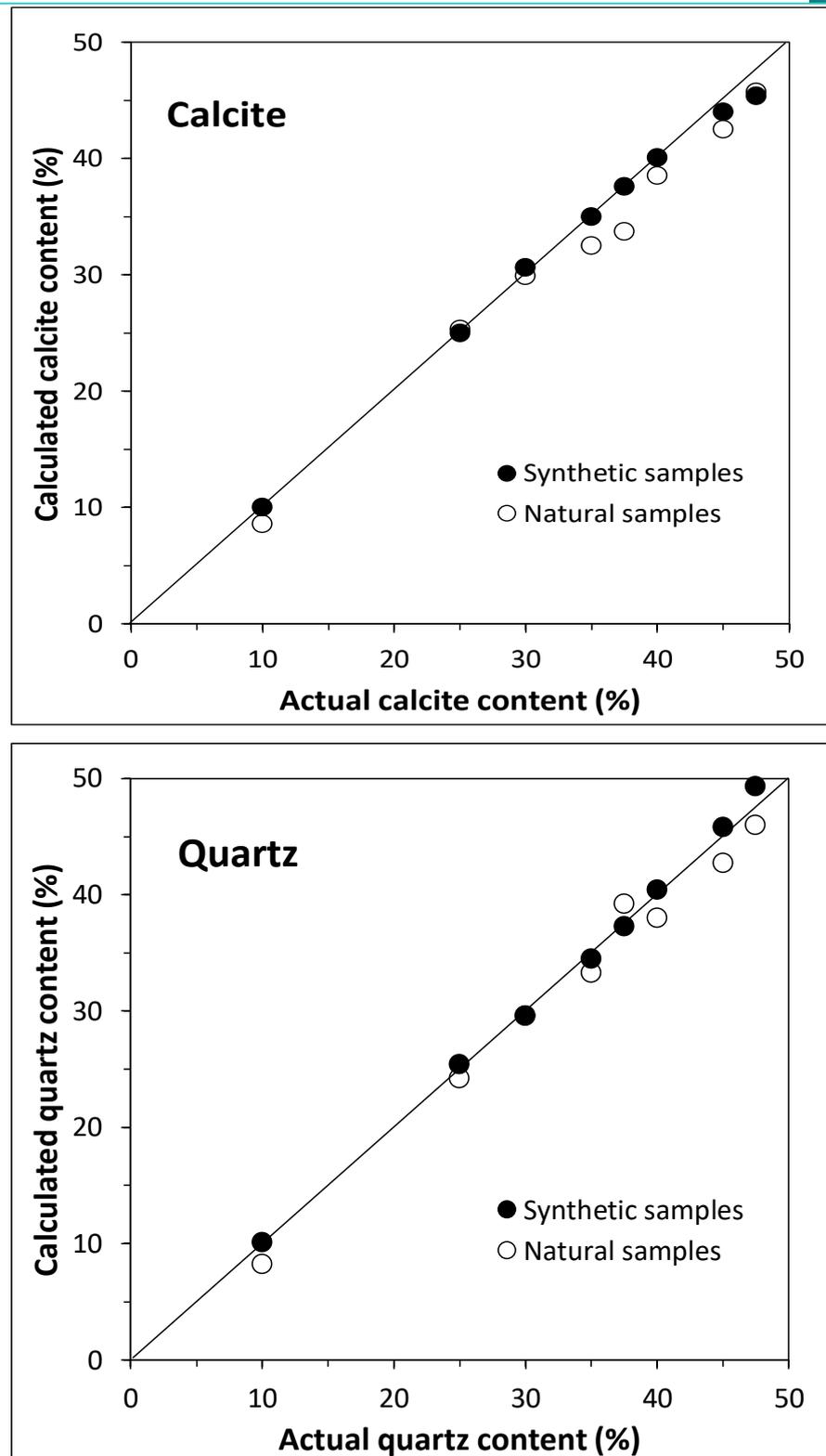
Fig. 4: Actual vs calculated concentrations of synthetic and natural calcite (top) and quartz (bottom)
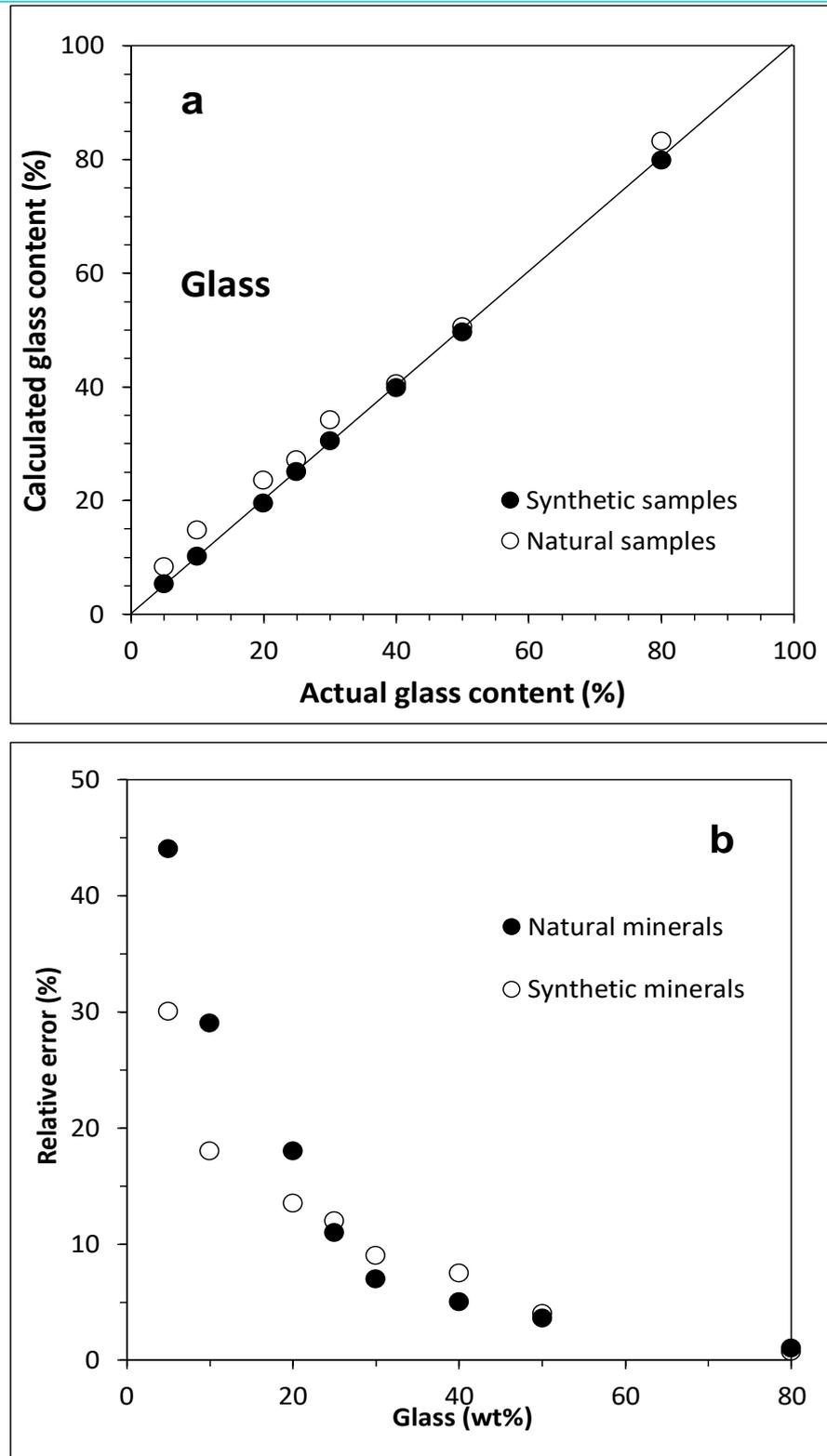
Fig 5: a) Actual vs calculated concentrations of amorphous matter in mixtures of natural and synthetic minerals b) Relative error of determination of amorphous matter in mixtures of natural and synthetic minerals.

