Trace elements in phosphorites of different provenance

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Abstract
28 samples of phosphorite from 12 deposits were analyzed for 20 trace elements, besides 7 samples data gathered from the literature. In total, were studied 35 samples of phosphorites from 19 deposits of 9 countries. The trace elements phosphorites of this work in decreasing order of mean abundance are (mg/kg): Sr (1228) > B (330) > Cr (176) > V (121) > Mn (102) > U (82) > Ni (25.9) > Cd (23.1) > Cu (20.9) > Zn (20) > Mo (17.1) > As (12.1) > Pb (7.4) > Co (6.6) > Se (5.6) > Th (3.4) > Sb (1.6) > Ag (0.97) > Sn (0.88) > Tl (0.7). These data also were compared with complementary literature data. Hierarchical cluster analysis allows us the following features: 1) The samples from Bayovar-Sechura are distinguished and grouped mainly in the same cluster. 2) The samples from Morocco, except the Youssoufia deposit, are grouped in a cluster. 3) The samples from Florida (US) are grouped with homogeneity except the deposit Lee Creek Mine. 4) The Geological Age is distinguished and grouped with homogeneity, except in few cases where the action of some other factors could weaken the importance of Geological Age.

Key Words
Rock phosphate, trace elements, chemical analysis, statistical analysis, provenance.

Introduction
Sustainable agriculture is based upon moderate use of agrochemicals. Some of them, such as phosphate rocks, contain abundant trace elements (Bech *et al.* 2009). Among them, Cu, Zn and Mo are essential nutrients, but high levels of others such as Cd, Pb, As, Se and U are undesirable for the possible transfer from soils to the human food chain. Phosphorite ores of different geographical provenance can vary substantially in trace elements contents. Nevertheless phosphorites from different origin contain a distinctive trace element assemblage. So it should be possible to identify the origin of a particular rock phosphate by its trace element pattern. Therefore to minimize environmental and healthy risks is important to know the phosphorite trace element assemblages, and use suitable phosphorites of the known provenance with a low potential toxic trace element contents. The aim of the present work is the estimation of 20 trace elements: Ag, As, B, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Tl, U, V and Zn of phosphorites of deposits from various origins.

Material and methods
Studied samples
Table 1 gives 35 studied phosphorite samples, 28 analyzed by the authors and 7 culled from the literature. The geographic provenance is indicated in the same table. Moreover, we compare the average of these 35 samples with those of complementary literature.

Analytical methods
Aqua regia extracts were used to estimate the pseudototal values of these elements, following standard procedures (ISO 1466 2002) and measured with ICP-AES and ICP-MS. Quality control and detection limits were detailed in Bech *et al* (2009).

Statistical methodology
Trace element concentrations in phosphate of different provenance are reported by computing the mean, the standard deviation, the standard error and the range. To complete the data description other statistics (minimum, 25th, 50th and 75th percentiles and the maximum) are also summarized. Correlations between the trace element concentrations are investigated by using the Spearmen's correlations based on ranges without any distribution assumption. Multivariate relationships between trace element and sample units are analyzed by performing a cluster analysis. Data analysis was performed using standard packages of the R statistical computing project.

Results and discussion

Statistical data

Table 2 (not shown) consists of the summary statistics of the trace elements in the studied phosphorites. The trace elements in phosphorites of this work in decreasing order of mean abundance are (mg/kg): Sr (1228) > B (330) > Cr (176) > V (121) > Mn (102) > U (82) > Ni (25.9) > Cd (23.1) > Cu (20.9) > Zn (20) > Mo (17.1) > As (12.1) > Pb (7.4) > Co (6.6) > Se (5.6) > Th (3.4) > Sb (1.6) > Ag (0.97) > Sn (0.88) > Tl (0.7). There is a very high level of Sr (that constitute a “first group”) followed by other groups of elements: second group: with relative high concentrations: B, Cr, V, Mn and U; third group, with moderate concentrations: Ni, Cd, Cu, Zn, Mo and As; fourth group with relative low concentrations: Pb, Co, Se and Th; fifth group, with very low concentrations: Sb, Ag, Sn and Tl. Table 3 (not shown) gives the comparison between the trace element averages in the phosphorites of this work with those of complementary literature data. The ratio: this study average, tsa, versus complementary literature data average, clda, give 3 groups of trace elements: Group I (tsa/clda<0.54): Ag, Mn, Pb, Sn and Th.Group II (0.54 < tsa/clda < 1.22) : As, Cd, Co, Cr, Cu, Ni, Sb, Sr, U and V.Group III(tsa/clda>1.22): B, Mo, Se, Tl and Zn.

