Chapter 3
Characterization of phosphate rocks

Characterization studies of phosphate rock (PR) samples should provide data on: (i) the composition of the apatite, other phosphate minerals and gangue minerals; (ii) the relative amounts of mineral species present (estimated); and (iii) the particle size of the various minerals in the rock fabric, etc. It is possible to combine this information with a comprehensive chemical analysis to determine the distribution of chemical species among the mineral components.

Based on such an evaluation, it is possible to estimate the potential for beneficiation, suggest possible beneficiation routes, and make a preliminary assessment of the suitability of PRs for various fertilizer production processes and/or their applicability for direct application.

PHOSPHATE ROCK MINERALOGY

Sedimentary apatites

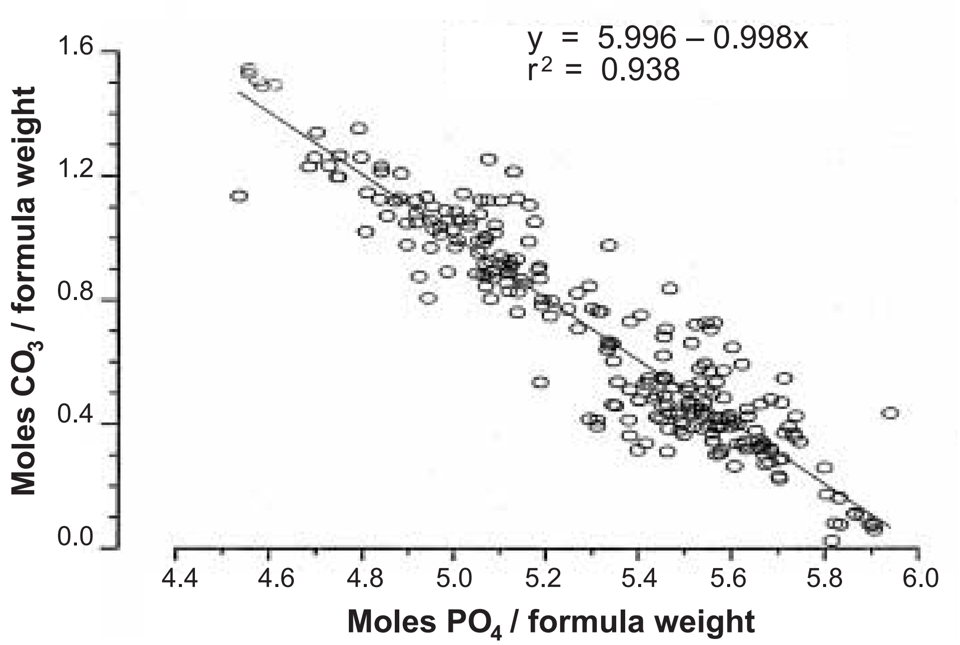
Most sedimentary deposits contain varieties of carbonate-fluorapatite that are grouped under the collective name francolite (McConnell, 1938). In establishing a series of systematic relationships between francolites, various authors (McClellan and Lehr, 1969; McClellan, 1980; McClellan and Van Kauwenbergh, 1990a) have used X-ray diffraction (XRD), chemical analysis and statistical methods to show that the contents of calcium (Ca), sodium (Na), magnesium (Mg), phosphorus (P), carbon dioxide (CO_2) and fluorine (F) can describe most francolites adequately.

Most importantly, carbonate substitutes for phosphate in a 1:1 ratio (Figure 3), and the maximum amount of substitution is 6–7 percent CO_2 by weight. Both cation and anion substitutions compensate net charge imbalances. The incorporation of CO_2 into the francolite structure is accompanied by increased fluorine contents. In francolites, the unit-cell *a* dimension (*a* value) decreases from 9.369 +/- 0.001 Å to approximately 9.320 +/- 0.001 Å with maximum carbonate substitution (Figure 4). The index of refraction also decreases systematically with increasing carbonate substitution.

Sedimentary PRs from insular and cave deposits often contain carbonate apatites that have a lower F content than stoichiometric fluorapatite and may contain significant amounts of hydroxyl in their structures. Although some of these carbonate apatites may meet the francolite definition (significant CO_2 with more than 1 percent F) (McConnell, 1938), they have crystallographic, chemical and other physical properties that differ substantially from those of francolites that contain excess fluorine (McClellan and Van Kauwenbergh, 1990b; Van Kauwenbergh and McClellan, 1990a; Van Kauwenbergh, 1995).