5. Discussion

This study has shown that Rietveld refinement based on whole pattern fitting is a very promising method for quantification of the amorphous matter content in rocks. Even in mixtures in which there was no direct visual evidence for the presence of amorphous matter, the method determined the abundance of amorphous matter with sufficient accuracy. The accuracy of the quantitative determinations depends on the particle size of the minerals present in the mixtures (quartz and calcite) due to the microabsorption effect, and the difference between the particle size of the internal standard and the minerals. The greater accuracy in the quantitative determinations observed in the mixtures with synthetic minerals is attributed to both the very fine particle size of calcite and quartz and the negligible difference between the particle sizes of the minerals and the corundum internal standard. The small particle sizes of minerals decrease the possibility for preferred orientation in addition to microabsorption.

By contrast the particle size of the natural minerals was considerably larger. Actually, optimum refinement was obtained by assuming average particle size of 10 μm. The problem might be solved by applying a different sample preparation protocol, with use of micronization to decrease the average particle size further. The influence of the combination of particle size and preferred orientation may be observed indirectly by the overall gradual decrease in the relative error in the amount of quartz with increasing amorphous matter content (Table 2). Calcite displays perfect cleavage along $(10\bar{1}1)$ plane which contribute considerably to the preferred orientation, that causes greater errors during the quantitative analysis. The sharp increase in the relative absolute error for both minerals at very high glass content (80 wt. %) should be looked for to the incomplete mixing of the two minerals with the glass.

The XRD traces of the mixtures of both the synthetic and natural minerals showed the existence of a hump in the range 18-35 °2θ characteristic of the amorphous matter only in mixtures containing more than 25% and 30% glass respectively. For lower glass contents the hump was not visible, although the area of the hump attributed to the amorphous matter gradually increased with

increasing glass content (Table 1). Hence, the sensitivity of XRD is not adequate to distinguish the subtle increase of the background due to amorphous matter at low-moderate glass loadings. This indicates that the lack of the hump is not a safe criterion for the recognition of amorphous matter at low amorphous matter contents and that the presence or absence of amorphous matter should be verified and quantified by the use of an internal standard. Rietveld refinement is a very promising technique in this aspect. Nevertheless, particle size should be carefully controlled for optimum results. It is suggested that particle size for more accurate determinations of amorphous matter should be lower than 10μm, preferably less than 5μm and that sample preparation should be carefully made to avoid preferred orientation of mineral phases.

