



STANDARD CHARACTERIZATION OF PHOSPHATE ROCK SAMPLES FROM THE FAO/IAEA PHOSPHATE PROJECT

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Abstract. Phosphate rocks (PR) are phosphate-bearing minerals that vary widely in their inherent characteristics and consequently their agronomic potential. In the framework of a FAO/IAEA networked research project, the evaluation of the agronomic effectiveness of natural and modified PR products under a variety of soil climate and crop management conditions was carried out. The characterization of phosphate rocks is the first and essential step in evaluating their suitability for direct application. If several PR sources are utilized, standardized methods should be used for comparison purposes to determine their agronomic potential. This paper describes the standard characterization of phosphate rock products utilized in the project, in particular the mineralogical and crystallographic analyses, physical analyses, chemical composition and solubility in conventional reagents. A total of 28 phosphate rock samples from 15 countries were collected and analyzed in specialized laboratories. The data on mineralogy, chemical composition and solubility in conventional reagents are closely interrelated. An arbitrary classification of the reactivity of the PR samples was made based on the solubility indices in conventional reagents. On another hand, the results of the crystallographic parameters, calculated indices of absolute solubility, specific surface and porosity reflect the variability of the physical state and the sample pre-conditioning treatment of the analyzed products. A proper characterization of phosphate rock samples should provide the maximum of basic information that can be obtained in a cost-effective manner in normal chemical laboratories. Based on the results of this characterization, the following determinations are recommended: a description of the sample, major elemental (total P, Ca, Mg) composition, solubility in conventional reagents (neutral ammonium citrate, citric and formic acid) and particle size analysis. The classification of PR samples for direct application as fertilizers requires the definition of standards. It should be noted that the European standards are very strict with regard to solubility and particle size. The studies carried out under this project are part of the efforts to provide some guidelines for the provision of such standards in other environmental conditions, in particular tropical acid soils. Follow-up studies are required to evaluate the agronomic effectiveness of the PR, i.e. actual performance of the PR under study as affected by a specific set of soil, crop, climate and management conditions. In a final phase, it would be required to relate the results agronomic potential from the study with those of actual agronomic effectiveness and several other socioeconomic criteria for developing adequate Decision Support Systems for PR application.

1. INTRODUCTION

In many acidic soils in developing countries, P deficiency is the main limiting factor for crop production and, therefore, requires the application of P fertilizers for optimum plant growth and production of food and fibre. However, in most developing countries superphosphates, which are the commercially available phosphatic fertilizers, are not produced locally and their supplies to resource-poor farmers is rather limited [1]. On the other hand, many developing countries possess deposits of phosphate rock (PR) minerals [2]. Many years of research have shown that PR can be used for direct application in agriculture and it is most effective when used in acid P-deficient soils. [3]. As this is commonly the case in most tropical soils, direct application of PR is considered an agronomic and economically attractive alternative to the use of more expensive water-soluble P fertilizers such as superphosphates [1, 4].

Considering the direct application of PR products, several factors affect their agronomic effectiveness or their capability to supply phosphorus to crops. These have been extensively described in several reviews for temperate [3] and tropical agriculture [1]. The various factors may be grouped into

three main categories, i) inherent PR factors, ii) soil factors and iii) plant factors. The PR products or materials differ widely in their geological origin, mineralogical, chemical and physical properties and consequently in their effectiveness [1, 5, 6]. It is, therefore, essential to identify and select PR products of good quality and suitable for direct application, in particular to tropical acid soils [7].

In the frame of the FAO/IAEA networked research project on “The use of nuclear and related techniques for evaluating the agronomic effectiveness of P fertilizers, in particular rock phosphates” the agronomic effectiveness of natural and modified PR products was evaluated under different soil, climate and crop conditions [8]. In addition to the individual characterization studies performed by the participating investigators, a standard characterization of the soils and PRs employed in the project was carried out with financial support of the World Phosphate Institute. The standard characterization was conducted to obtain direct and comparable information on the suitability of PRs for direct application and to better interpret the results from the agronomic evaluation, including the creation of a database for using a phosphate model.

This paper describes the standard characterization of phosphate rock products utilized in the project, in particular the mineralogical and crystallographic analyses, the chemical composition and solubility in conventional reagents, and the physical analyses. The results are synthesized and additional correlation studies are presented. Also, guidelines for their characterization are given.

2. MATERIALS AND METHODS

A total of 28 phosphate rock samples from 15 countries were collected for mineralogical as well as chemical and physical analyses (Table I). From these, two were granulated, 11 ungrounded and 15 ground samples. The exact origin of the products, and the treatments performed, if any, were not specified. Eight extra samples (2 PRs from Venezuela and 6 imported PRs from Malaysia) were received only for mineralogical characterization.