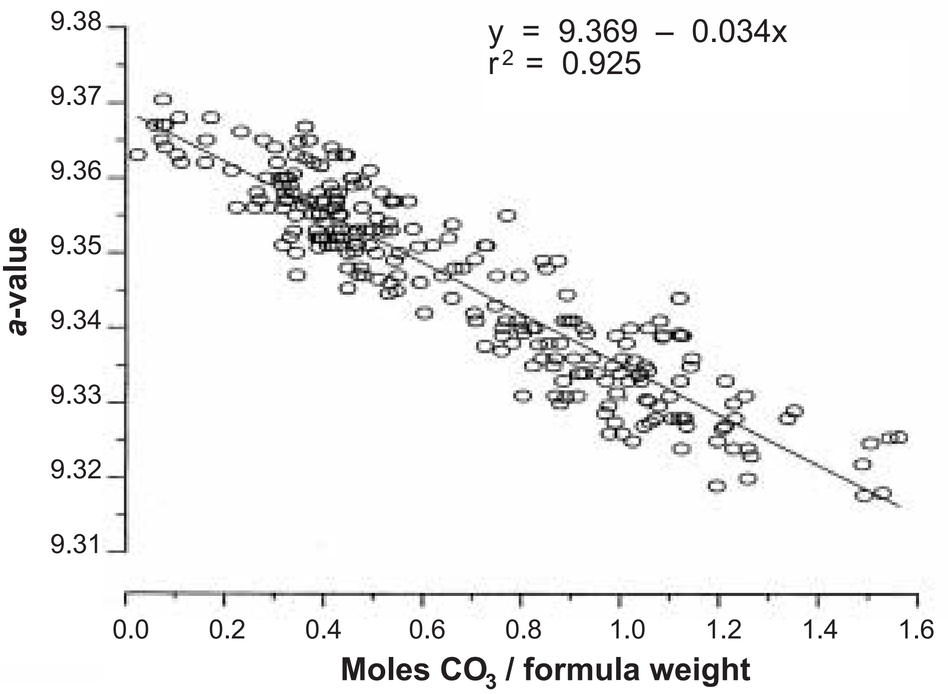
Some carbonate apatites do not fit well within either the excess fluorine francolite series or the hydroxyl-fluor-carbonate apatite series and perhaps belong in an intermediate class. PRs from deposits at Sechura, Peru, and Mejillones, Chile, fit into this category. The carbonate apatites in these rocks have unit-cell *a* dimensions that fall clearly into the range of the francolite series

FIGURE 3
Excess fluorine francolites, correlation of moles of CO_3^{-2} with PO_4^{-3} per formula weight



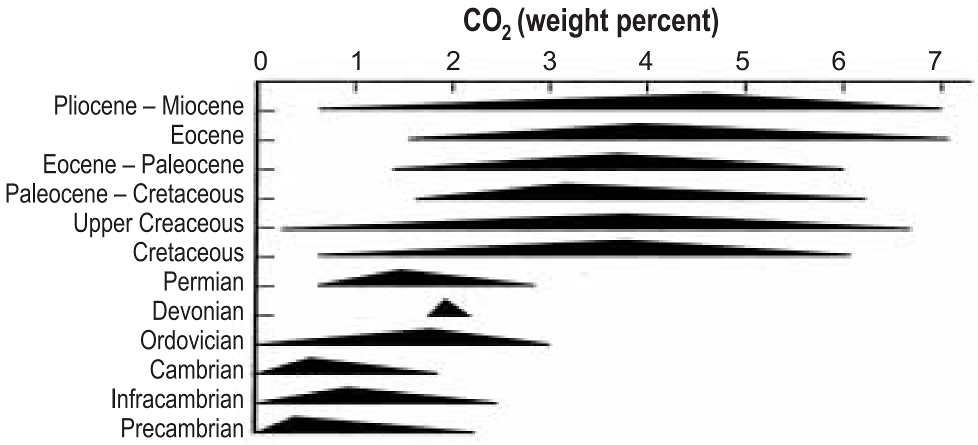
Source: McClellan and Van Kauwenbergh, 1990a.

