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AUI GEOLOGIE

Mineralogy of the sands from the Romanian Black Sea Coast

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Abstract

In the present paper, beach sediments from the Black Sea coast have been studied in order to establish their composition and decipher their origin. The study area is composed of fine and very fine sand. A total of 25 samples were selected for mineralogical analyses; the heavy and light minerals were identified through X-ray diffraction, using a Shimadzu LabX XRD-6000 diffractometer with a Cu anticathode. The samples analyzed can be divided into two categories: those gathered in the southern part of the study area (Eforie-Vama Veche) are predominantly composed of calcite (15 samples), while those collected from the northern sector (Năvodari-Constanța) are predominantly made up of quartz (10 samples). The X-ray diffraction patterns of the mineral concentrates indicate the presence of quartz, feldspars, a mixture of carbonate minerals, hematite, and albite. The heavy minerals identified are pyroxenes, amphiboles, muscovite, rutile, and garnet. The sands of the Romanian seaside have contents similar to those of sediments from other coastal areas of the world in terms of light minerals, with a higher content of carbonates and quartz and a lower content of clay minerals.

Keywords: Black Sea coast, XRD, minerals, coastal sediments.

1. INTRODUCTION

The Romanian Black Sea shore requires particular attention given that, in recent years, both anthropogenic pressure and an increase in sea level have left their marks upon its status. Overfishing, coastal erosion, and eutrophication, pollution with heavy metals, chlorinated pesticides, petroleum-based products, sewage, as well as the extension of construction projects have had a negative impact upon marine ecosystems, the coastal population, and, certainly not least, the economy of the area. A number of measures aimed at the prevention and protection of the Romanian seaside should, therefore, be implemented.

Part of the research dedicated to the

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marine geology of Romania, the present paper seeks to develop an image of the mineralogy and sedimentary processes of coastal sand. The data obtained is intended to provide detailed knowledge of the mineralogical composition of the sediments on the Romanian coast and the conditions which characterized their depositional environments.

The Romanian section of the Black Sea coast has a length of 244 km and is characterized by a lower, less jagged shore, which continues underwater with the continental shelf.

From a geographic and sedimentary point of view, the Romanian seaside is divided into the following two units:

– the northern unit has a length of approximately 165 kilometers and is characterized by low, simple or complex, barrier beaches, composed of sandy sediments, mainly of Danubian origin, and gentle submarine slopes;

– the southern unit extends over a length of about 83 kilometers, with cliffs and narrow beaches at the base of the cliffs or blocking the valleys of the tributaries of the Black Sea. The unit is covered predominantly by limestone cliffs of various heights, ranging from 3 to 35 meters, short sections of sandy beaches at the mouths of rivers and in harbours (Midia, Constanta, Mangalia), and submarine slopes steeper than in the northern area.

The coastline is highly varied, having slightly wavy shapes, with pronounced capes and deep bays extending into Dobrogea valleys, with cliffs, beaches, and sand strips. Cliffs, which represent two-thirds of the length of the coast, have heights ranging between 20 and 40 m. Thus, at Cape Singol (at the point “Pescărie”, marking the entry into Mamaia), the height of the cliffs increases southward up to 35 m before dropping back to 10-15 m, only to reach about 40 m at Cape Tuzla and Eforie, drop back to 10-20 m in Costineşti and Mangalia, and then increases again in Vama Veche (Romanescu, 2006).

The main coastal areas of Romania are Năvodari, Mamaia, Eforie Nord, Eforie Sud, Costineşti, Saturn, Jupiter, Venus, Neptune, 2 Mai, Vama Veche, all located in Constanța County. Romania's coastline is constantly subjected to erosion, a phenomenon which has intensified over the past 30 years because of the construction of the reservoirs of Iron Gates I and II. This has led to the amount of sediment brought from the Danube to the Black Sea being reduced to half, and to a disturbance in coastal sediment balance. Additional factors in the process of coastal erosion are the decreased intake of beach sediment, the loss of sediment as a result of the building of dykes, and the collapse of sea walls because of the geotechnical instability of the top of slopes and/or wave action at their base. The extent of coastal erosion varies from one sector to another.