The majority of samples were reported to be phosphate rocks of commercial grade, after washing or beneficiation. Some have been directly obtained from the mine deposits, others have undergone some manufacturing process such as partially acidulation (Venezuela) or fusion (Brazil).

The chemical analyses, including solubility in conventional reagents and the physical analyses (particle size, specific area and porous volume) were performed at the “Centre d’Etudes et de Recherches des Phosphates Minéraux”, CERPHOS, Casablanca, Morocco [9]. The specific methods used are indicated in Table II. The mineralogical and crystallographic determinations were made at the “Centre de Recherches Pétrographiques et Géochimiques” of the “Centre National de Recherches Scientifiques” (CNRS), Nancy, France, by X-ray diffraction on compacted, non-oriented powder preparations. A total of 32 samples were analysed for mineralogical content.

3. RESULTS AND DISCUSSION

The results from the analyses performed on the PR samples have been grouped according to the type of analyses.

First of all, it should be noted that the available general information on the phosphate rock samples is very poor and incomplete. In many countries phosphate rocks are not available on a commercial scale. A description of the phosphate rock should include the origin of the rock sample (country and location of the deposit), type of deposit (geological formation), and pre-treatment/conditioning of the sample, if any, i.e. washing, grinding, beneficiation, heating, degree and kind of acidulation, granulation, etc. Most of this information can be obtained from the supplier.

The full set of analytical data for the mineralogical and crystallographic determinations, chemical and solubility in conventional reagents and textural analysis is not given in this paper. Rather, the summary tables from these results are presented and discussed.

3.1. Mineralogy

The main mineral content of the PR samples is shown in Table III. Apatite is the predominant mineral averaging 75%, ranging from 46–56% (China-Jingxiang, Russia, Brazil-Patos) to 90-95% (Togo 1, Morocco 2, Tunisia 2). These values are roughly equivalent to the percentage P₂O₅ content (Table VII).

Two other minerals of interest to agriculture are calcite and dolomite as sources of Ca and Mg. A relatively high content of calcite is observed for Morocco 3, Jordan 1, and Jordan 3 (14%) and Venezuela-Monte Fresco (28%). Dolomite content is high in Thailand-Racha Buri (34%), Morocco 1 (22%), and China-Jingxiang (21%), resulting also in high contents of CaO and MgO (Table VI). It is expected that these phosphates when applied in acidic soils would produce an important liming effect due to its Ca and Mg supply [10, 11].

Conversely, useless silica (quartz) contents are high in Russia PR (40%), Venezuela-Navay (35%), Brazil-Patos (30%) and China-Jinning (27%), Venezuela-Riecito (24%) and China-Jinxiang (23%). This mineral constitutes generally an exogangue, and needs to be removed in order to increase the P₂O₅ content of the final product and to decrease transportation and grinding costs [12, 3].

TABLE I. LIST OF PHOSPHATE ROCK (PR) SAMPLES UTILIZED IN THE PROJECT

PR Denominations	Country/Origin	Source	Analysis
ALGERIA	Algeria	IMPHOS	MINER/CHEM/PHY
MOROCCO 1	Morocco	IMPHOS	MINER/CHEM/PHY
MOROCCO 2	Morocco	IMPHOS	MINER/CHEM/PHY
MOROCCO 3	Morocco	IMPHOS	MINER/CHEM/PHY
TUNISIA 1	Tunisia	IMPHOS	MINER/CHEM/PHY
TUNISIA 2	Tunisia	IMPHOS	MINER/CHEM/PHY
TUNISIA 3	Tunisia	IMPHOS	MINER/CHEM/PHY
JORDAN 1	Jordan	IMPHOS	MINER/CHEM/PHY
JORDAN 2	Jordan	IMPHOS	MINER/CHEM/PHY
JORDAN 3	Jordan	IMPHOS	MINER/CHEM/PHY
SENEGAL	Senegal	IMPHOS	MINER/CHEM/PHY
MINJINGU	Tanzania	IMPHOS	MINER/CHEM/PHY
TOGO 1-	Togo	IMPHOS	MINER/CHEM/PHY
COMMERCIAL			
TOGO 2-HIBOGAN	Togo	IMPHOS	MINER/CHEM/PHY
PATOS	Brazil	Participant CRP	MINER/CHEM/PHY
YOORIN	Brazil	Participant CRP	CHEM
BAHIA INGLESA	Chile	Participant CRP	MINER/CHEM/PHY
TRINIDAD DE	Cuba	Participant CRP	MINER/CHEM/PHY
GUEDES			
NAVAY	Venezuela	Participant CRP	MINER
RIECITO	Venezuela	Participant CRP	MINER/CHEM/PHY
RIECITO PAPR	Venezuela	Participant CRP	CHEM
MONTE FRESCO	Venezuela	Participant CRP	MINER
MAARDU	Estonia/Lithuania	Participant CRP	MINER/CHEM/PHY
POLPINO	Russia	Participant CRP	MINER/CHEM/PHY
JINGXIANG	China	Participant CRP	MINER/CHEM/PHY
JINNING	China	Participant CRP	MINER/CHEM/PHY
RACHA BURI	Thailand	Participant CRP	MINER/CHEM/PHY
PETCHA BURI	Thailand	Participant CRP	MINER/CHEM/PHY