FIGURE 4
Excess fluorine francolites, variation in unit-cell *a* value with increasing CO_3^{-2} for PO_4^{-3} substitution



Source: McClellan and Van Kauwenbergh, 1990a.

Figure 5
Variation of CO_2 contents in excess fluorine francolites of various geological ages



Notes: 472 samples, 165 deposits; peak of triangle represents average CO_2 content.
Source: McClellan and Van Kauwenbergh, 1991.

(9.320–9.370 Å). However, samples from these deposits exhibit higher carbonate contents and chemical reactivities than calculations based on excess fluorine francolite models would indicate.

Francolites are metastable with respect to fluorapatite and can be altered systematically through the combined effects of weathering, metamorphism and time (McClellan, 1980). PRs from the same sedimentary deposit may contain apatites with widely differing properties because of geologic conditions and post-depositional alterations (Van Kauwenbergh and McClellan, 1990b; McClellan and Van Kauwenbergh, 1991). Older sedimentary rocks generally contain francolites with a limited amount of carbonate substitution while younger sedimentary PRs may have compositions that span the francolite model (Figure 5).

Igneous apatites

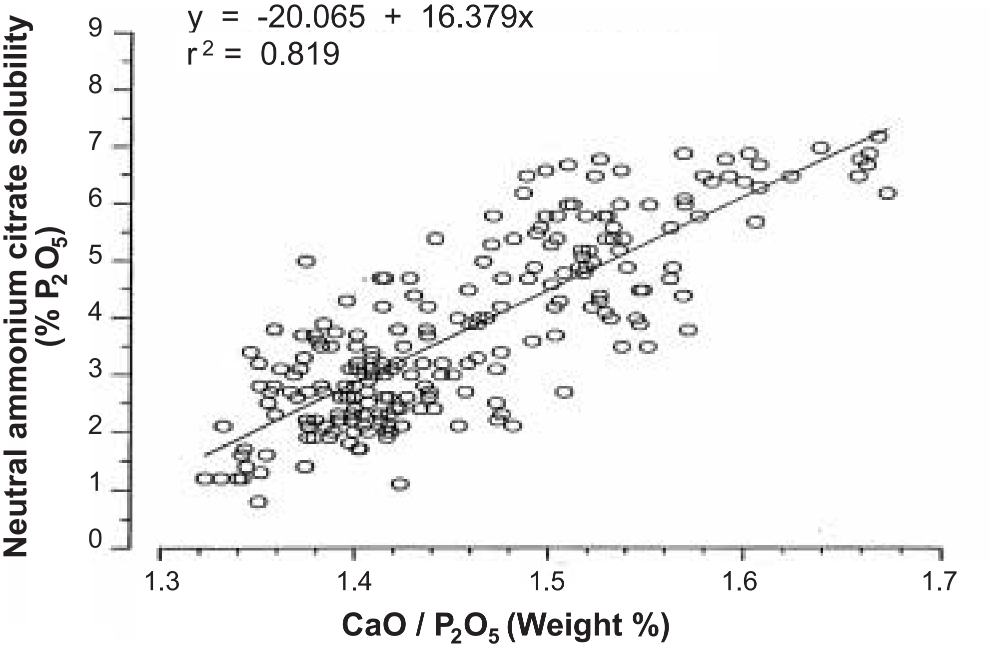
Primary crystalline apatite from igneous sources may be of fluorapatite, hydroxyapatite or chlorapatite varieties, and pure apatites of the varieties will contain slightly more than 42 percent P_2O_5. A continuous series exists between the fluorapatite and hydroxyapatite end members.

Other minerals in PRs

A total P_2O_5 analysis of a potential ore is not a dependable criterion for estimating the apatite content and evaluating a phosphate deposit. Probably the most common secondary phosphate–weathering minerals are members of the crandallite series. Wavellite is also a common aluminium phosphate formed during weathering. The most common non-phosphatic accessory minerals associated with sedimentary PRs are quartz, clays and carbonates (dolomite and calcite). Carbonate-cemented PRs are particularly noteworthy because of their abundance. Quartz can occur as detrital grains or as microcrystalline varieties. Siliceous cement can be particularly difficult to detect in samples using optical microscopy because of its anisotropic nature and appearance similar to microcrystalline francolite.