Inter-elemental correlations

Table 4 (not shown) give us the positive and negative correlations between the trace elements of phosphorites of the present study. To measure the correlation we have used the Spearman correlation coefficient. Several trace elements exhibit significant positive interelemental correlations which point to their common enrichment processes in phosphorites. This was found between: Ag-Sb (r=0.76), Ag-V (r=0.61), Ag-Zn (r=0.84), Cd-Zn (r=0.60), Co-Mn (r=0.65), Cr-Ni (r=0.60), Cu-Ni (r=078), Mn-Pb (r=0.66), Sb-U (r=0.69), Sb-V (r=0.76) and U-V (r=0.68). Significant negative correlation was found between: B-Co (r=-0.53), Co-Sb (r=-0.53), Co-U (r=-0.51). Co-Zn (r=-0.58) and Se-Sn (r=-0.51).

Hierarchical cluster analysis

To describe underlying group similarities between samples we have analyzed the three data sets (Table 1) with hierarchical cluster analysis (Figure 1). We observe:

1) The samples from Bayovar-Sechura are distinguished and grouped mainly in the same cluster.
2) The samples from Morocco, except the Youssoufia deposit, are grouped in a cluster.
3 The samples from Florida (US) are grouped with homogeneity except the deposit Lee Creek Mine.
4) The Geological Age is distinguished and grouped with homogeneity, except in few cases where the action of some other factors could be weaken the importance of Geological Age.

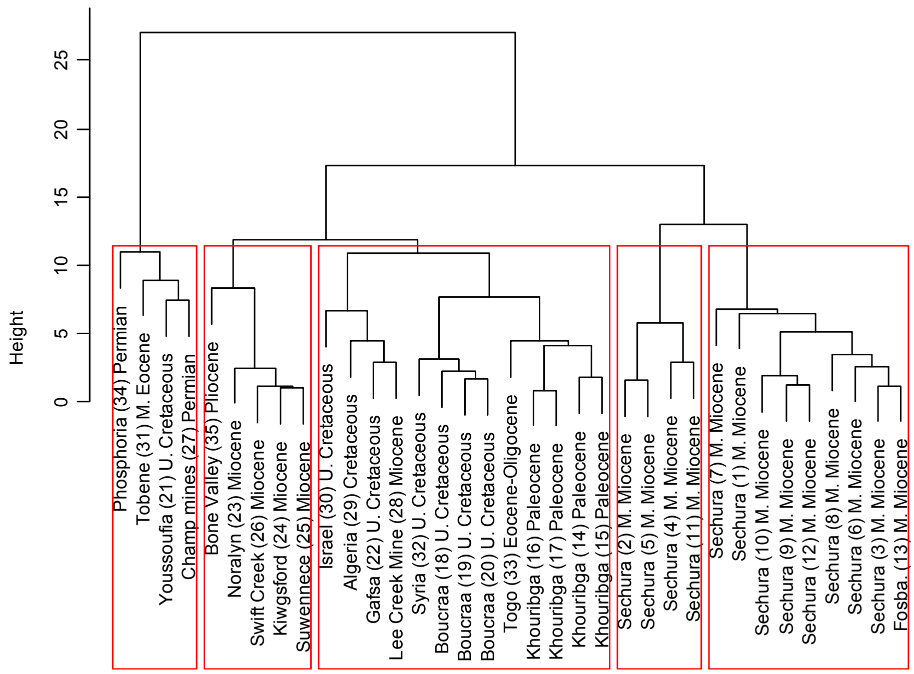

Figure 1.

