Fractionation of Pb in Soil of Abandoned Pb Mine by SEM-EDX and XRD

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ABSTRACT: Mining activity has been associated with environmental pollution problem all through ages. Rhandirmwyn Pb mine was one of the most important mine site areas in South Wales. At present, the mine waste and adits in the area are regarded as main sources of Pb pollution in the area. Therefore, scanning electron microscopy coupled with energy dispersive X-ray spectrometer (SEM-EDX) were used for the identification of fractional forms of Pb that are liable to leach out/down from the soil matrix of the abandoned mine site to surface-and-underground water bodies of the nearby localities, and to determine its association with soil components using X-ray diffraction (XRD). Among the fractional forms of Pb, Galena, Anglesite, Cerussite, Mimetite and Pyromorphite were identified as the fractions of Pb found in the soils of Nantymwyn (Rhandirmwyn) abandoned mine, of which Anglesite was the most abundant fraction observed. Being the most soluble fraction of Pb among the five Pb minerals observed dissolution of this fraction from the abandoned mine is highly possible and could be a source of contamination of soils and surface-and-ground water sources of localities in the vicinity of the spoil mines. However, results of XRD indicated that the bulk chemistry of the soil samples is dominated by quartz followed by aluminosilicates (comprise of illite and kaolinite and traces of pyrite, albite and orthoclase), all of which could be sink for Pb and could possibly influence the mobility of the metal.© JASEM

INTRODUCTION

Rhandirmwyn Pb mine is one of numerous abandoned lead mine in the South Wales, where early mining practices have resulted in spoil heaps of mine waste, rich in potentially toxic metals being exposed to weathering and leaching. The spoil heaps have the potential to cause pollution of the environment due to mobilisation.

Mines throughout the world, whether active or derelict, have become a persistent source of toxic metal contamination, particularly in soils and surface-and-ground water. As such, wherever there are metalliferous spoils associated with disused non-ferrous metal mines stand to present a broad spectrum of environmental problems. This is particularly relevant to North and Mid Wales as a former major mining area for non-ferrous metals. Mining activities ceased long before statutory controls on mining waste were established and thus, Pb pollution load of the mine waste sites in Rhandirmwyn requires pollution inventory scan regularly. Because, the primary fear, which has been instituted in the mind of people living in the vicinity of the abandoned mine site, is that the abandoned mine site could impact detrimental effect on the environment and hence there need for reclamation/remediation of the site.

As soil matrix is heterogeneous, attention has to be focused on the interaction of various forms of Pb with different soil constituents. This is because accurate description of complex interactions of Pb forms in soils is a pre-requisite tool in predicting their behaviour in soil environment (Selim and Spark, 2001; Adamu et al., 2013). The dispersion of Pb contaminants from the abandoned mine site into the immediate surroundings depends on its release and transport tendencies (Salomons, 1995; Selim and Spark 2001). Therefore, characterisation of Pb in soil should go beyond a simple determination of total content. This is because total metal concentrations provide little or no insightful information on the potential mobility and bioavailability of toxic metals (Arenas-Lago et al., 2015; Adamu et al., 2013; Adamu et al., 2011). It is the geochemical phases of toxic metals that will yield information more pertinent in the transfer of metals along soil-water-plant-animal-human chain (Rattan et al., 2005; Salomons, 1995).

The geochemical status and potential mobility of Pb could be estimated via mineralogical method. The solid metal phases can be determined directly or indirectly. The indirect method involves identification of fractions of a metal binds to soil by sequential extraction, whereas the direct method uses spectroscopic instruments to identify mineral