FIGURE 6

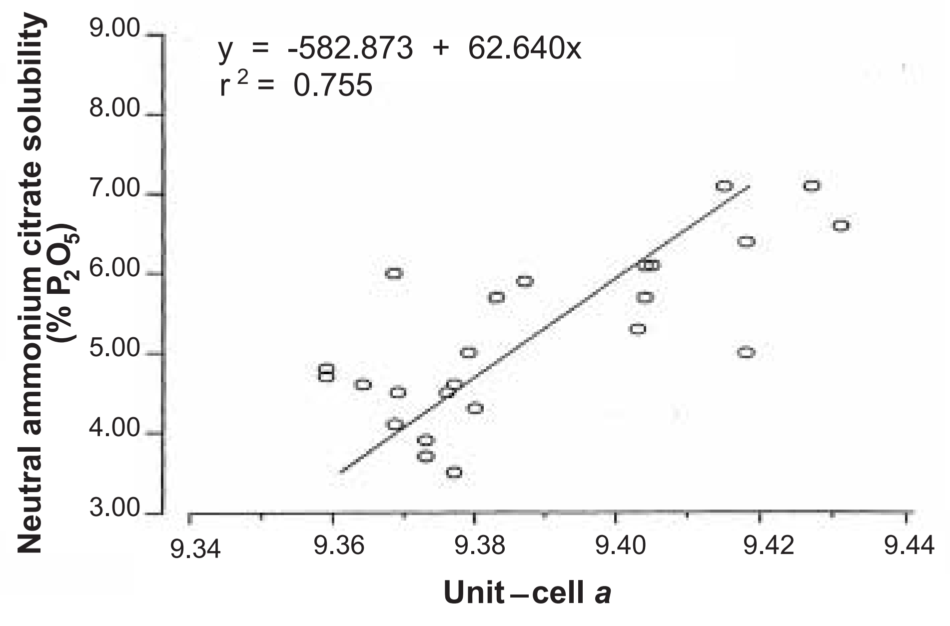
Relationship of the CaO/P_2O_5 weight percent ratio to NAC-soluble P_2O_5, excess fluorine francolites



Source: Van Kauwenbergh, 1995.

FIGURE 7

Unit-cell *a* dimension versus NAC solubility of hydroxyl-fluor-carbonate apatites



Source: Van Kauwenbergh, 1995.

Other silicates found in sedimentary PRs can include feldspars and micas (biotite and muscovite). Clay minerals found in sedimentary PRs include illite, kaolinite, smectites and palygorskite/sepiolite. Zeolites, including clinoptilolite and heulandite, are occasionally found in PRs.

Common minerals associated with igneous apatite include nepheline, alkali feldspars, micas, pyroxenes and amphiboles. Calcite, dolomite and magnetite are common minerals associated with carbonate apatite deposits. Weathering may leach and remove carbonates and some silicates leaving resistant minerals such as apatite, magnetite, pyrochlore and zircon in the residuum over the deposit.

PHOSPHATE ROCK SOLUBILITY TESTS

Apatite solubility

The three solutions commonly used to measure the solubility (reactivity) of direct application phosphate rock (DAPR) are neutral ammonium citrate (NAC), 2-percent citric acid (CA), and 2-percent formic acid (FA). The methods used to measure the solubility of PR rock stem from procedures used to analyse conventional water- and citrate-soluble phosphate fertilizers. Unless standard procedural steps are observed strictly, solubility figures obtained by different experimenters on the same rock sources using the same methods may show considerable disagreement (Hammond *et al.*, 1986b).

The NAC solubility of francolites with a maximum known amount of CO_3 substitution ($CaO/P_2O_5 \cong 1.67$) is about 7 percent P_2O_5 (Figure 6). This value decreases with decreasing CO_3 substitution to about 1–2 percent P_2O_5 for sedimentary francolites with very little CO_3 substitution ($CaO/P_2O_5 \cong 1.33$). PRs containing carbonate-apatite with low fluorine contents and OH- substitution may have solubilities in various extraction media as high as the most highly substituted francolites (Figure 7). NAC solubilities of igneous apatites are generally about 1–2 percent P_2O_5 or about the same as sedimentary francolites with little carbonate substitution.

