

Apatite from Alkaline Complexes – Geological Aspects, Behaviour in Mineral Processing and Characterisation Techniques

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ABSTRACT

Several mineral resources have been recognised to alkaline igneous rocks. In general, these mineralisations present low P grades, so a complex concentration process is required to achieve commercial grade concentrates. This process is guided not only by the ore characteristics, such as apatite grain size and liberation degree, gangue minerals and slimes content, but also by different apatite varieties, iron oxy-hydroxide surface coating and roughness. The main techniques applied to apatite and phosphate ore characterisation, such as optical microscopy, cathodoluminescence (CL) microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), surface techniques and magnetic separation are discussed, aiming to evaluate distinct apatite varieties and their technological behaviour.

INTRODUCTION

Phosphate deposits associated to alkaline igneous rocks are very distinct from the most important world phosphate resources from sedimentary origin; they are characterised by their low P grades and complex mineralogy, explained by the diversified composition of the apatite bearing rocks. Several mineral resources have been recognised worldwide in such intrusions (Notholt, Sheldon and Davidson, 1989); apatite primary mineralisation is associated mainly to carbonatites (sovitites, beforites, ferrocarbonatites), pyroxenites and related to metassomatic processes in glimmerites, fenites and syenites. In Brazil, apatite is the most ubiquitous mineral and occurs in significant concentrations in at least 12 alkaline-carbonatitic complexes.

Apatite deposits have been recognised in fresh rocks, but mainly in their overlying weathering mantles in tropical and subtropical regions, reaching more than 150 m thick. In fact, among the several deposits exploited in Brazil, just Jacupiranga fresh carbonatites are actually mined. It is emphasised that the weathering process is directly responsible for the economical character of the phosphate deposits as a result of the enrichment by eluvial (residual) or colluvial processes.

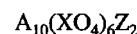
In general, these mineralisations usually present P_2O_5 grades from four to 15 per cent w/w. Although it requests, necessarily, a complex concentration process by froth flotation and wet

magnetic separation to reach a final concentrate grade from 35 to 36 per cent of P_2O_5 , which are basically used in fertiliser industry, production of sodium tripolyphosphate (STPP) and raw materials for the feed industry. These concentrates have rather strict specifications and most impurities are related to the presence of specific minerals in the phosphate ores. Therefore an adequate knowledge of the nature and distribution of the mineral assembly in the deposit is required for controlling the flotation plant products and mine planning purposes.

APATITE

There are known to be a few hundred that contain the tetrahedrally coordinated phosphate (PO_4^{3-}) anion; however, only a few species are relatively common and only the apatite mineral group (with grades between 14 per cent and 18.5 per cent P) constitute the valuable phosphorous minerals that are economically exploited.

Apatite presents a general formula:



where A = Ca, Pb, Sr, Zn; in the Be, Cd, REE, Sc, Mg, Mn, ...; X = P; the, V, S, C, itself, Cr, ...; and Z = F, OH, Cl, Br.

Pure members of the apatite group are almost non-existent because of the frequent and varied substitutions in their crystal structure.

The anionic content of the monovalence site (channels; Z_2) defines three main types of apatite (pure members – solid solution): fluorapatite ($Ca_{10}(PO_4)_6F_2$); hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$); chloroapatite ($Ca_{10}(PO_4)_6Cl_2$) (Toledo and Pereira, 2001).

According to the observed variations in chemical composition, CO_3^{2-} substitutes PO_4^{3-} in carbonate-apatites (McConnell, 1973; Le Geros and Le Geros, 1984); incorporation of F⁻ or OH⁻ accompanies this substitution and a deficit in Ca^{2+} ions may even occur. Carbonate-apatites are type 'A' when CO_3^{2-} substitutes F⁻ in the 'Z' site or type 'B' when CO_3^{2-} replaces PO_4^{3-} in 'X' sites. These two apatite varieties have distinct physicochemical behaviour as well as infrared absorption spectra.

As stated by Fischer and McConnell (1969), the compositional variability due to various substitutions (mainly in anionic site) establish some physical properties of the mineral, such as specific gravity, birefringence, magnetic susceptibility, solubility and others, etc. In general, substitutions in 'A' site have the greatest overall effect on unit cell parameters, while substitutions in the 'X' site affect the 'a' and 'c' dimensions differently, resulting in anisotropy. Besides, little variations are related to substitutions in the 'Z' site.