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components ((Selim and Spark 2001). Of the two techniques, fractionation of metals in soil by sequential extraction is the most commonly employed. However, main problem associated with extraction techniques is that each of the extractants may affect the soil components in a different way and artefacts occur. Besides, the method depends largely on different factors such as the choice and order of the extractants, the length of the process, the solid/liquid ratio, and the procedure of sample preparation and conservation (Filgueiras et al., 2002). Because of these problems, several authors have recommended using direct techniques in order to identify how toxic metals are associated with the different soil components (Beesley and Marmiroli, 2011; Cerqueira et al., 2012, Cerqueira et al., 2011; Moral et al., 2005) and thereby complete the information on the solid phases that directly retain toxic metals. Different direct characterisation methods were chosen, such as Field Emission Scanning Electron Microscopy (FE-SEM) with Energy dispersive X-ray Spectroscopy (EDX), X-ray diffraction (XRD) and Time of Flight Secondary Ion Mass Spectrometry (TOFSIMS) for detecting and identifying toxic metals in the different geochemical soil phases (Arenas-Lago et al., 2015; Cerqueira et al., 2011; Kierczak et al., 2008). Although the techniques are semi-quantitative methods, but provide detailed information about the nature of the soil components and possible interactions with toxic metals. Gee et al. (1997), for example, investigated mineralogy of smelting slags and the response of specific mineral forms to natural weathering processes and potential release into the environment. Similarly, the objective of this research was to investigate and predict the mobility and dispersion of Pb from the abandoned spoils into the nearby aquatic and terrestrial environmental compartments using the direct technique involving a combination of SEM-EDX and XRD.

MATERIAL AND METHODS

The Rhandirmwyn mine (Fig. 1) is located in the village of Rhandirmwyn (52.0790° N, 3.7750° W) which is 10 kilometres (6.23 miles) north of the market town of Llandovery in the Dinefwr District of South East Dyfed which before the local government reorganisation lay in Carmarthenshire (Hughes, 1992). Rhandirmwyn village extends along both sides of the Tywi (Towy) river, some two miles north of Cilycwm village and extends up the Gwenffrwd valley towards Cwrt-y-Cadno as far as Bwlchyrhiw and then east across the mountains into Ceredigion and Breconshire (Powys).

Seven sampling points in the study area (Fig. 2) where selected based on the historical mine activity and in each sampling points five soil samples were randomly collected from the surface horizons of the mine spoil heaps using an Eijkelkamp sampler. They were then stored in polyethylene bags and taken to the laboratory. The soil samples from the same area were mixed, air dried, sifted through a 2 mm-sieve and homogenized. The pH was determined according to Slattery et al. (1999). The soil: water and soil: KCl ratio was 1: 2.5 for both measurements.

The morphology, structural distribution and particle chemical composition of samples containing ultrafine particles and minerals (crystalline and/or amorphous) were investigated using a JEOL JSM-6700f plus FE-SEM with charge compensation for all applications in both conductive and non-conductive samples. The FE-SEM was equipped with an Energy Dispersive X-ray spectrometer (EDX), and the mineral identification was made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes. Samples were set on a standard aluminium slide with carbon adhesive, coating them with layers of carbon for 20 nm thick. EDX spectra were recorded in the FE-SEM image mode.

Soil mineralogical analysis was performed in a Philips type powder diffractometer fitted with a Philips PW1710 control unit, Vertical Philips PW1820/00 goniometer and FR590 Enraf Nonius generator. The instrument was equipped with a graphite diffracted beam monochromator and copper radiation source [λ (Kα1) = 0.15406 nm], operating at 40 kV and 30mA. The X-Ray powder diffraction pattern (XRPD) was collected by measuring the scintillation response to Cu Kα radiation versus the 2θ value over a 2θ range of 2–70°. The identification and quantification of the crystalline phases were performed using an installed software programme (Crystal Impact). These extremely acidic conditions favour the mobility and availability of heavy metals in the soil (Cerqueira et al., 2011).

RESULTS AND DISCUSSION

The pH of the soil sample collected from all the sampling points of the study area was around 6 at the time of investigation. Consequently, this acidic soil condition could favour the mobility and availability of heavy metals in the soil (Cerqueira et al., 2011; Flis et al., 2011).