2. BLACK SEA SEDIMENTS

2.1 Black Sea sediments

Recent sedimentation in the Black Sea is governed by the deposition of allochthonous terrigenous sediments poor in carbonates, and the local generation of large quantities of biogenic carbonates (coccolithophorids) (Atanasiu, 1981).

The mineralogical composition of the detrital fraction indicates sources from the north and north-west (especially the Danube), on the one hand, and the south and east (the Caucasus), on the other (Stoffers and Muller, 1978). The northern origin is evidenced by the abundance of quartz and feldspar (with high quartz/feldspar and calcite/dolomite ratios, and a heavy mineral association dominated by garnet). Among the phyllosilicates, illite is predominant (over 50%, compared to the 10% represented by kaolinite and chlorite).

The southern origin is supported by the abundance of lithoclasts (limestone, volcanic and metamorphic rocks), and the prevalence, among the heavy minerals, of pyroxene and, among the clay minerals, that of montmorillonite (over 50%).

2.2 Sediment distribution

The distribution of sediments is influenced by the main factors of sediment dispersal, namely waves and currents. Time also plays a very important role. Sediment values are even higher when ripples act for a longer period. Erosion and accumulation are strictly controlled by the relationship between the hydrodynamic regime caused by the agitation of waves, the submarine morphology of the coast and the texture of beach sediment (Caraivan, 2010).

In coastal regions (littoral and continental shelf), waves and the currents they induce, as well as the coastal currents caused by the wind, are the main factors involved in sediment dispersion. Coastal sediments are dominated by terrigenous sand – terrigenous-biogenic or biogenic-terrigenous, depending on the prevailing fraction. Shells belonging to the genera *Mya*, *Mytilus*, *Venus* and *Cardium* bring a 10-60% contribution to the composition of shore and beach sand. The significant contribution of rivers is stored in deltas, lagoons and coastal fronts (Vespremeanu, 2005).

Conchiferous carbonate sediments predominate in the Danube shelf, with over 50% $CaCO_3$, mixed with clay minerals.

3. SEDIMENT MINERALOGY

3.1 Coastal sediment mineralogy

The main factors affecting mineralogical composition are the following: the selective sorting of minerals under hydrodynamic equivalents, the different degree of resistance to abrasion of minerals, postdepositional chemical processes, the different sedimentation rates, sediment maturity, and the progressive dilution induced by the distancing from the source of sediment.

Coastal sediments are composed of a light fraction and a heavy fraction.

The analyses performed on Romanian coastal sediments have revealed that the light fraction is represented by terrigenous minerals, predominantly quartz, feldspars, micas and chlorites. It was found that the percentage of feldspars and micas decreases with the distance from the shoreline. Within the light mineral fraction, quartz is predominant, occurring as sub-rounded grains.

Coastal sands generally display good sorting, and always contain bioclasts, sometimes in large quantities.

The coastal system accumulates siliciclastic sediments represented by gravels, oligomictic (quartz) or polymictic (consisting of clasts of various mineral species) sands, moderately sorted, together with eolianite and tempestite (Buzgar, 2000).

3.2 Mineralogy of surface sediments

According to the literature, the following mineralogical characteristics can be summed up for Romanian coastal sands:

The coarse fraction of the surface sediments of the continental shelf is characterized by a varied mineralogical content, depending on the source of the material and the marine hydrodynamic agents. The mineralogical analysis of the sand fraction provides the ability to track the surface distribution of mineral species and thereby determine their conditions of accumulation (Fulga, 2004, 2008).

The category includes light mineral particles of terrigenous material (quartz and feldspar, rock fragments and micas), biogenic material and glauconite.

Quartz and *feldspar* are the main components of the fraction. Quartz occurs as colorless grains, sub-rounded or more intensely processed as a result of post-depositional processes. Feldspar (plagioclase) displays prismatic shapes and polysynthetic mackles. Microline is often present. The highest frequency of quartz and feldspar (45%) occurs along the shoreline.

Rock fragments are generally underrepresented. The most common lithic fragments are represented by terrigenous detritus material (shale, limestone and quartzite).