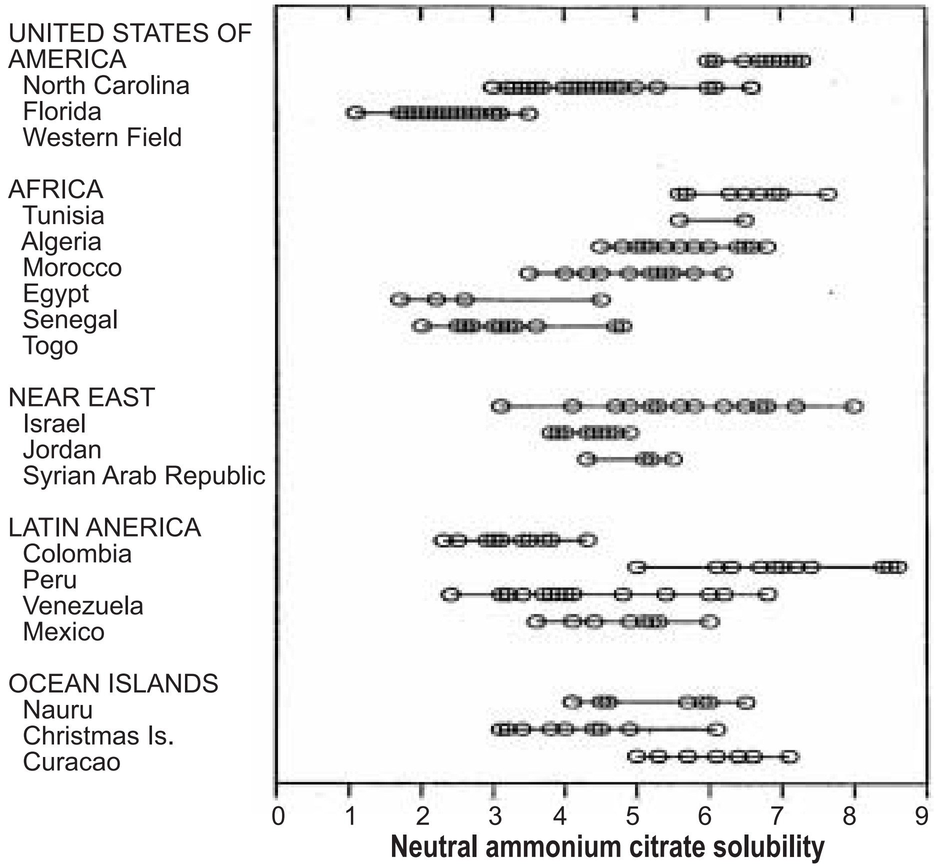
Table 5 shows the data on solubility in NAC, 2-percent CA and 2-percent FA for some selected PRs (in order of decreasing CO_3 substitution). The two PRs that probably show the most consistently high NAC solubilities are North Carolina (the United States of America) and Gafsa (Tunisia). The Central Florida (the United States of America) and Tennessee (the United States of America) samples have less carbonate substitution and lower solubilities. The

TABLE 5
Solubility data on selected phosphate rock samples

Sample	Type	Total P_2O_5	Apatite[a] CO_3 subst.	Solubility[b] (% P_2O_5)			
				Neutral ammonium citrate		2% citric acid	2% formic acid
				1st extraction	2nd extraction		
				(wt. %)			
North Carolina (United States of America)	Sedimentary	29.8	6.4	7.1	6.6	15.8	25.7
Gafsa (Tunisia)	Sedimentary	29.2	5.8	6.6	6.8	11.9	18.6
Central Florida (United States of America)	Sedimentary	32.5	3.2	3.0	3.2	8.5	8.2
Tennessee (United States of America)	Sedimentary	30.0	1.6	2.5	2.7	8.7	6.9
Araxa (Brazil)	Igneous	37.1	0	1.7	1.7	3.5	3.9

a. Based on statistical models developed at the IFDC.
b. All samples ground to -200 Tyler mesh (-75 μm) under similar conditions.

