Study of Toxic Elements in Iron Ores from the *Ojos Negros* District (Teruel, Spain)

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ABSTRACT

The main objective of this work was to know the amount of toxic elements associated to iron ores from the mine of *Ojos Negros* (Teruel, Spain). These toxic elements are phosphorus, sodium and potassium in order of importance. The presence of phosphorus in iron minerals increases the fragility of iron and steel products, and alkaline elements produce complex carbonates which affect the normal function of the blast furnace and their refractory materials. In this sense 148 samples were analysed, corresponding to different depths of three drillings located in the zone called *Tio Elias*, sited in the mountain range of *Sierra Menera*, near the location of *Ojos Negros*; one of the most important iron mines of the Iberian Peninsula. A mineralogical and chemical characterization of these samples was carried out. Correlations between the studied toxic elements (Na_2O, K_2O y P_2O_5) and the major constituents showed that Na and K were in a close relation with micaceous minerals from slates like moscovite and paragonite, reaching values about 2.5 % for $Na_2O + K_2O$, while P showed concentrations lower than 0.32% and was in close relation with Mg-Ca carbonates, iron oxides and iron hydroxides like ferrihidrite and goethite.

INTRODUCTION

Iron is the fourth element more abundant in the nature. Its deposits are known from antiquity and they were used in numerous applications. In this sense, Spain has been one of the word leading iron producers during the last part of the 19th and the first quarter of the 20th centuries (Zitzman and Neumann-Redlin, 1976). Nowadays, Spain has abundant reserves of this element. An example is the *Ojos Negros Complex (Teruel, Spain)*, one of the larger Spanish iron ores (Fernández-Nieto, 1977).

Several aspects must be taken into account to consider an iron deposit economically profitable, such as appropriate volumetric measurement, chemical composition, physical composition relating to the grain size and geographical location. In particular, aspects concerning to chemical composition are very important, since the mean contents of certain elements should be restricted to the established limits to prevent that companies can drive back the raw material if they do not fulfil the necessary requirements.

The main objective of this work is to know the amount of those chemical elements associated to iron ores from the mine of *Ojos Negros (Teruel, Spain)*. Among these elements, the presence of phosphorus above a determined level increases the fragility of iron and steel products and forces the election of a particular industrial process. Then, there is a general trend to reduce costs avoiding the employment of mineralizations with high phosphorus contents. Phosphorus could be also a problem if it is solubilised since it could cause ecological impacts in surface waters (Haygarth, 2005, Haygarth *et al*, 2005). On the other hand, alkaline elements (sodium and potasium) produce complex carbonates, which are deposited in the refractory materials affecting the normal function of the blast furnace.

The *Ojos Negros Complex* is sited at a height of 1500 m in the mountain range of Sierra Menera. This mountain range is located between *Teruel* and *Guadalajara* provinces and it is limited by *Tajo* (western slope) and *Ebro* (eastern slope) river basins. This zone is located in the central part of the *Iberian Range*, in the called *Rama Castellana* or *Celtiberics Chains*, which consists of small *Mesozoic* massifs cored by a *Palezoic* basement and separated by basins filled by detrital rocks during the *Tertiary* and *Quaternary* periods. *Sierra Menera* is a *Paleozoic* massif composed by goethite gossans formed from weathering processes (Villena, 1976). It is hosted by *Ordovician* and *Silurian* basement rocks (western of Iberian Range). The basal portion of the stratigraphic sequence consists of quartzites and graywackes of *Early Ordovician* age with intercalations of sandstones and iron oolitic layers (Herranz *et al*, 2003). It is overlaid by a *Late Ordovician* carbonate-dominated succession, known as the *Pobo limestones* (Villena, 1976) which is divided into three members: (i) quartzites and sandstones with silty intercalations, (ii) an irregularly distributed sequence of marls, shales and carbonates (*Cabezo limestones*) including Mg-Fe carbonates and (iii) dolostones, iron oxides and hydroxides and clays (see Figure 1).

The strata-bound orebodies are preferentially located on the flanks of *Sierra Menera* anticline. At the south, five *Paleozoic* massifs crop out (Villena, 1976; Fernández-Nieto *et al*, 1977, 1979, 1981 and 2003) and they are mainly composed of Mg-Fe carbonates (belonging to siderite-magnesite series) and dolomite, with a gangue of quartz, clay minerals and calcite.