Finally, this study involved only anhydrous minerals, which do not adsorb water on their surface, hence their density is very close to the theoretical one described in the literature and included in the database of the BMGN code. Nevertheless, in cases of minerals which adsorb water such as smectites or zeolites, quantitative analysis under uncontrollable relative humidity conditions will lead to misleading results regarding the presence of amorphous matter. It is suggested that special analytical protocols in which the relative humidity has been taken into account are designed for the quantitative analysis of such minerals. This is beyond the scope of this work.

6. Conclusions

Application of the Rietveld approach allowed quantitative determination of amorphous matter in mixtures of natural and synthetic quartz and calcite in 1:1 ratio. However, amorphous matter was not visible when present in proportion as much as 25% in the mixtures of synthetic minerals and 30% in their natural counterparts. Therefore, visual inspection of XRD traces is not a safe criterion for identification of amorphous matter in fine grained sediments and soils, even when the remaining phases are well crystallized. Addition of a suitable internal standard and use of Rietveld refinement is recommended as a standard method for identification and quantitative determination of the amorphous matter, provided that particle size of the phases present is strictly controlled.

7. References

Barker, J.M., Santini, K., 2007. Perlite. In: Elzea Kogel, J.E., Trived, N.C., Barker, J.M., Trukowski S.T (Eds) *Industrial Minerals and Rocks, Commodities, Markers and Uses* 7th Ed), SME, Littleton CO, 685-702pp.

Bell, F. G., 1996. Lime stabilisation of clay minerals and soils. *Engineering geology,* 42, 223-237.

Benito, R., Garcia-Guinea, J., Valle-Fuentes, F.J., Recio, P., 1998. Mineralogy, geochemistry and uses of the mordenite–bentonite ash-tuff beds of Los Escullos, Almería, Spain. *Journal of Geochemical Exploration*, 62, 229-240.

Bish, D.L. & Plötze, M., 2011. X-ray powder diffraction with emphasis on qualitative and quantitative analysis in industrial mineralogy. in: G.E. Christidis (Ed) *Advances in the characterization of Industrial Minerals*. EMU Notes in Mineralogy vol 9, Mineralogical Society of Great Britain and Ireland, London, 35-76 pp.

Blanco Valera, M., Martínez Ramírez, S., Ereña, I., Gener, M., & Carmona, P., 2006. Characterization and pozzolanicity of zeolitic rocks from two Cuban deposits. *Applied Clay Science*, 33, 149–159.

Breese R.O.Y., Bodycomb, F.M., 2007. Diatomite. In: Elzea Kogel, J.E., Trived, N.C., Barker, J.M., Trukowski S.T (Eds) *Industrial Minerals and Rocks, Commodities, Markers and Uses* 7th Ed), SME, Littleton CO, 333-450 pp.

Christidis, G.E., 2001. Formation and growth of smectites in bentonites: a case study from Kimolos Island, Aegean, Greece. *Clays and Clay Minerals*, 49, 204-215

De La Torre, A.G., Bruque, S. & Aranda, M.A.G., 2001. Rietveld quantitative amorphous content analysis. *Journal of Applied Crystallography*, 34, 196-202.

Guidobaldi, Cambi, C., Cecconi, M., Deneele, D., Paris, M., Russo, G., Vitale, E., 2018. Multi-scale analysis of the mechanical improvement induced by lime addition on a pyroclastic soil. *Engineering Geology*, 221, 193-201.

Hill, R.J., 1991. Expanded use of the Rietveld method in studies of phase abundance in multiphase mixtures. *Powder Diffraction*, 6, 74-77

Massazza, F., 1993. Pozzolanic cements. *Cement and Concrete Composites,* 15, 185-214.

Mertens, G., Snellings, R., Van Balen, K., Bicer-Simsir, B., Verlooy, P., & Elsen, J., 2009. Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity. *Cement and Concrete Research*, 39, 233–240.

Post, J.E. & Bish, D.L., 1989. Rietveld refinement of crystal structures using powder X-ray diffraction data. in: Bish, D.L., Post, J.E (eds): Modern Powder Diffraction. *Reviews in Mineralogy*, 20, 277-308.

Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2, 65-71.

Snellings R., Machiels L., Mertens G. & Elsen J., 2010. Rietveld refinement strategy for quantitative phase analysis of partially amorphous zeolitised tuffaceous rocks. *Geologica Belgica*, 13, 183-196.

Suherman, P.M., Van Riessen, A., O'Connor, B., Li, D., Bolton, D. & Fairhurst, H., 2002. Determination of amorphous levels in Portland cement clinker. *Powder Diffraction*, 17, 178-185.