TABLE II. LIST OF STANDARDS METHODS FOR PR SAMPLES OF DIRECT APPLICATION

Chemical Element	Method
P ₂ O ₅ TOTAL ISO 6598	Dissolution of the sample using hydrochloric-nitric acid digestion. After dissolution, precipitation of the orthophosphate ions as quinoleine phosphomolibdate, the acid solution is passed at about 75°C through a filter, washed, dried with acetone. The obtained precipitate is weighed.
CaO	Dissolution of the sample using perchloric acid. The calcium is chelated in alkaline medium using excess amounts of EDTA. This excess is titrated with a calcium solution of known concentration in the presence of magnesium to make the change more visible.
MgO	Dissolution of the sample using perchloric acid digestion. Measurement of the magnesium content, by Atomic Absorption Spectrometry (AAS) with an air/acetylene flame, in presence of lanthanum nitrate as matrix modifier and at a wave length of 285.2 nm, or alternatively by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES).
K ₂ O	Dissolution of the sample using perchloric acid digestion. Measurement of the potassium content by AAS with an air/acetylene flame at a wavelength of 766.5 nm, or alternatively by ICP-ES.
Na ₂ O	Dissolution of the sample using perchloric acid digestion. Measurement of the sodium content by AAS with an air/acetylene flame at a wavelength of 766.5 nm, or alternatively by ICP-ES.
Fe ₂ O ₃	Dissolution of the sample using perchloric acid digestion. Measurement of the iron content by AAS with an air/acetylene flame at a wavelength of 372 nm, or alternatively by ICP-ES.
Al ₂ O ₃	Dissolution of the sample using perchloric acid digestion. Measurement of the aluminium content by AAS with an air/acetylene flame at about a wavelength of 309.3 nm, or alternatively by ICP-ES.
SiO ₂	Dissolution of the sample using hydrofluoric acid digestion. Measurement of the silica content by AAS with a nitrous oxide/acetylene flame at a wavelength of 251 nm.
SO ₃	Dissolution of the sample using perchloric acid digestion. The concentration of sulphates is determined either by turbidity (precipitation of BaSO ₄ by the reaction of sulphate ions present in the solution and a calibrated BaCl ₂) or by ICP-ES.
Cu	Dissolution of the sample using perchloric acid digestion Measurement of the copper content by AAS in an air/acetylene flame at a wave length of 324.8 nm or alternatively by ICP-ES.
Mn	Dissolution of the sample using perchloric acid digestion. Measurement of the manganese content by AAS in an air/acetylene flame at a wave length of 279.5 nm or alternatively by ICP-ES.

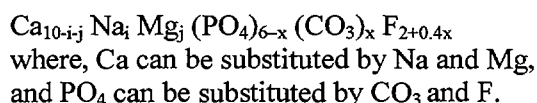
TABLE II (CONTINUED)
LIST OF STANDARDS METHODS FOR PR SAMPLES OF DIRECT APPLICATION

Chemical Element	Method
Zn	Dissolution of the sample using perchloric acid digestion Measurement of the zinc content by AAS in an air/acetylene flame at a wave length of 213.9 nm, or alternatively by ICP-ES.
Cd	Dissolution of the sample using perchloric acid digestion Measurement of the cadmium content by AAS in an air/acetylene flame at a wavelength of 228.8 nm, or alternatively by ICP-ES.
Cr	Dissolution of the sample using perchloric acid digestion Determination of the chromium content by ICP-ES or alternatively by colorimetry (in acid medium the bichromate ions Cr_2O_7 produce in reaction with diphenylcarbazide a violet color that is measured by Spectrophotometry at a wavelength of 540 nm).
Ni	Dissolution of the sample using perchloric acid digestion Measurement of the nickel content by AAS in an air/acetylene flame at a wave length of 232 nm, or alternatively by ICP-ES.
F	Dissolution of the sample by nitric acid. Determination of the fluorine concentration with an ionometer using a fluoride specific electrode.
Solubility test citric acid/ formic acid (EEC Method)	Extraction of phosphorus from ground and sieved (to 63 microns) phosphate samples using citric acid or formic acid solution while shaking at a temperature of about 20°C.
Solubility test citric acid (New Zealand Meth.)	Extraction of phosphorus from ungrounded phosphate samples with a solution of citric acid while shaking at a temperature of about 20°C.