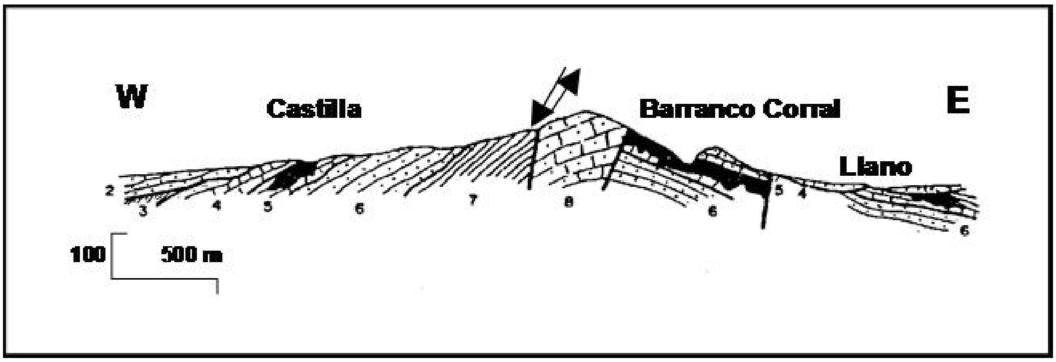

Figure 1: Schematic cross section in the *Sierra Menera* unit.
1. Quaternary 2. Buntsandstain 3. Ampeletic slates 4. Quartzites
5. Cabezo limestones and ore formation 6. Colmenarejos quartzites
7. Venta graywackes 8. Armoricans quartzites.

EXPERIMENTAL

Sampling zone

Sampling was carried out in the area called *Tio Elias*, located in the NE slope of *Sierra Menera*. The orebody was according with the sandstones and quartzites from the surroundings. Materials have a low crystalline grade. They are very hydrated and plenty of holes, showing recent deposits (Urquiza et al, 1985). A total of 148 samples corresponding to different depths of three drill holes (TE1, TE2 and TE3) were analysed. A bore B-50 in continuous wined (one sample per meter) was used except in the sterile zone where samples were collected at different depths.

Procedures

The mineralogical composition were analyzed by X-Ray Diffractometry (XRD) (Shultz, 1964; Barahona, 1974, Brindley, 1980) using a Siemens D-5000 diffractometer with a wolfram cathode and iron anode working at 30 mA and 40 kV. Scans from 3 to 65 degrees with 2θ/min speed were made with slits of entrance and divergence of 0.18 and 1° respectively.

For the chemical analysis, samples were dried at 110ºC and they were subjected to a particle homogenization using a ball grinder until reaching a particle size of 74 µm. Digestion of samples was carried out in the following way: 0.1 g of homogenized sample was treated two hours in closed vessels at 130-160ºC with a mixture of 4 mL aqua regia and 2 mL concentrated hydrofluoric acid. 10 mL of saturated boric acid solution was added to the obtained solution and it was diluted to 25 mL with water. Al, Ca, Fe, Mg and Mn were determined by Flame Atomic Absorption Spectrometry (FAAS), using a Perkin Elmer 503 spectrometer, while Na and K by Flame Atomic Emission Spectroscopy in a Cornning spectrometer.

Two types of digestion procedures were carried out in order to determine the phosphorus content in the samples,. When they were lower than 0.05%, 1 g of sample was treated with 30 mL of (1+1) nitric acid and heated until nitrous vapours appeared. Then 10 mL of 2.5% potassium permanganate and 10 mL of hydrogen peroxide were added to obtain a colourless liquid. Finally 10 mL of 2% ammonium vanadate were added and the solution heated and filtered through a 238 paper filter. The obtained solution was poured into a 100 mL volumetric flask, 10 mL of 5% ammonium molybdate were added and it was diluted to the mark.

When the phosphorus contents were higher than 0.05%, 1 g of sample was treated with a mixture of 25 mL percloric acid, 18 mL nitric acid and 7 mL hydrochloric acid and heated until percloric vapours were obtained. Solution was filtered through 242 paper filter and diluted to the mark in 100 mL volumetric flask. An aliquot of 10 mL of this solution was taken and treated with 10 mL of 1% bismuth nitrate, 10 mL of 2% ammonium molibdate and 2 mL of 2% ascorbic acid. It is diluted to the mark in 100 mL volumetric flask.