The most common *micas* are muscovite and biotite. Through their lamellar habitus, micas have a hydraulic behavior different from that of quartz grains (Caraivan, 2010). The high mica content indicates areas of maximum deposition of fine material.

The *organogenic material* consists of fragments of mollusk shells (aragonite), ostracods and foraminifera. They provide information on the marine environment and, to a lesser extent, the transport medium. The analysis has revealed a 0.063 to 0.125 mm fraction containing less than 30% organogenic fragments in the case of the inner shelf, compared to that of the outer shelf, which exceeds 30%. There is also a correlation between the characteristics of the light fraction and the heavy mineral association, which is predominantly composed of amphibolite.

4. MATERIALS AND METHODS

4.1 The data set available

In order to study the mineralogical composition of the sand on the Romanian coast of the Black Sea, 25 samples were collected. The location of these samples is shown in Figure 1.

4.2 The pre-selection method

After grinding, the samples were subjected to XRD analyses at the Faculty of Physics of the „Alexandru Ioan Cuza” University of Iaşi.

The determination of the minerals within the samples was performed so as to determine the proportions of light and heavy minerals, along with the mineral associations.

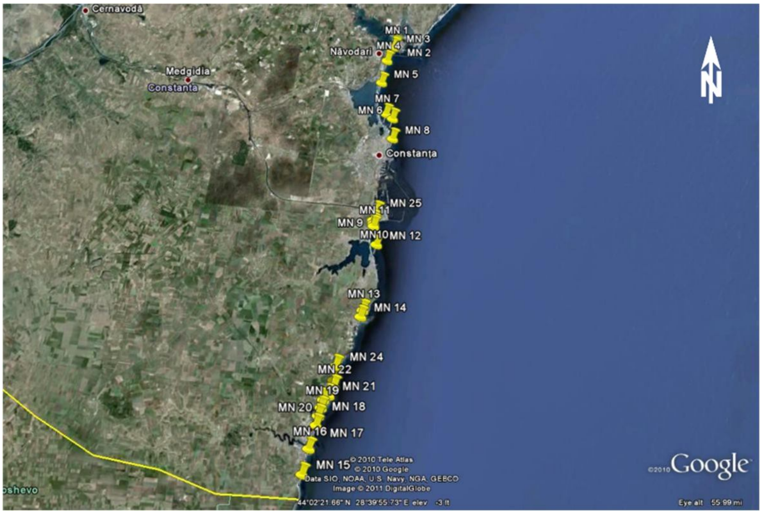

Fig. 1 Romanian coastline. Location of samples.

4.3 X-ray diffraction analysis (XRD)

The XRD technique is most commonly used to identify minerals, particularly for fine-grained materials whose size is too small to be studied through light microscopy. Furthermore, XRD analysis can provide information about the crystalline structure of the mineral and the nature of isomorphic substitutions.

The method relies on the reflection and refraction of X-rays by the crystal structure. Refraction angles depend on the density and spacing of the planes of the crystal with the highest atomic density, which vary from one crystalline structure to another. The maximum distance between the planes with the highest atomic density, the main parameter in XRD analysis, is called "reticular distance" and noted with the letter ***d.***

The analysis performed is based on Snell's law, and the equipment used was a Shimadzu LabX XRD–6000 diffractometer.

5. RESULTS AND DISCUSSION

The sediments discharged by the Danube River have a high ratio of siliciclastic minerals. The heavy mineral input at the entry is small. The proportion of organogenous elements within beach structures is higher, compared to that of sandy river sediments. In the Cap Singol-Vama Veche area, coastal deposits have a high ratio of carbonates and the terrigenous material is replaced by remnants of shells ($CaCO_3$ up to 85-95%).

Heavy minerals, accessory minerals of pre-existing rocks that are sometimes relict minerals, appear concentrated in fine arenites. The morphological and chemical characteristics indicate nearly standard crystallization conditions, allowing the use of heavy minerals as important indicators of source areas. Moreover, their mechanical and chemical resistance, together with the high resistance to abrasion of some of them, act as accurate indicators of mature sediments.