Figure 8
NAC solubilities of sedimentary PRs from various countries



Source: Van Kauwenbergh, 1995.

igneous-derived Araxa (Brazil) sample, with essentially no carbonate substitution, has the lowest solubilities in this set of samples.

The measured ranges (maximum and minimum) in NAC solubilities of PRs from various countries may show great variability (Figure 8). Impurities such as calcite, dolomite and gypsum may cause interferences in solubility measurements (Axelrod and Gredinger, 1979). It may be necessary to remove carbonates that interfere with and suppress solubility measurements. It is possible to remove carbonates using Silverman's solution (tri-ammonium citrate solution, pH 8.1) (Silverman *et al.*, 1952). NAC-soluble P_2O_5 values may increase substantially when carbonates are extracted. All the data presented in this chapter were obtained using extracted samples or samples containing no detectable carbonates.

The specific surface area of phosphate particles has a pronounced effect on apparent solubility. Sedimentary phosphate particles containing highly substituted francolites are composed of microcrystalline aggregates. In sedimentary PRs, the geometric outer surface of phosphate particles contributes only a small portion of the specific surface area. The specific surface area, including internal porosity, of sedimentary rocks may be more than 20 times the specific surface area of igneous rocks, which are composed of solid apatite crystals. Studies for the Tennessee Valley Authority (Lehr and McClellan, 1972) indicate that PRs with the highest citrate solubilities often have the highest surface areas.

Grinding provides ‘fresh’ particle surfaces, increases geometric surface area, and increases solubility measurements. Studies by the International Fertilizer Development Center (IFDC) of two PRs with high NAC solubilities indicated that grinding from plus 200 mesh Tyler (75 µm) to 100-percent minus 200 mesh increased specific surface area from 40 to 50 percent. The NAC P_2O_5 solubilities of these PRs and a third rock increased from about 60 to 120 percent with grinding to minus 200 mesh. However, previous experimental reviews (Rogers *et al.*, 1953; Cooke, 1956; Khasawneh and Doll, 1978) concluded that any increase in PR solubility rarely justified grinding to a size less than 100 mesh for agronomic use.

CLASSIFICATION OF PHOSPHATE ROCKS BASED ON SOLUBILITY

There is no widely accepted simple system for classifying and grading PRs for direct application according to solubility measurements. Diamond (1979) proposed a threefold classification system (low, medium and high reactivity) according to NAC, 2-percent CA and 2-percent FA solubilities (Table 6). The system was based on IFDC data for the relative effectiveness of extraction media and the results of a wide variety of laboratory experiments and field trials.

TABLE 6
Proposed classification of PR for direct application by solubility and expected initial response

Rock potential	Solubility (% P_2O_5)		
	Neutral ammonium citrate	Citric acid	Formic acid
High	> 5.4	> 9.4	> 13.0
Medium	3.2-4.5	6.7-8.4	7.0-10.8
Low	< 2.7	< 6.0	< 5.8

Source: Diamond, 1979.

Hammond and Leon (1983) proposed a system with four solubility rankings (high, medium, low and very low) based on relative agronomic effectiveness (RAE) and NAC-soluble P_2O_5 (Table 7). This study consisted of a relative comparison of PRs from several sedimentary, igneous and metamorphic sources based on a greenhouse experiment using *Panicum maximum* grass grown in an acid soil. These and additional data were analysed further by statistical methods to show that the low and very low classifications were composed of sedimentary francolites with very low carbonate substitution and igneous PRs (Leon *et al.*, 1986). The RAE values depend not only on the inherent PR properties (NAC solubility) but also on soil properties and crop species/varieties (Khasawneh and Doll, 1978).

TABLE 7
Ranking system for some South American PRs by solubility and RAE

Soluble P_2O_5 in NAC (% P_2O_5)	RAE[1] (%)	Solubility ranking
> 5.9	> 90	High
3.4-5.9	90-70	Medium
1.1-3.4	70-30	Low
< 1.1	< 30	Very low

[1] RAE = [(yield of ground PR) - (yield of check)]/[(yield of TSP) - (yield of check)] x 100.