In both cases, a standard solution of 1 $g.L^{-1}$ of phosphorus was prepared by dissolution of potassiumdihydrogenphosphate in water. Aliquots of this solution was taken and treated in the same way that samples in order to prepare a calibration curve. All measurements were made by using a spectrophotometric method where standards and samples were treated with the reactive vanadium-molibdate and determined at 430 or 725 nm (Jackson, 1976). All measurements were referred to a blank solution.

Finally, a statistical processing of data was made in order to establish correlations between the chemical elements (Na, K and P) and the major constituents independently for each drill hole.

RESULTS AND CONCLUSIONS

Geological and mineralogical composition

Geological and mineralogical composition of the three drill holes are shown in Figure 2 and 3.

The drill hole number TE 1 was sited in the western zone. It is well mineralized with a depth of 119 m, showing three different zones. The first 56 m were composed by fine grains of quartzites in shades from grey to yellow-reddish. Dispersed micaceous layers were detected with intercalations of grey slates. The mineralized zone (53 m) was in a red colour due to the presence of powdered iron materials with diverse compact degrees. It could be detected the presence of goethite, hematite, quartz, carbonates (calcite, dolomite and magnesite) and traces of phyllosilicates. Finally, the last zone was formed by two lithologies. One of them was the nearest to the mineralization with slates, quartz (60%) and muscovite (well crystallised). The second one, located at the bottom, was a dark pelitic zone with a decrease of the iron ore and a high level of micaceous minerals, quartz, dolomite, siderite and goethite.

The drill hole number TE 2 was located at the eastern of TE 1. It is the drill hole with a minor mineralization with 111 m of depth. The first 18 m were compact and greasy and they were composed by black slates. The second length (32 m) was composed by medium- to thick-grain quartzites with eventual slates. At the bottom of the drill hole it could be distinguish three parts: an upper zone composed by quartz and carbonates (magnesite and dolomite), an intermediate zone where quartz, goethite, hematite an iron-magnesium carbonates were detected and finally, a dolomitic zone with goethite.

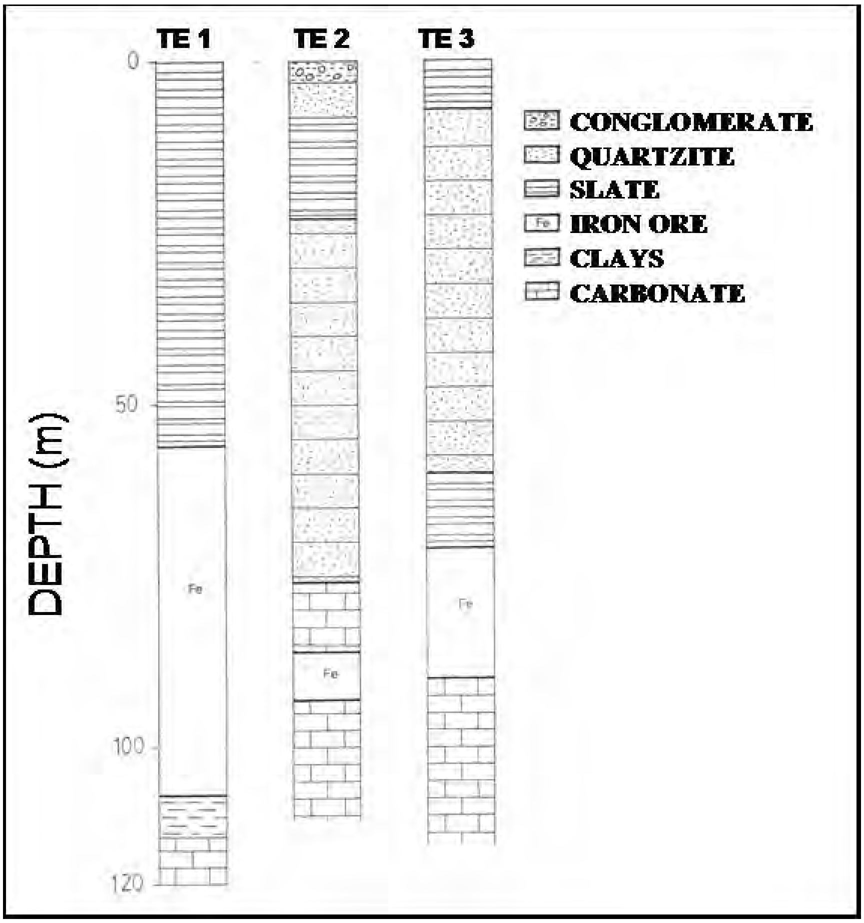

Figure 2: Geological composition of drill holes.