FE-SEM with EDS is used to investigate the morphology, structural distribution, and chemical composition of samples containing ultrafine particles and minerals (crystalline and/or amorphous). The results presented are representative of all the soils studied (Fig. 3) and shows that forms of the Pb exists in the study area are mainly of Anglesite, Cerrusite and traces of Galena, Pyromorphite and Mimetite. Noticeably, with the application of this technique, among the five forms of Pb in the abandoned mine site, Anglesite and Cerrusite are the most commonly found and then followed by traces of Galena,

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Pyromorphite and Mimetite (Table 1). The fact that Galena which is the primary ore of the Pb was found in trace and completely not observed in some locations of the study area indicates that the area has undergone a series of secondary mineralization that resulted in the formation of Mimetite, Cerussite, Anglesite and Pyromorphite. This was much earlier comfirmed by Bevins et al. (2010) that secondary mineralization was well developed in the study area and resulted in the formation of Mimetite, Cerussite, Anglesite and Pyromorphite from Galena. In general, mineralogical form of Pb can be changed by natural processes from compounds such lead sulphide (PbS) and lead chloride ($PbCl_2$) to lead sulphate ($PbSO_4$), carbonate ($PbCO_3$) and phosphate ($Pb_3(PO_4)_2$) (Thornton et al., 2001). Therefore, it is possible that most of the Galena ore in the area might have been oxidised during the secondary mineralisation process which resulted in prevalence of secondary minerals in the area (Table 1). In addition, Hester and Moore, (1997) also confirmed that secondary minerals of Pb are formed when galena weathers. The secondary mineralisation of Galena as the primary Pb-bearing mineral occurred when oxidised and forms a rim in its outer parts to prevent further oxidation (Joeng and Lee, 2003). The rim is formed by Cerussite ($PbCO_3$) (reaction 1) and Anglesite ($PbSO_4$) (reaction 2), both of which were identified as the major fractions of Pb found in the soils of Nantymwyn (Rhandirmwyn) abandoned mine.

$$Pb^{2+} + H_2CO_3 + 2H_2O \rightarrow PbCO_3 + 2H_3O^+ \quad (1)$$
$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \quad (2)$$
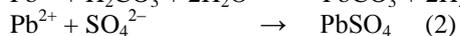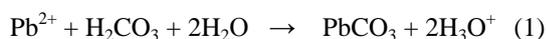
Henceforth and from the environmental risk assessment purview, both Cerussite (reaction 3) and Anglesite (reaction 4) can release Pb as the pH of soils of the study area were found mostly around 6 and thus, Pb from the heaps of spoil mines could potentially be released into, and may pose a serious environmental and health threat to, the nearby living localities.

$$PbCO_3 + 2H_3O^+ \rightarrow Pb^{2+} + 3H_2O + CO_2 \quad (3)$$
$$PbSO_4 + 2H_3O^+ \rightarrow Pb^{2+} + H_2SO_4 \quad (4)$$
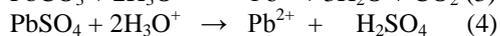
From the viewpoint of XRD results, the bulk chemistry of the spoil heaps (where most of the samples were obtained) is dominated by abundant quartz, aluminosilicates e.g. illite, kaolinite, and traces of pyrite and Feldspars e.g. albite, orthoclase (Fig. 4). Therefore, the quartz and aluminosilicates may serve as sink for the Pb and other toxic minerals in the Nantymwyn mine, which may possibly reduce their mobility in the environment. However, because of the complexity of the soil-waste system, with its myriad of surface types and solution composition, such a generalisation may not hold true. In addition, the natural sorption capacity of the major minerals observed also largely depends on the pH of the soil environment, which either directly or indirectly affects several mechanisms of metal retention by soils (Mclean and Bledsoe, 1992). In addition, It has been pointed out that Pb maximum retention onto soil surface increases with high pH value of soil system, since in general, maximum retention of cationic metals occurs at pH>7 (Harter, 1983). Therefore, as the pH of the soil environment of the spoil mines were mostly around 6, therefore, the retention of Pb on the soil of the study area was relatively weak. Therefore, Pb could significantly be released into the nearby aquatic and terrestrial environmental compartments, which in turn could lead to a serious environmental and health problem to localities in the vicinity.