3.2. Crystallography

The results of a and c axes of the hexagonal crystal of the apatite contained in the PR samples are presented in Table IV. The unit cell a dimension is indicative of the degree of carbonate substitution for phosphate, decreasing as the mole ratio of CO_3/PO_4 increases. Thus, the axis is a key factor determining the chemical reactivity of the PR containing carbonate apatite [13, 6].

The composition of carbonate-apatites can be expressed by the following general formula [14, 5]:



These isomorphic substitutions modify the crystallographic parameters. A particular feature is the F content. The PR with a high degree of isomorphic substitution of carbonate for phosphate has a F content near or higher than that of theoretical fluor-apatite to charge balance the replacement of carbonate for phosphate [15].

TABLE III. MINERALOGICAL COMPOSITION OF PHOSPHATE ORES (IN %)

Phosphates	Apatite	Calcite	Dolomite	Quartz	Feldspar	Kaolinite	Mica
Algeria	84		10	2.5			
Morocco 1	65		22	12			
Morocco 2	93		1.5	2.5			
Morocco 3	82	14					
Tunisia 1	85	2	3	3			
Tunisia 2	90	4	1.5	1.5			
Tunisia 3	85	6	1	6			
Jordan 1	70	14		12			
Jordan 2	80	4		11			
Jordan 3	73	14		11			
Senegal	83	3		11			
Minjingu	80	3					
Togo 1, Commercial	95			3			
Togo 2, Hibogan	80			13		1.5	
Brazil 1, Patos	55			30	2	2.5	5
Bahia Inglesa	62			18	13		1.5
Trinidad de Guedes	85	2.5		7			
Riecito	70	1		24	5		
Monte Fresco	65	28		7			1
Navay	60			35	2.5	1.5	
Maardu	70	3.5	5.5	17	1		
Polpino	56			40			2
Jingxiang	46	8	21	23	1		
Jinning	58		11	27			3
Malaysia - Jordan	85	7		7			
Malaysia - China	80		4.5	13			2
Malaysia - Tunisia	82	4	4.5	2.5			
Malaysia - N. Carolina	90			6.5			
Malaysia - Christmas Island	88		2				
Malaysia - Morocco	85	8	1.5	1.5			1.5
Thailand - Racha Buri	50	3	34	6		2	
Thailand - Petcha Buri	85	8					1.5

From the value of the a axis it is possible to calculate the coefficients of the general formula, using the following empirical relations:

$$a = 9.374 - 0.204 [x/(6-x)]$$

$$CO_3/PO_4 = [x/(6-x)]$$

$$i = 1.327 [x/(6-x)]$$

$$j = 0.515 [x/(6-x)]$$

Table V shows the calculated empirical formulae of the different apatites under study. All but three PR samples (Morocco 3, Jordan 1 and Russia) show different degrees of isomorphic substitution in their structure confirming their carbonate apatite nature. It may be also noted that the ratio CO_3/PO_4 increases in the PRs with high CO_3 isomorphic substitution as well as the F content. Almost all, except those mentioned above, can be considered as "excess fluorine" PRs because they contain fluorine in excess of the two moles per formula weight [15]. However, they do not exceed three that may cause injury to grazing stock through fluorosis.

TABLE IV. CRYSTALLOGRAPHIC PARAMETERS OF APATITES
(UNIT CELL DIMENSION IN ANGSTROMS, Å)

Phosphates	a axis	c axis
Algeria	9.339	6.904
Morocco 1	9.360	6.904
Morocco 2	9.339	6.896
Morocco 3	9.366	6.904
Tunisia 1	9.346	6.904
Tunisia 2	9.353	6.904
Tunisia 3	9.339	6.900
Jordan 1	9.366	6.904
Jordan 2	9.353	6.900
Jordan 3	9.353	6.900
Senegal	9.391	6.904
Minjingu	9.339	6.888
Togo 1, Commercial	9.384	6.896
Togo 2, Hibogan	9.377	6.904
Patos	9.394	6.888
Bahia Inglesa	9.339	6.892
Trinidad de Guedes	9.318	6.884
Riecito	9.415	6.904
Monte Fresco	9.394	6.908
Navay	9.380	6.900
Maardu	9.394	6.900
Polpino	9.366	6.912
Jingxiang	9.377	6.888
Jinning	9.349	6.884
Malaysia - Jordan	9.366	6.904
Malaysia - China	9.387	6.896
Malaysia - Tunisia	9.339	6.900
Malaysia - N. Carolina	9.339	6.892
Malaysia - Christmas Island	9.394	6.896
Malaysia - Morocco	9.360	6.904
Thailand - Racha Buri	9.391	6.890
Thailand - Petcha Buri	9.429	6.896