The last drill hole (number TE 3) with 115 m of depth was located at the north of the drill hole number TE 2. The first length (70 m) was composed by compact quartzites of thick grains in grey-white to yellow tones with eventual slate beds. In the second length (45 m) iron ores in shades of red were presented with quartz and phyllosilicates increasing the dolomitic materials with the depth.

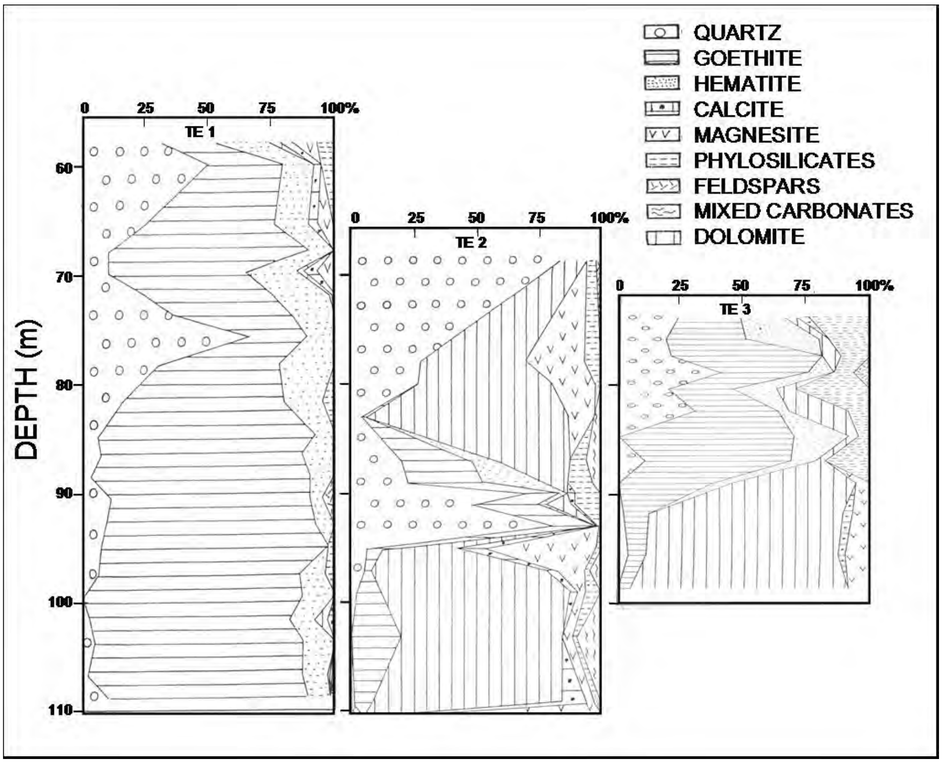

Figure 3: Mineralogical composition of drill holes.

Chemical and statistical analysis

Chemical elements such as Al, Ca, Fe, K, Mg, Mn, Na and P were determined as described above. Their results have been expressed as percentages of their respective oxides (see Table 1). In this table the average and the standard deviation as well as the maximum and minimum values obtained for each element are shown for each length established in TE 1, TE 2 and TE 3 drill holes.

Considering the iron ore length, the highest mean percentage in the iron content (61.7%) was found in TE 1, with a maximum value of 75.1%, followed by TE 3 (51.0%) with a maximum value of 64.3%, being TE 2 the least mineralized with average content of iron about 40.2% and maximum value of 56.3%. TE 1 was the drill hole with a higher grade of mineralization, but at the same time presents the highest amounts of Na, K and P associated to the iron ore. It is remarkable the amount of K (1.70%) with a maximum value of 26.0% compared with the other ones (TE 2 with an average value of 0.047% and maximum value of 0.090% and TE 3 with an average value of 0.035% and maximum value of 0.060%). TE 1 also showed the highest average values for Mn and Ca. TE 2 has the highest average values for Al and TE 3 for Mg and similar average value for P (0.085%) than TE 1 (0.087%).

In the length above iron ore, it is remarkable the higher amounts of Al (18.4%) and K (0.70%) in TE 1, Ca (4.99%) and Mg (3.68%) in TE 2 as well as the lower amounts of Fe (2.43%), Mn (0.08%), Na (0.013%) and K (0.031%) in TE 3.

In the length under the iron ore, it is noticeable the higher amounts of Al (20.0%), Na (0.54%), K (0.91%) and P (0.036%) in TE 1, Ca in TE 2 and TE 3 with average values of 20.0 and 26.0%, respectively.