The heavy fraction within the sediment never exceeds 5%. More than 40 heavy minerals have been identified, a great degree of mineralogical diversity being recorded in the Danube Prodelta and south of it, on the continental shelf. Most of these minerals are rare or occasional, with only six heavy minerals (rutile, garnet, amphibole, epidote, pyroxene, zircon) constituting less than 90% of the heavy fraction.

The diffractograms of the samples analyzed are available in Annex A.

The interpretation of the diffractograms reveals that the sands of samples MN1-MN5 and MN7, collected from the coast of Năvodari (up to the entry into Constanta), have a siliciclastic character, the minerals subordinated to quartz being calcite, dolomite, albite and orthoclase. In the samples collected from locations close to Năvodari, iron minerals occur. Figure 2 shows the X-ray patterns of the sample MN4 (Năvodari – south-Mamaia), where quartz is the main mineral.

MN6 and MN8 exhibit characteristics slightly different from those of the samples collected nearby, probably due to the stronger anthropogenic influence within the industrial city of Constanța and the area around its port.

Starting with samples MN9-MN13, collected from the beaches of Eforie Nord, Eforie Sud, Tuzla and Costineşti Village, the characteristics of the sand change. The main mineral is calcite, and the secondary ones are quartz, hematite, aragonite, muscovite and dolomite. Of the heavy minerals, rutile and diopside occur.

In samples MN15 (Fig. 3)-MN25, with the exception of MN20 and MN21, on the one hand, and MN17 and MN18, on the

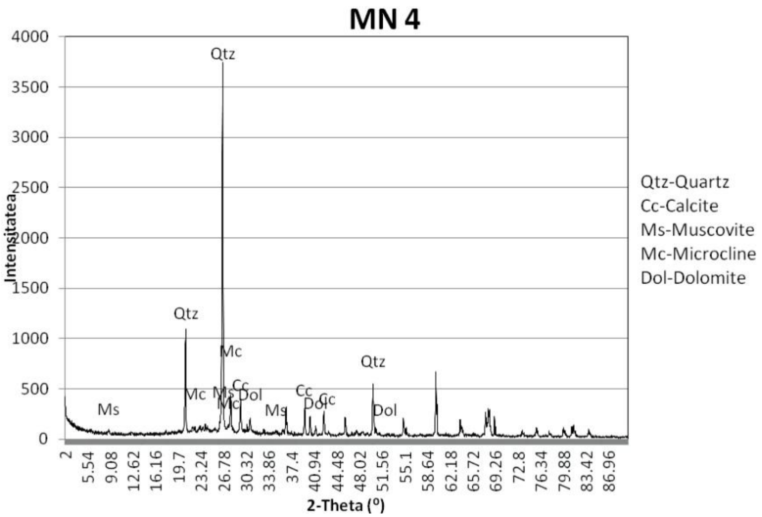

Fig. 2 X-ray patterns of sample MN4.

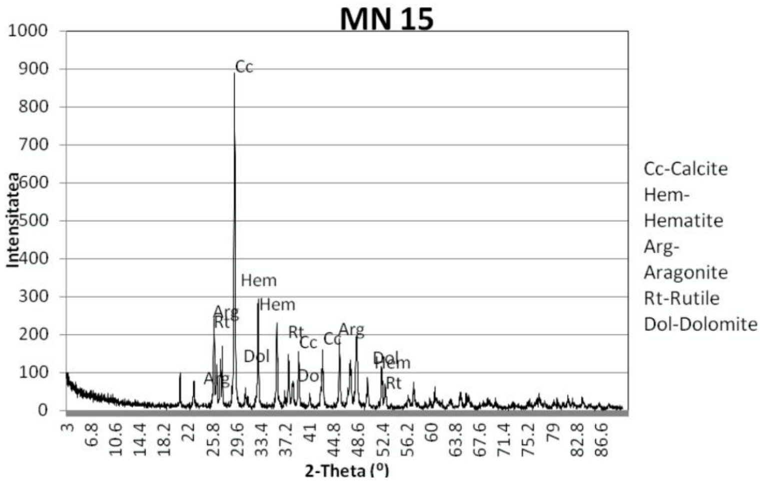

Fig. 3 X-ray patterns of sample MN15.

other, which will be discussed further on, the main mineral are calcite, hematite, dolomite, and, subordinated or not, aragonite. The latter is proof that these beaches are covered with sands containing shell debris.