Several authors have attempted to relate chemical reactivity of sedimentary apatites to their mineralogical characteristics. Thus, indices of absolute solubility, which are defined as the ratio between the percentages of soluble P in a given reagent (neutral ammonium citrate, citric acid, formic acid) to the total P content of the apatite, can be calculated. By this way, the variations in the apatite content of the ores, and the P content in the apatite can be eliminated. Based on a study with 50 phosphate rocks, using the same a axis the following relations have been proposed to estimate indices of absolute solubility [14]:

$$\begin{aligned}
 \text{Neutral ammonium citrate} &= 421 (9.369 - a) \\
 \text{Citric acid} &= 611 (9.378 - a) \\
 \text{Formic acid} &= 1.091 (9.376 - a)
 \end{aligned}$$

TABLE V. EMPIRICAL FORMULAE OF APATITES

Phosphates	Ca	Na	Mg	PO ₄	CO ₃	F	CO ₃ /PO ₄
Algeria	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Morocco 1	9.875	0.090	0.035	5.614	0.385	2.154	0.069
Morocco 2	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Morocco 3	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Tunisia 1	9.749	0.181	0.070	5.275	0.724	2.289	0.137
Tunisia 2	9.813	0.135	0.052	5.439	0.560	2.224	0.103
Tunisia 3	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Jordan 1	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Jordan 2	9.813	0.135	0.052	5.439	0.560	2.224	0.103
Jordan 3	9.813	0.135	0.052	5.439	0.560	2.224	0.103
Minjingu	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Bahia Inglesa	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Trinidad de Guedes	9.496	0.363	0.141	4.707	1.292	2.516	0.274
Polpino	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Jingxiang	9.778	0.161	0.062	5.344	0.655	2.262	0.123
Malaysia - Jordan	9.929	0.051	0.020	5.773	0.226	2.090	0.039
Malaysia - Tunisia	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Malaysia - N. Carolina	9.686	0.226	0.088	5.120	0.879	2.351	0.172
Malaysia - Morocco	9.875	0.090	0.035	5.614	0.385	2.154	0.069

The data on calculated indices of absolute solubility using the “*a* axis” of PR are presented in Table VI. Based on these criteria, the most reactive PR products were Trinidad de Guedes from Cuba, followed by Algeria, Morocco 2, Tunisia 3, Tanzania, and Chile. It should be also noted that there were some limitations to these calculations. From a total of 33 determinations of the “*a* axis”, only 19 could be used. The other values were higher than 9.374 Å and, thus would produce negative values. Among the 19 useful values, seven were identical, thus the technique was not sensitive enough to discriminate among PR sources. For this reason, it was not possible to draw clear conclusions with regard to their chemical reactivity from the crystallographic analysis.

Thus, the crystallographic analysis provides valuable information for determining the reactivity of phosphate rocks. Indeed, the dimensions of the unit-cells *a* and *c* of the apatite are indicators of the size of the crystals and their degree of substitution. The reactivity and chemical solubility would increase with the carbonate substitution for phosphate [13, 6, 1].

These results provide a good theoretical basis for the grouping of PR samples. However, it should be noted that sedimentary phosphate rocks are complex mineral mixtures and even PRs from the same deposit may contain apatite with widely differing properties. The carbonate-fluorapatites are metastable and can be modified under the combined effects of weathering, metamorphism and time [15].

On another hand, these determinations are expensive and require specialized laboratories and skilled staff, therefore, they should be reserved only for basic studies to characterize main phosphate deposits.

3.3. Chemical analysis

The data from the elemental quantitative analysis provide a complete picture of the chemical composition in terms of major elements (P, Ca, Mg), intermediate (Si, F, Fe, etc.) and microelements, (Zn, Cu, Ni, Mn). The full data are not shown.

TABLE VI. INDICES OF ABSOLUTE SOLUBILITY OF PHOSPHATE ROCKS
CALCULATED FROM *a* AXES (IN % OF THEORETICAL P₂O₅ CONTENT)

Phosphates	Neutral Ammonium Citrate	Citric Acid	Formic Acid
Algeria	12.63	23.82	46.91
Morocco 1	3.79	10.99	17.45
Morocco 2	12.63	23.82	46.91
Morocco 3	1.26	7.33	10.91
Tunisia 1	9.69	19.55	32.73
Tunisia 2	6.74	15.27	25.09
Tunisia 3	12.63	23.82	46.91
Jordan 1	1.26	7.33	10.91
Jordan 2	6.74	15.27	25.09
Jordan 3	6.74	15.27	25.09
Minjingu	12.63	23.82	46.91
Bahia Inglesa	12.63	23.82	46.91
Trinidad de Guedes	21.49	36.66	63.27
Polpino	1.26	7.33	10.91
Jinning	8.42	17.71	29.45
Malaysia - Jordan	1.26	7.33	10.91
Malaysia - Tunisia	12.63	23.82	46.91
Malaysia - N. Carolina	12.63	23.82	46.91
Malaysia - Morocco	3.79	10.99	17.45

A summary of the main elemental composition of the studied PR samples is given in Table VII. The total P₂O₅ contents are very variable, ranging from 15–17% (Russia, Chile) to 35–36% (Senegal, Togo), with an average of 27%. Phosphate rocks containing less than 20% P₂O₅ need to be beneficiated, in order to bear the transportation costs. According to European regulations, a minimum of 25% P₂O₅ is required [16].