Conclusion: Based on the results obtained from mineralogical analysis of the of Nantymwyn (Rhandirmwyn) derelict mine still consists of Pb of different fractions, which are originated from the primary Pb bearing mineral (PbS) as a result of secondary mineralisation process. The results revealed that Anglesite was found to be the most frequent and soluble among the five forms of Pb observed in the area. Hence, the soil of spoil heaps of Nantymwyn (Rhandirmwyn) abandoned mine site could potentially be a source of contamination to nearby aquatic and terrestrial environmental compartments. On the other hand, the XRD analysis revealed that the soils of all the seven locations studied are dominated by quartz and aluminosilicates, which could bind Pb and affect its mobility, but with the acidic nature of the soil of the locations Pb could be leached into the environment and be source of contamination. Therefore, as the inhabitants of the Rhandirmwyn community are proposing to turn the site into a recreational and/or residential area for the sake of environmental management and utilisation, the Nantymwyn (Rhandirmwyn) derelict mine must first be remediated to avoid recurrent Pb poisoning in the area after reclamation.

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Table 1. Forms of lead observed from SEM-EDX analysis

Locations	Forms of lead observed				
	Galena PbS	Anglesite $PbSO_4$	Cerussite $PbCO_3$	Mimetite $3Pb_3As_2O_8PbCl_2$	Pyromorphite $3Pb_3P_2O_8PbCl_2$
1	1	2	1		
2	2	3			1
3		1	7		
4		8	1		
5		4			1
6		2	1	2	
7	5				

Note: Any number greater than 1 under the mineral forms means that the mineral form was observed in more than one location within the sampling area.
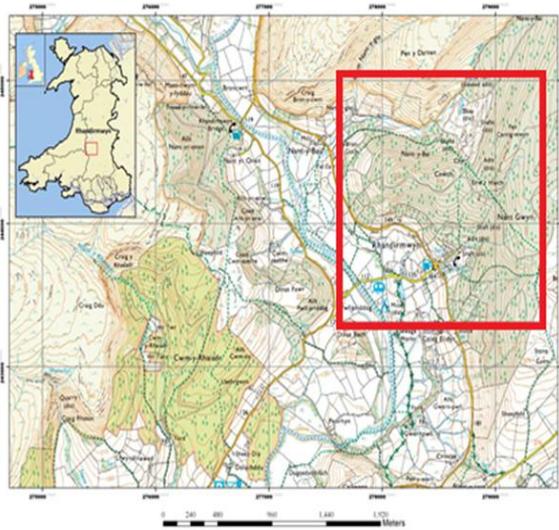

Fig 1. Location map showing the study area in regional context. Digimap
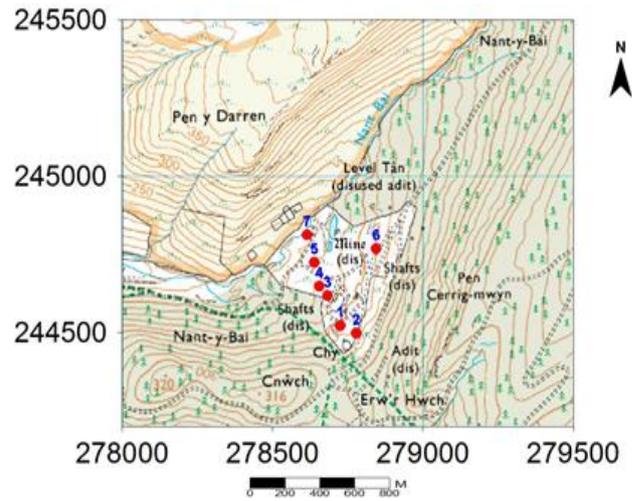
Fig 2. Showing soil sampling locations

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Compound present: Pbs(galena)

Compound present: $3Pb_3As_2O_8PbCl_2$ (Mimetite)