Calcite and quartz occur as primary minerals in samples MN14, MN20 (Fig. 4) and MN21, collected from the southern sector, perhaps as a result of the sand-replenishing activities that are often carried out in the area of the Costineşti Obelisk, Venus Beach and Cap Aurora, where storms have been quite frequent recently, and, in order to preserve the beach, large amounts of sand have been brought from other areas and mixed with the ancient sands.

Samples MN17 and MN18, collected from the beaches of the city of Mangalia, are different, probably due to anthropogenic and port-related activities, as well as to sanding.

The XRD diffractograms of the samples are characterized by a mixture of carbonate minerals, quartz and feldspars. The samples can, thus, be divided into two categories: those in the south (Eforie-Vama Veche), predominantly composed of calcite (15 samples), and those of the northern sector (Năvodari-Constanța), where quartz is predominant (10 samples). MN20 and MN21 belong to the southern sector, where the main mineral is quartz, followed by calcite and aragonite.

The interpretation of XRD patterns has revealed a similar trend for the samples in each category, with the exception of MN6, collected from the beach of Constanța, in which rutile and hematite occur in high proportions. The clay minerals present are vermiculite and montmorillonite, but their contribution to Romanian coastal sands is very low.

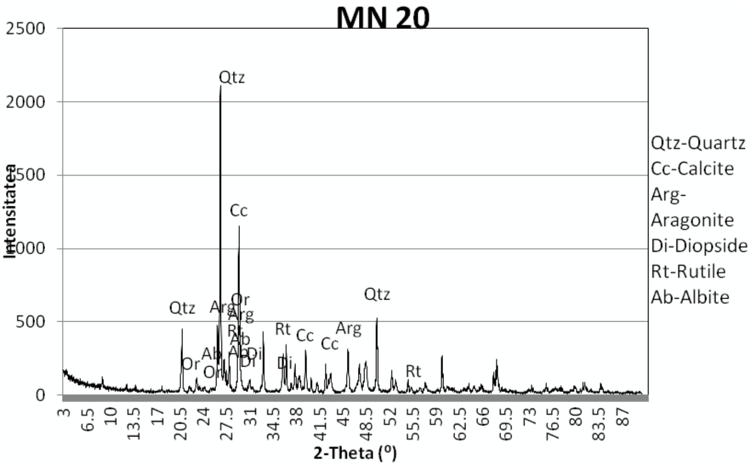

Fig. 4 X-ray patterns of sample MN20.

6. CONCLUSIONS

Based on the XRD analyses performed on the 25 surface sediment samples collected from the entire Romanian Black Sea coast, we could delineate the following two zones: the Năvodari-Constanța zone, where siliciclastic sands prevail, and the Vama Veche-Eforie zone, where sands rich in calcite are predominant.

The main minerals identified in the Năvodari-Constanța zone are the following: quartz, calcite, dolomite, albite, hematite, orthoclase, microcline, and muscovite.

In nearly all of the samples collected from the Vama Veche-Eforie zone, biogenic calcite is predominant. Quartz, hematite, aragonite, muscovite, dolomite, albite and gypsum have also been identified.

The mineralogical analysis of the sand fraction provides the ability to track the surface distribution of minerals and, thus, determine their conditions of accumulation.

The results were compared with other studies conducted on several coastal areas of the world (Sundararajan et al., 2009; Vidinha et al., 2004), revealing that the sands of the Romanian seaside are similar when it comes to light minerals, with higher content of carbonates and quartz, and lower contents of clay minerals.