The CaO contents varied from 24% (Russia) to 52% (Morocco 3), with an average of 41%. Most PR contains values above average. Phosphate rocks suitable for direct application supply more calcium than phosphorus to the soil, thus having some amendment effect [17].

The MgO contents (3–4% in Thailand Racha Buri and China Jingxiang) are not negligible and probably come from dolomite. Brazil 2 Yoorin, with 12% MgO, corresponds to a manufactured product, i.e., fused phosphate.

The CO₂ contents, with an average of 4%, may be originated from two sources, i.e., free carbonates and isomorphic substitution in the apatite. In the case of China JX (12%) and Thailand RB (11%), it probably comes from carbonates (dolomite).

The SiO₂ contents confirm the significant presence of quartz minerals in PR. Russia, China JN, and Brazil 1, Patos PR had 46%, 36%, and 31% SiO₂, respectively (data not shown).

Concerning microelements content, it is noticeable that Brazil 2, Yoorin ranks first for most of these elements and that both PR samples from Thailand, RB and PB are very rich in Mn and Zn. The Cd content seems not to be a problem, with an average of 17 ppm, and only three PR products have more than 50 ppm (Senegal, Togo, Morocco 2).

Regarding the chemical analyses, the major elements (P, Ca, Mg and CO₂) can be determined routinely in chemical laboratories and the information provided is useful for agricultural purposes [17]. The P₂O₅ is essential for calculating the rates of PR application and the CaO and MgO for estimating the potential amendment effect of the PR. In this study, the average contents of CaO and P₂O₅ in the PR samples were 41% and 27%, respectively.

TABLE VII. CHEMICAL COMPOSITION (IN %)

Phosphates	P ₂ O ₅	CaO	MgO	CO ₂
Algeria	28.90	47.95	1.46	7.66
Morocco 1	26.65	44.02	2.24	8.29
Morocco 2	31.84	50.05	0.41	5.35
Morocco 3	32.05	52.01	0.27	6.59
Tunisia 1	29.55	48.23	0.47	6.14
Tunisia 2	30.29	49.63	0.51	5.88
Tunisia 3	28.12	47.39	0.45	6.59
Jordan 1	30.62	47.67	0.25	4.28
Jordan 2	30.64	47.39	0.30	3.74
Jordan 3	30.32	50.47	0.23	6.24
Senegal	35.51	50.05	0.06	1.96
Minjingu	28.73	42.90	1.91	4.37
Togo 1, Commercial	36.09	49.77	0.10	1.78
Togo 2, Hibogan	27.92	38.70	0.29	1.25
Patos	25.45	31.40	0.21	0.45
Yoorin	17.69	27.06	12.70	0.71
Bahia Inglesa	17.22	28.88	0.72	3.92
Trinidad de Guedes	31.09	45.71	0.23	3.21
Riecito	29.45	38.98	0.08	2.23
Riecito PAPR 40%	26.37	30.56	0.13	0.89
Maardu	30.08	44.30	0.83	4.37
Polpino	15.07	24.68	0.32	2.94
Jingxiang	19.24	35.47	3.93	12.30
Jinning	21.39	30.98	0.95	2.67
Racha Buri	23.23	38.27	4.92	11.72
Petcha Buri	34.81	46.27	0.05	4.72

3.4. Solubility in conventional reagents

The results of the solubility tests in neutral ammonium citrate, 2% citric acid and 2% formic acid, are presented in Table VIII (values expressed in % of total P₂O₅). These are the three commonly used extractants for measuring solubility of PR. Comparisons of these solubility tests have been made by some authors [18].

The solubility of PR is measured in conventional reagents such as organic acids, which simulates the extraction power of the root similar to the determination of available soil P. Neutral ammonium citrate is a mild extractant that generally gives a good correlation with P uptake by plants and it is recommended in the USA [19]. On the contrary, relatively strong extractants such as citric (used in Brazil) and formic (used in Europe) acids usually extract more phosphorus because of the higher acidity of these extracts. Of these, the 2% formic acid is much more concentrated than the others because of differences in molecular weight.