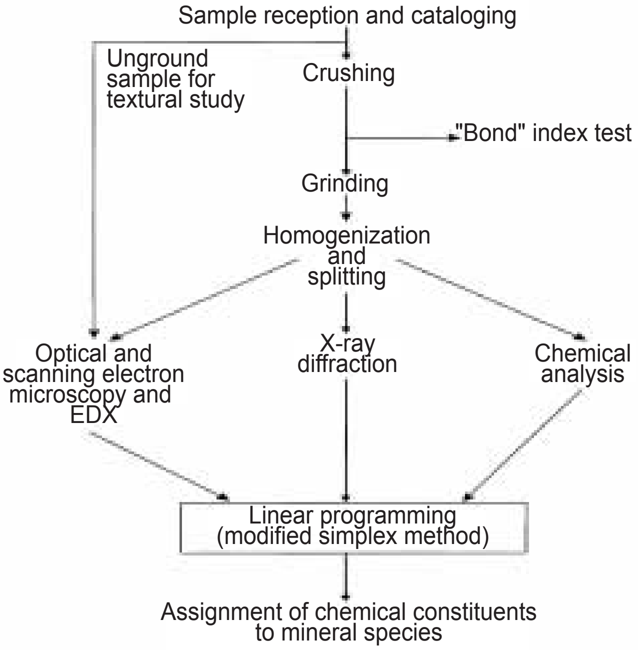
Source: Hammond and Leon, 1983.

The P_2O_5 content and solubility of DAPR constitute what the consumer purchases. However, grade may not be critical in laboratory evaluations of solubility. Lehr and McClellan (1972) showed that NAC solubilized a relatively constant amount of P_2O_5 in successive extractions of the same sample. While the extracted P_2O_5 remained relatively constant, the total P_2O_5 content of the sample decreased. A fairly constant amount of NAC-soluble P_2O_5 was obtained for all mixtures that contained at least 50 percent PR (or about 20 percent P_2O_5). Confusion in interpreting solubility data begins when the extracted P_2O_5 is expressed as a percentage of total P_2O_5. For example, a 30-percent P_2O_5 rock with a 7-percent P_2O_5 NAC extraction value could be expressed as 23 percent of total P_2O_5. A sample containing the same rock (and apatite) could be diluted to 20-percent P_2O_5. At a 7-percent P_2O_5 NAC-extraction value, the NAC-soluble P_2O_5 as a percentage of total P_2O_5 would be 35 percent. This number is higher and might appear better to a prospective buyer. However, the PR would not be any more soluble, and the customer would buy and transport less nutrient and more gangue minerals.

CHARACTERIZATION METHODS

FIGURE 9

Flowsheet of the PR characterization process at the IFDC



The flowsheet in Figure 9 shows an 'ideal' sequence of the steps followed at the IFDC in a detailed characterization of a PR deposit. This scheme is based on experience and can be modified to accommodate specific samples or situations.

Where the sample consists of rock fragments, unground samples are processed to thin sections for optical microscopy and textural studies. The remaining rock fragments are then crushed and ground to be relatively free flowing. These can be homogenized, split and sampled (about minus 0.63 cm). Unconsolidated samples may be screened to determine particle-size distributions, and each size fraction may be analysed chemically.

Microscopic methods include optical and scanning electron microscopy (SEM). Optical microscopy is used to identify mineral species, specify the types of mineral particles, examine the texture of consolidated rocks, and estimate the percentage of various minerals and the liberation and grain size of various components. Samples can be examined as grain mounts or as thin sections.

The texture of PRs can be very important. Consolidated rocks need to be crushed and ground in order to liberate the phosphate particles. Usually, a rock has to be ground to about one-half the grain diameter of the mineral particle of interest or primary gangue mineral in order to achieve the liberation (80 percent mono-mineral particles) needed for beneficiation. Computerized image analysis can be useful in estimating phosphate grain or gangue mineral sizes. While the phosphate grains and gangue mineral grains may occur in some rocks as distinct particles, some rocks contain significant amounts of gangue minerals occluded within phosphate particles.

Cement-particle relationships are also important. If the phosphate grains break cleanly from the cement, it may be possible to make a highly effective separation. If the phosphate grain boundaries and cement are highly intergrown (i.e. locked), separation may be difficult.