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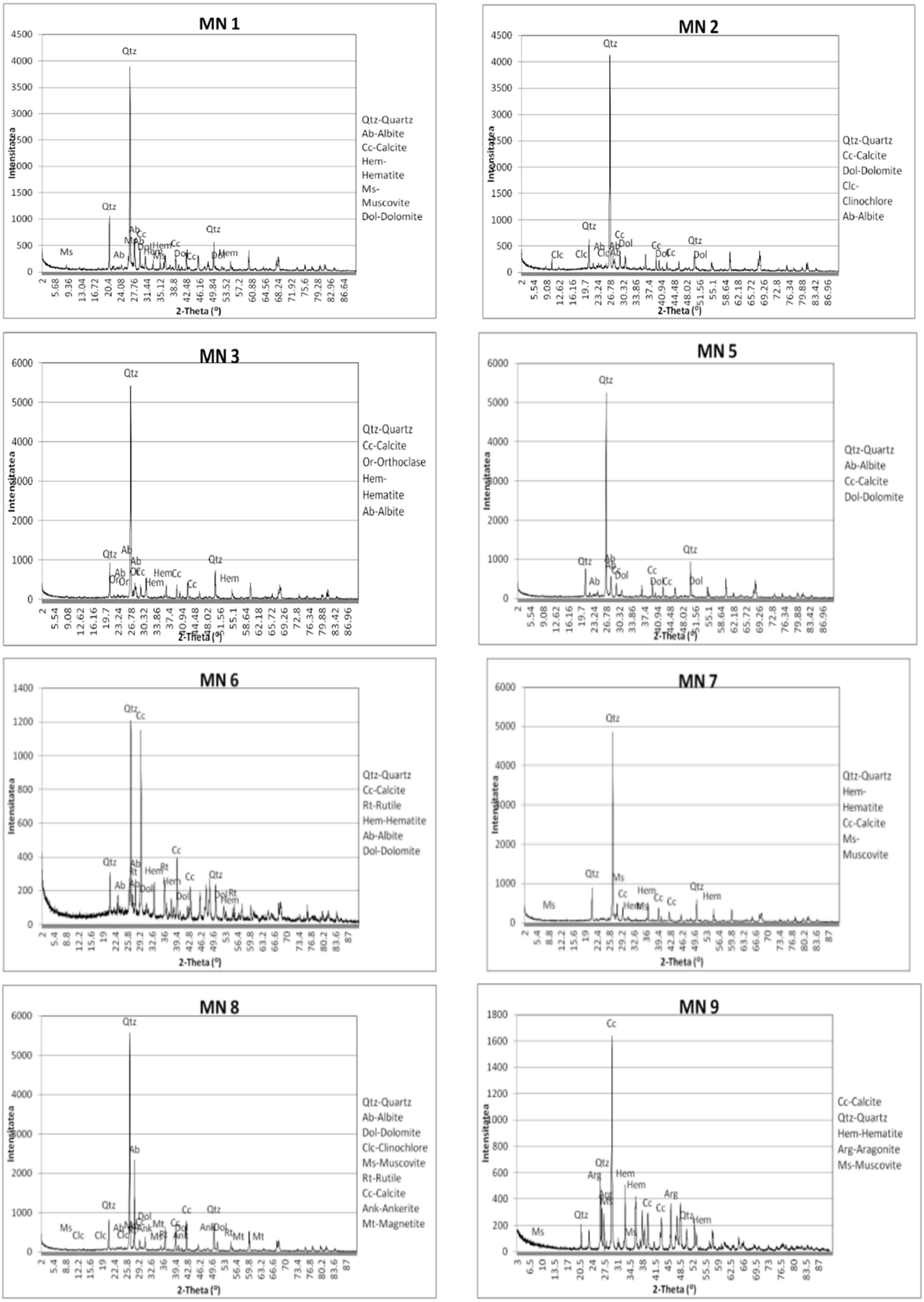
ANNEX A. X-ray patterns of sand samples



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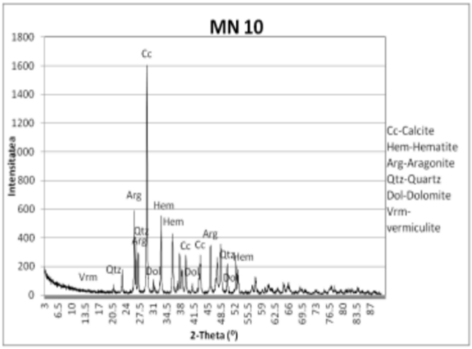