Table 1.

Set 1: Samples of naturally occurring rocks of Bayovar-Sechura analyzed in this work				
Country	Deposit	Bed	Geological Age	Sample No.
Peru	Area I	I-C	Middle Miocene	1
Peru	Area I	I-B-A	Middle Miocene	2
Peru	Area I	I-1	Middle Miocene	3
Peru	Area I	I-1-2	Middle Miocene	4
Peru	Area I	I-1-2-3	Middle Miocene	5
Peru	Area I	I-3	Middle Miocene	6
Peru	Area II	II-1	Middle Miocene	7
Peru	Area II	II-5	Middle Miocene	8
Peru	Area II	II-6	Middle Miocene	9
Peru	Area II	II-7-top	Middle Miocene	10
Peru	Area II	II-7-volcanic tuff	Middle Miocene	11
Peru	Area II	II-7-base	Middle Miocene	12
Set 2: Samples obtained from commercial sources analyzed in this work				
Country	Deposit	Phosphate producer		
Peru	Fosbayóvar	Minera Bayovar	Middle Miocene	13
Morocco	Khouribga KIID	Office Chérifien des Phosphates	Paleocene	14
Morocco	Khouribga KIISB	Office Chérifien des Phosphates	Paleocene	15
Morocco	Khouribga KIISL	Office Chérifien des Phosphates	Paleocene	16
Morocco	Khouribga KIIC	Office Chérifien des Phosphates	Paleocene	17
Morocco	Boucraa BGA	Phosphates de Boucraa, S.A.	Upper Cretaceous	18
Morocco	Boucraa BGB	Phosphates de Boucraa, S.A.	Upper Cretaceous	19
Morocco	Boucraa BGC	Phosphates de Boucraa, S.A.	Upper Cretaceous	20
Morocco	Youssoufia YN	Office Chérifien des Phosphates	Upper Cretaceous	21
Tunisia	Gafsa	Compagnie des Phosphates de Gafsa	Upper Cretaceous	22
Central Florida, USA	Noralyn	Imc-Agrico	Miocene	23
	Kiwgsford	Imc-Agrico	Miocene	24
North Florida, USA	Suwennece	Occidental Chemical Co.	Miocene	25
	Swift Creek	Occidental Chemical Co	Miocene	26
Idaho, USA	Champ mines	NU-West Industries	Permian	27
North Carolina, USA	Lee Creek Mine	TexasGulf Inc.	Miocene	28
Set 3: Samples of literature data				
Country	Deposit	Reference		
Algeria	Undeterminated	Sattouf (2007)	Cretaceous	29
Israel	Undeterminated	Sattouf (2007)	Upper Cretaceous	30
Senegal	Tobene	Samb (2002)	Middle Eocene	31
Syria	Undeterminated	Sattouf (2007)	Upper Cretaceous	32
Togo	Undeterminated	Sattouf (2007)	Eocene-Oligocene	33
USA	Phosphoria Formation	Gulbrandsen (1966)	Permian	34
Florida, USA	Bone Valley	Altschuler (1980)	Pliocene	35

Conclusions

The trace elements in phosphorites of this work in decreasing order of mean abundance (mg/kg) are: Sr (1228) > B (330) > Cr (176) > V (121) > Mn (102) > U (82) > Ni (25.9) > Cd (23.1) > Cu (20.9) > Zn (20) > Mo (17.1) > As (12.1) > Pb (7.4) > Co (6.6) > Se (5.6) > Th (3.4) > Sb (1.6) > Ag (0.97) > Sn (0.88) > Tl (0.7). Several trace elements exhibit significant positive interelemental correlations which point to their common enrichment processes in phosphorites. The negative correlations are in agreement with the geochemical affinities between these pairs of elements. In the case of positive correlations, the agreement geochemical is only partial: There are different factors, not only geochemicals, of enrichment of trace element phosphorites. The cluster analysis allowed three main groups: Bayovar-Sechura, Morocco, except the Youssoufia deposit, and Florida (US), are grouped with homogeneity except the deposit Lee Creek Mine.

References

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