When it is not possible to identify minerals by optical microscopy and/or XRD methods, SEM techniques and energy dispersive X-ray analysis (EDX) can be very useful in determining cement/phosphate grain relationships and whether the cement breaks cleanly from the grains. SEM and EDX provide for much higher magnifications and allow close examination of textures of phosphate and gangue mineral surfaces.

XRD is used to identify minerals, qualitatively estimate their concentrations, and determine the unit-cell dimensions of the apatite. Each mineral has a unique XRD pattern composed of a series of peaks. Computer search-match programs ease the complexities of identifying mineral species in complex mixtures considerably.

Special techniques may be needed for clay mineral identification including particle-size separation and concentration. Samples may then be air-dried, treated with organic vapours, and/or also heat-treated to differentiate the clay minerals.

XRD data from apatite and an internal standard can be processed using least-squares computer techniques to determine the unit-cell *a* and *c* dimensions. A common problem encountered in the data analysis is the presence of overlapping and interfering peaks. Iron and aluminium phosphates and carbonates (calcite and dolomite) have peaks that overlap with apatite peaks. These peaks may be removed during the course of data processing. Chemical extraction techniques may also be used to remove carbonates prior to XRD analysis.

Chemical analyses of most PRs usually include CaO, P_2O_5, F^-, Cl^-, SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, MnO, MgO, CO_2, S, organic C, free water, and loss on ignition (LOI). Commercially available standards are used to calibrate analytical methods.

The mineral identifications, determined by XRD, SEM, EDX and optical microscopy methods, and the chemical analyses are equated using several computer methods developed at the IFDC. These methods use a chemical/mineral mass-balance calculation that results in an approximate modal analysis (Figure 10).

The characterization of PR sources, mainly the chemical composition, reactivity and particle size, is the first and essential step in evaluating their suitability for direct application, in particular for comparison purposes in agronomic trials (Chien and Hammond, 1978; Truong *et al.*, 1978; Hammond *et al.*, 1986b). In the framework of an FAO/IAEA networked research project, the agronomic effectiveness of PR sources from several deposits worldwide has been evaluated under different soils, climate and crops conditions (IAEA, 2002). In addition to the individual characterization studies performed by the participating investigators, a complete standard characterization including mineralogical and crystallographic, physical, chemical composition and reactivity analyses was made using 28 PR samples from 15 countries in specialized laboratories. This standard characterization was necessary in order to obtain direct and comparable information on the suitability of the studied PRs for direct application and to better interpret the results from the agronomic evaluation, including the creation of a database for model testing and the development of a decision-support system. Truong and Zapata (2002) have synthesized the information on the methods utilized and results obtained. They have also provided some guidelines for PR characterization for direct application.

FIGURE 10
Diagram showing the approximate modal analysis of phosphorite sample No. 1

Major components	Total	Calcite	Dolomite	Francolite	Pyrite	Quartz	Unassigned
Ca0	48.30	0.94	0.25	47.10			
P_20_5	30.42			30.42			0.00
F	3.78			3.78			0.00
Cl	0.00						0.00
$Si0_2$	1.79					1.79	0.00
Al_20_3	0.38						0.38
Fe_20_3	0.53				0.53		0.00
Na_20	0.90			0.82			0.08
K_20	0.10						0.10
Mn0	0.00						0.00
Mg0	0.47		0.06	0.41			
$C0_2$	5.83	0.74	0.26	4.28			0.55
S	1.10				0.43		0.67
Total	93.61	1.69	0.57	86.71	0.96	1.79	1.79
-0=F	1.59			1.71			
-0=Cl	0.00						
Total	92.01	1.69	0.57	85.00	0.96	1.79	
Volatiles							
L0I	11.38						
H_20	1.31						
Organic C	1.38						

Francolite: A = 9.326999

Theoretical Index of Refraction (N25) = 1.604

Theoretical Absolute Citrate Solubility = 17.7%

Predicted A0AC Citrate-Soluble P_20_5 = 6.3%

Ca0/P_20_5 Ratio, Francolite = 1.55

Ca0/P_20_5 Ratio, Whole Rock = 1.59

Ca0/P_20_5 Ratio, (-Calcite) = 1.56

R_20_3/P_20_5 Ratio = 0.03

$(R_20_3 + Mg0)/P_20_5$ Ratio = 0.05