A statistical study of chemical data were carried out in order to establish correlations between the primary chemical elements of this investigation (Na_2O + K_2O and P_2O_5) and the major elements more representative of the surrounding rocks (Al_2O_3 and CaO/MgO). From the results obtained, in Figure 4 (1-3) are shown those more relevant.

Relation between alkaline elements (Na_2O + K_2O) and the content of Al_2O_3 was only remarkable for TE 2 drill hole (Figure 4-1). Bulk of samples are locate is a small area (A). The rest of samples correspond to the upper length. Among them, two populations could be observed (B and C). One of them (B) was in close relation with materials composed by quartz and slates from the top of the mineralization, where dioctaedric micas of muscovite type and paragonite with structural K and Na were detected. There were the highest contents of Al_2O_3 and values of Na_2O + K_2O near 2.5%. The second population (C) showed a notable reduction of Al_2O_3 contents (< 4.5%) while alkaline elements were between 1.2 and 1.8%. In general, dispersion of alkaline elements was higher due to their higher mobility compared with aluminium.

DRILLHOLE TE-1	**0-56 m**				**56-111 m**				**111-119 m**			
Nº Samples	14				45				5			
	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**
Fe_2O_3	5.33	2.07	2.47	8.93	61.7	7.96	38.0	75.1	11.85	5.82	5.01	19.7
MnO	0.29	0.58	0.03	2.24	2.92	0.65	2.16	6.47	1.01	0.78	0.18	1.95
Al_2O_3	18.4	4.68	10.4	24.4	1.52	3.82	0.19	26.0	20.0	8.53	8.26	27.1
CaO	3.68	4.10	0.01	14.0	3.53	2.71	<0.01	11.3	7.22	7.61	2.10	20.5
MgO	2.77	2.72	0.12	9.08	2.08	1.55	<0.01	6.22	2.80	2.82	1.24	7.83
Na_2O	0.43	0.34	0.03	1.16	0.61	0.43	0.02	1.31	0.54	0.33	0.12	0.95
K_2O	0.70	0.44	0.11	1.44	1.70	3.75	0.14	26.0	0.91	0.51	0.34	1.63
P_2O_5	0.025	0.010	0.014	0.046	0.087	0.046	0.002	0.206	0.036	0.012	0.025	0.055
DRILLHOLE TE-2	**93-110 m**				**87-93 m**							
Nº Samples	24				6				11			
	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**
Fe_2O_3	6.27	10.6	0.82	52.0	40.2	11.15	22.1	56.3	14.8	10.3	4.84	40.9
MnO	0.27	0.48	<0.01	2.28	1.67	0.43	0.97	2.29	0.69	0.56	0.27	2.28
Al_2O_3	5.38	4.99	0.96	15.1	2.54	0.44	2.08	3.22	1.21	0.74	0.49	2.23
CaO	4.99	7.18	0.21	22.7	1.59	2.84	0.01	7.31	20.0	7.29	7.60	29.8
MgO	3.68	5.43	0.01	18.0	1.56	2.53	0.01	6.61	14.8	2.35	8.21	16.9
Na_2O	0.40	0.55	<0.01	1.68	0.037	0.018	0.020	0.070	0.021	0.011	0.010	0.040
K_2O	0.44	0.60	0.01	1.95	0.047	0.022	0.030	0.090	0.034	0.020	0.010	0.070
P_2O_5	0.028	0.063	0.001	0.320	0.057	0.018	0.037	0.076	0.023	0.010	0.008	0.041
DRILLHOLE TE-3	**0-72 m**				**72-92 m**				**92-114 m**			
Nº Samples	10				20				13			
	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**	$\bar{x}$	**σ**	**Minimum**	**Maximum**
Fe_2O_3	2.43	2.58	0.76	9.31	51.0	11.5	11.2	64.3	6.64	2.00	4.32	12.3
MnO	0.08	0.11	0.01	0.34	2.63	0.63	0.56	3.78	0.42	0.21	0.24	1.09
Al_2O_3	1.77	1.06	0.83	4.36	1.32	0.65	0.26	3.02	0.84	0.66	0.19	2.10
CaO	3.85	9.18	0.11	29.8	2.58	5.51	0.01	24.1	26.0	7.85	0.38	30.8
MgO	2.23	5.67	0.01	18.2	2.39	3.25	0.68	16.0	15.7	5.53	0.46	26.4
Na_2O	0.013	0.009	<0.01	0.030	0.023	0.017	<0.001	0.060	0.032	0.023	0.010	0.090
K_2O	0.031	0.012	0.020	0.050	0.035	0.018	<0.001	0.060	0.043	0.028	0.010	0.110
P_2O_5	0.031	0.026	0.009	0.101	0.085	0.076	0.016	0.300	0.015	0.011	0.007	0.046