Compound present: $PbSO_4$ (Anglesite)

Compound present: $PbCO_3$ (Cerussite)
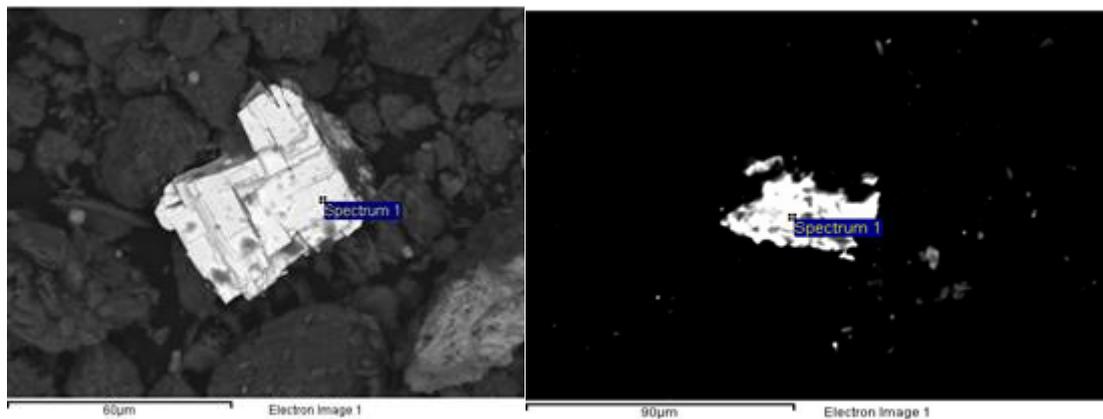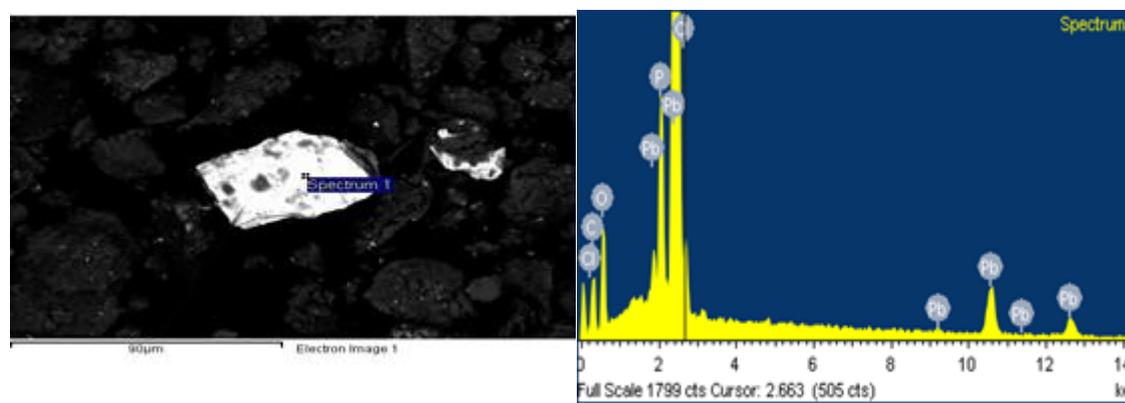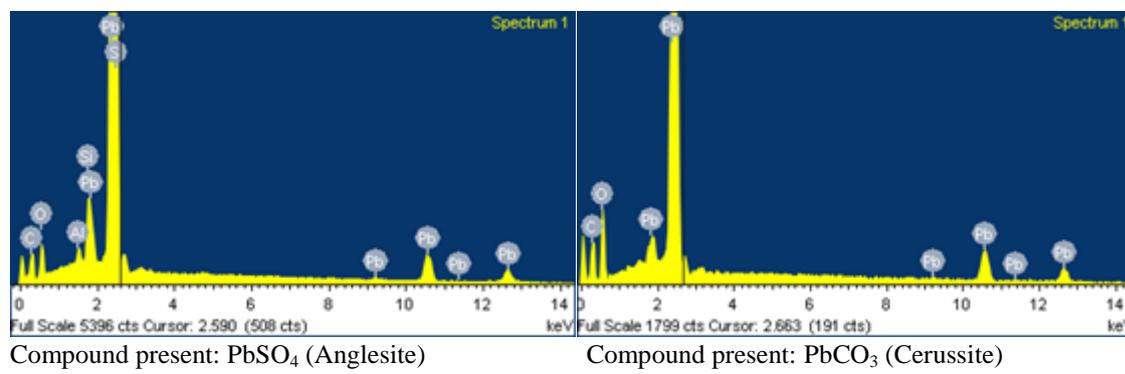