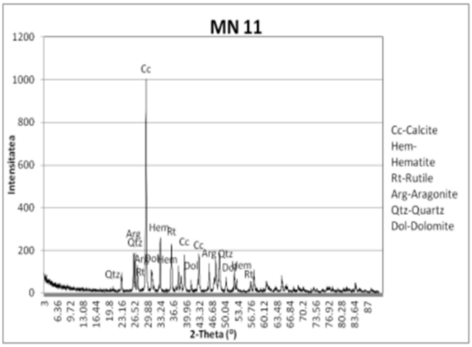

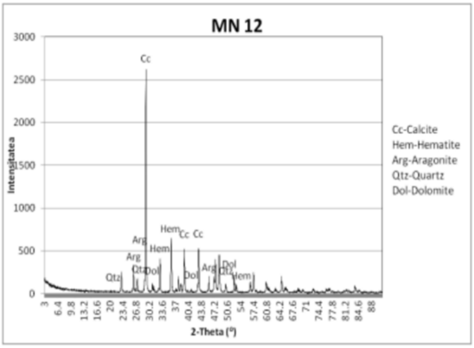

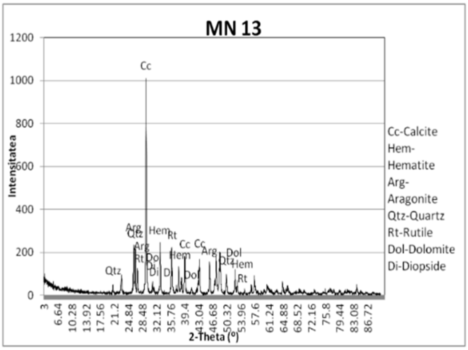

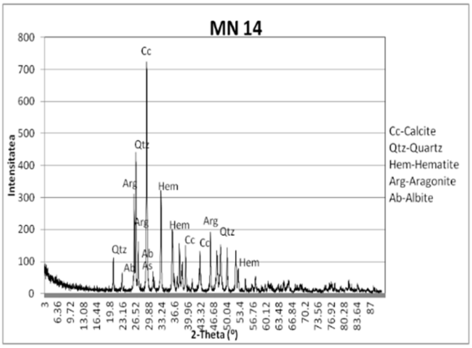

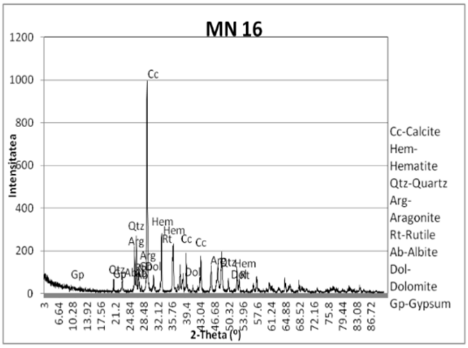

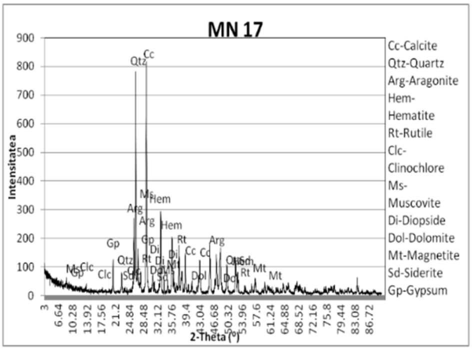

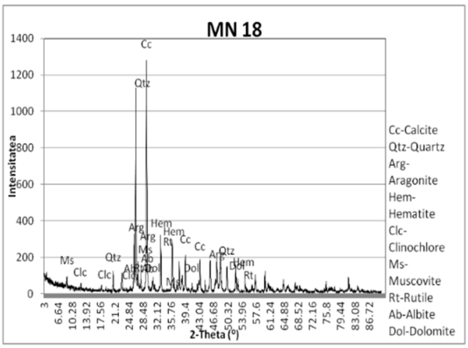

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