TABLE 1. Chemical composition expressed in percentage ($\bar{x}$ = average value, σ= standard deviation)

Figure 4-2 represents the correlation between P_2O_5 and CaO/MgO for the TE 3 drill hole. Some anomalies were presented in relation to depth. It could be observed a group of samples with values of P_2O_5 lower than 0.04% corresponding to the top (A) and the bottom (B) of the drill hole. The rest of samples, were from the mineralization zone (C), showing a great dispersion in phosphorus content (average value of 0.085 ± 0.076%) and a relation CaO/MgO lower than 1. It could be also observed a sterile zone that can not be explained at the moment but probably it corresponded to samples of lithologic units which are not present in this study.

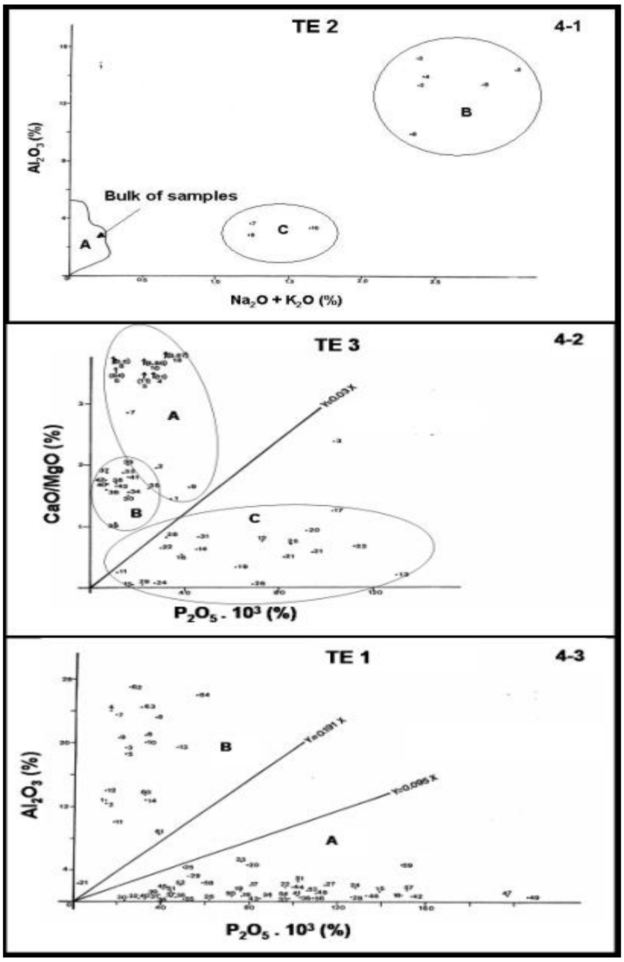

Figure 4: Correlations between the primary chemical elements and major elements.

Figure 4-3 shows the correlation between P_2O_5 and Al_2O_3 for TE 1 drill hole. It could be observed a great dispersion of samples into two regions (A and B). Region A comprised samples of the mineralization zone with very low Al_2O_3 content and variable contents of P_2O_5. In region B samples from upper and lower length zones are mixed without apparent relation. Between region A and B there is a sterile zone. The explanation would be the same that in Figure 4-2.

From the studies carried out we can conclude that Na and K were in a close relation with micaceous minerals from slates like muscovite and paragonite and in a minor proportion with feldspars associated to quartzites. P was in close relation with Mg-Ca carbonates, iron oxides and iron hydroxides like ferrihidrite and goethite. According to Stoddat *et al*, 1983 the presence of reefs in the surroundings of the mineralization could be a primary source of phosphorus.

On the other hand, the subaerial character of the mineralization together with its high porosity and the predominance of hemihydrated phases (goethite) over anhydrous phases (hematite) were indicative of deposition conditions later to metamorphism stages (Fernandez Nieto, 1981) dating the age of karstification in the Middle Pliocene.

The powdered character of the mineralization was due to the existence of small particles (0.2-3.0 μm) with an incipient degree of crystallization and low cohesion among them.

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