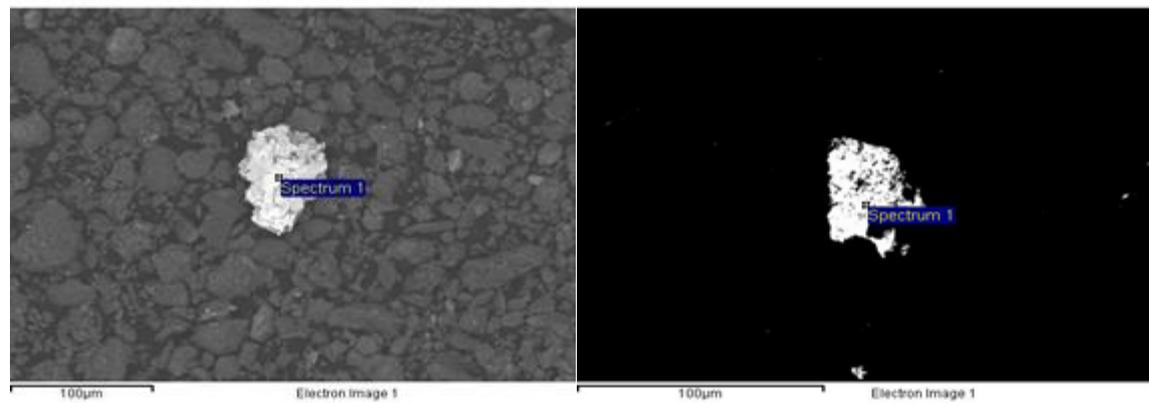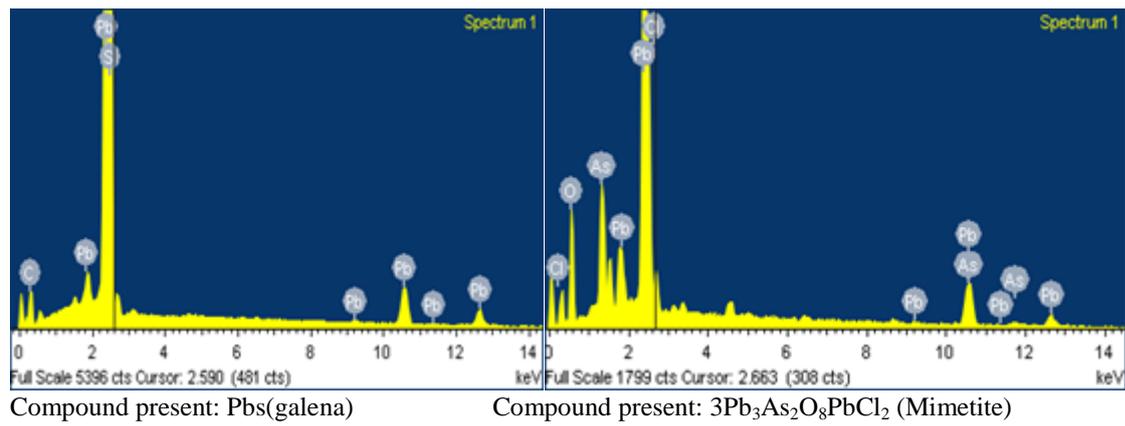
Fig 3. The mineral forms of lead observed in the samples by SEM-EDX analysis.