TABLE VIII. SOLUBILITY TESTS IN CONVENTIONAL REAGENTS
(% OF TOTAL P₂O₅)

Phosphates	Neutral Ammonium Citrate	Citric Acid	Formic Acid
Algeria	23.0	38.6	71.2
Morocco 1	26.0	38.4	60.4
Morocco 2	20.2	33.1	60.1
Morocco 3	16.7	29.9	56.5
Tunisia 1	27.6	41.7	75.8
Tunisia 2	22.7	41.3	72.5
Tunisia 3	21.3	40.3	73.6
Jordan 1	33.1	26.0	27.4
Jordan 2	24.0	36.2	55.9
Jordan 3	31.1	31.2	52.1
Senegal	12.4	21.5	25.6
Minjingu	28.9	44.9	69.9
Togo 1 Commercial	13.6	20.1	19.8
Togo 2 Hibogan	15.4	24.6	23.8
Patos	6.4	22.0	18.1
Yoorin	80.2	99.2	77.6
Bahia Inglesa	34.3	51.6	60.1
Trinidad de Guedes	23.1	29.3	25.5
Riecito	12.1	32.5	32.8
Riecito PAPR 40%	31.6	58.5	54.3
Maardu	29.1	28.5	32.9
Polpino	31.8	48.2	46.8
Jingxiang	6.6	8.8	11.6
Jinning	16.5	24.2	24.0
Racha Buri	37.0	55.6	64.4
Petcha Buri	25.7	38.9	51.9

A first classification was made based on the combination of these three solubility tests. The PR samples in study were classified into four distinct groups according to their reactivity (Table IX-A).

The European solubility standards for phosphates as fertilizers are very strict. A minimum of 55% solubility in 2% formic acid is required [16]. Table IX-B displays the classification of the PR samples according to their solubility in 2% formic acid. Four categories of long-term reactivity were identified (Table IX-B).

Both classifications provide a similar but not identical grouping of the PR samples in study. The first one, using the solubility data in the three reagents, expresses the average short and long term effects of PR whereas the second, with only formic acid solubility, appears to be more related to the long-term effect of PR.

It should be also pointed out that these classification data based on chemical solubility in conventional reagents are quite different from the classification using the indices of absolute solubility (Table VI).

All these solubility determinations can be made in normal chemical laboratories. At least the solubility in formic acid should be determined because it is stable, reproducible, easy to handle and the results enable to discriminate the chemical reactivity of different phosphates. It is advisable, however, to use more than one solubility test in evaluating the PR chemical reactivity [5, 20].

TABLE IX. CLASSIFICATION OF PR REACTIVITY ACCORDING TO SOLUBILITY INDICES IN CONVENTIONAL CHEMICAL REAGENTS AND SOLUBILITY IN FORMIC ACID

A) CONVENTIONAL CHEMICAL REAGENTS			
Group I	Group II	Group III	Group IV
Racha Buri	Jordan 3	Maardu	Jinning
Tunisia 1	Jordan 2	Jordan 1	Senegal
Bahia Inglesa	Petcha Buri	Morocco 3	Togo 2
Minjingu	Morocco 2	Trinidad de Guedes	Togo 1
Tunisia 2		Riecito	Jingxiang
Tunisia 3			
Polpino			
Algeria			
Morocco 1			

B) FORMIC ACID			
Group I (> 70%)	Group II (60-70%)	Group III (50-60%)	Group IV (< 50%)
Tunisia 1	Minjingu	Morocco 3	Polpino
Tunisia 2	Racha Buri	Jordan 2	Maardu
Tunisia 3	Bahia Inglesa	Jordan 3	Riecito
Algeria	Morocco 1	Petcha Buri	Jordan 1
Yoorin	Morocco 2		Senegal
			Trinidad de Guedes
			Jinning
			Togo 2
			Togo 1
			Patos
			Jingxiang

3.5. Particle size distribution

The results of the particle size analysis in % of product passing through 45, 90, 165 and 320 microns sieves are presented in Table X. As the physical state of the initial samples was quite different (ground, ungrounded, granulated), it is not possible to make a direct comparison of the results across samples. For example, Morocco 3, ungrounded, had only 4.5% passing through 45 microns, while Estonia, finely ground, has 100% passing through all sieves. In this case, each phosphate should be examined individually and related to its agronomic effectiveness. From the data of Table X, it may be noted that 14 PR samples (about 60%) have 80% of the product passing through a 165 microns sieve. This determination is important and easy to be made.

In general, several reports indicate that P availability from PR is enhanced with increasing fineness of grinding. However, it is reported that a general cut-off point for most PR appears to be 100-mesh (150 microns) sieve [3]. Thus, there is no need to grind PR more finely than required for 80–90% of the product to pass 100-mesh [1]. According to European standards, PR products to be utilised as fertilizers should be finely ground, i.e. 90% of the product should pass through a 63 microns sieve and 99% of the product should pass through a 125 microns sieve [16].

Data on specific surface and porosity (volume of porous space) of the PR samples are not shown. These values depend on the origin of the PR and, also the degree of fineness.

TABLE X. PARTICEL SIZE DISTRIBUTION OF PHOSPHATE FRACTIONS
UNDER 400 MICRONS (IN % OF PRODUCT PASSING THROUGH)

Phosphates	45 microns	90 microns	165 microns	320 microns
Algeria	10.1	19.8	62.2	91.1
Morocco 1	35.3	47.9	69.1	92.2
Morocco 2	9.3	13.2	42.8	86.5
Morocco 3	4.5	7.3	30.9	80.9
Tunisia 1	69.1	83.8	97.2	100
Tunisia 2	68.8	80.2	90.9	97.9
Tunisia 3	63.8	76.9	91.5	98.6
Jordan 1	14.9	23.5	45.5	83.9
Jordan 2	62.4	87.0	98.3	100
Jordan 3	28.7	40.3	55.5	86.1
Senegal	8.6	31.1	61.5	90.1
Minjingu	55.2	75.6	89.5	97.3
Togo 1 Commercial	9.3	20.3	60.2	92.6
Togo 2 Hibogan	71.1	93.3	100	100
Patos	64.4	88.5	99.4	100
Bahia Inglesa	54.9	82.3	99.0	100
Trinidad de Guedes	13.1	16.2	29.4	77.5
Riecito	65.7	85.2	98.2	100
Maardu	100	100	100	100
Polpino	63.3	72.5	82.3	94.6
Jingxiang	59.5	71.6	83.2	94.9
Jinning	73.8	92.9	100	100
Racha Buri	66.2	84.8	97.7	100
Petcha Buri	45.9	61.5	76.6	93.2

3.6. Correlation studies

Attempts were made to relate some parameters determined in the characterisation, in particular to interpret the solubility data, which are considered indices of PR reactivity.

First, a correlation between the solubility measured in conventional reagents and the calculated indices of absolute solubility was run with the following results:

neutral ammonium citrate	$r = 0.15$
citric acid	$r = 0.07$
formic acid	$r = 0.14$

No relationship between both solubility groups was found. These results are in contrast to previous studies [5, 6]. It is likely that the crystallographic data were not sufficiently sensitive to discriminate between PR sources, thus the calculated indices of absolute solubility are not good indicators of their reactivity.

Secondly, the following correlations between the measured solubility in conventional reagents were made:

formic acid vs. neutral ammonium citrate	$r = 0.56$
formic acid vs. citric acid	$r = 0.72$
citric acid vs. neutral ammonium citrate	$r = 0.89$

The simple linear correlation coefficients show some relationship but they are not very close. This may be explained by the fact that the PR samples belong to contrasting solubility groups, thus each group requiring partial linear regression analysis. It was not possible to separate them further into different groups due to the lack of sufficient information on the PR samples. Other studies indicate that the presence of free carbonates in the PRs interfere with the solubility measurements [18].

Thirdly, correlations were made between the data of solubility in formic acid and other parameters, as follows:

formic acid vs. CO ₂ content	$r = 0.26$
formic acid vs. specific surface	$r = 0.31$
formic acid vs. porous volume	$r = -0.05$
specific surface vs. porous volume	$r = 0.24$

In the first correlation, no relationship was found. Here again, the PR samples belong to carbonate-apatites, with different degrees of isomorphic substitution and in some PRs, the CO₂ content represented mainly the free carbonates (Tables V and VII). Regarding the parameters of the physical analysis, specific surface and porous volume, the samples in study had contrasting particle size distribution due to the pre-treatment/conditioning of the samples received from the participants (Table X).

4. CONCLUSIONS

The characterization of phosphate rocks is the first and essential step in evaluating their suitability for direct application. If several PR sources are utilized, standardized methods should be used for comparison purposes to determine their agronomic potential.

The data on mineralogical and chemical composition and solubility in conventional reagents are closely interrelated. An arbitrary classification of the reactivity of the PR samples in four categories was made based on the solubility indices in conventional reagents. On another hand, the results of the crystallographic parameters, calculated indices of absolute solubility, specific surface and porosity reflected the large variability of the physical state resulting from preconditioning treatment of the received samples.

A proper characterization of phosphate rock samples should provide the maximum of basic information that can be obtained in a cost-effective manner by routine analysis in chemical laboratories. The following determinations are recommended: description of the sample, major elemental (total P, Ca, Mg) composition, solubility in conventional reagents (neutral ammonium citrate, citric and formic acid) and particle size analysis.

The classification of PR samples for direct application as fertilizers requires the definition of standards. The European standards were found to be very strict for this purpose. The studies carried out under this project should be considered as attempts to provide some guidelines for the provision of such standards in other conditions, in particular tropical acid soils where the PRs show great agronomic potential.

Follow-up studies are required to evaluate the agronomic effectiveness of the PR, i.e. actual performance of the PR under study as affected by a specific set of soil, crop, climate and management conditions. In a final phase, it would also be important to relate the results of this study with those of the agronomic effectiveness and several other socio-economic criteria for developing adequate PR Decision Support Systems.

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