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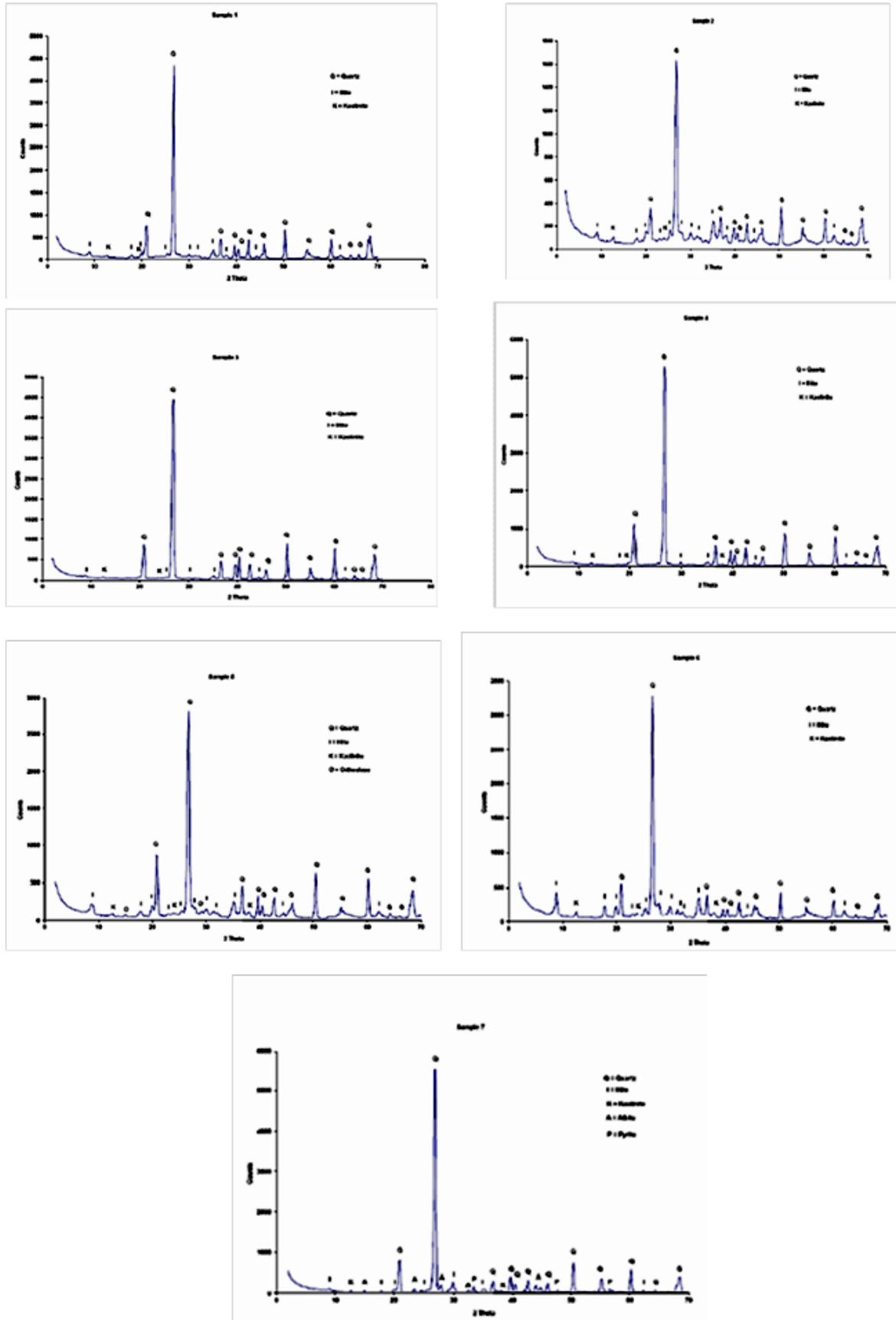
Figure 4. Soil mineralogical components observed during XRD analysis

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