Since substitutions affect the unit cell parameters of the apatite in several ways, the distortions are used to define apatite varieties by X-ray diffraction (XRD) coupled to chemical analysis and a range of other techniques, such as Fourier-transform infrared spectroscopy (FTIR), cathodoluminescence (CL) and scanning electron microscopy with energy and/or wave dispersive spectrometer (SEM-EDS/ WDS).

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MAIN CHARACTERISTICS OF THE PHOSPHATE DEPOSITS

The alkaline-carbonatitic complexes are typically formed by successive and distinct geological episodes that result in accentuated 3D intermingling of different rocks with remarkable variety in their mineral composition in the scale of few metres or even centimetres. The apatite is normally associated to several lithological units, as a result of distinct mineralisation pulses, consequently they may be of rather different varieties and P grades would change markedly over short distances.

The complex distribution of the primary rocks is therefore responsible for the main lateral variations and it is also reflected in their weathering mantles even considering the homogenisation provided by supergenic environments. These alteration profiles show an additional vertical zoning, more or less developed, according to the intensity and evolution of the weathering processes.

The apatite varieties recognised in Brazilian alkaline-carbonatitic deposits are essentially related to fluorapatite, carbonate-apatite, hydroxylapatite and carbonate-hydroxylapatite. Chloroapatite are absent in the alkaline igneous environment.

Significant mineralogical, textural and grain size variations are related to the vertical zoning in weathered deposits (Born and Kahn, 1990). A complete profile, not necessarily present in all deposits (particularly in carbonatites bearing complexes) may be subdivided into several layers from surface to the fresh rocks:

- Superficial red clay-rich lateritic cover and/or ferricrete.
- Non-apatitic layer, with varied contents of very fine secondary Ba, Sr, Fe and Al phosphates, not recovered by apatite froth flotation. The layer may be enriched in Nb, Ti, Fe, REE, Ba and Sr, sometimes in economic levels.
- Main apatite bearing earthy layer, frequently enriched in relation to the primary rocks. Carbonates were completely removed by leaching. Ferromagnesian silicates are totally decomposed; alteration of Fe-Mg phyllosilicates (biotite and phlogopite) into clay minerals and iron oxides occurred in the top level, while in the lower portions of the layer, the micaceous habit of strongly discoloured minerals, as vermiculite, hydrobiotite and chlorite may be still recognised. Chemically, high Fe_2O_3 contents, MgO up to two per cent and P_2O_5 enrichment typify this layer. In some deposits it is possible to identify hard and very rich phosphate crusts constituted by reprecipitated and cemented fine-grained apatite and carbonate-apatite with very fine disseminated iron oxides.

- This horizon is quite similar to the 'c' layer, with residual preservation of the original silicates and slight reduction of the P grades. At its basal portion, the humid material may acquire a greenish tint due to the colour of the primary micas, pyroxenes and/or amphiboles. Sometimes relict rock structures may still be recognised at undisturbed and moist surfaces.

Layer presenting little weathered silicate minerals with preserved original rock textures and structures on undisturbed surfaces; it corresponds to 'decomposed rock'. Carbonates, unusual at the top, become frequent at the lower portion of the layer, especially when the underlying fresh rocks are related to carbonatitic origin. Some relicts of serpentinised olivine may even be locally preserved.

- Very slightly weathered primary rocks, except for the serpentinised olivine; sulfides, mainly pyrite and pyrrhotite, may be common as accessory minerals.

It is remarkable that the secondary non-apatitic phosphates originated by the decomposition of apatite and predominant in the 'b' layer decrease sharply from top to bottom of the alteration profile and are almost absent in the two lower layers. Figure 1 illustrates the behaviour of the most important minerals in the weathering mantles overlying alkaline-carbonatitic rocks.

The systematic description of drill cores, mine benches, chemical analysis and simple hydrochloric acid tests for carbonates as well as colour and grain size observations provide sufficient elements to recognise the different vertical layers in the weathered profile and the main variations of the fresh rocks. In general, different ore types may be macroscopically recognised by their texture and colour characteristics, thus geological descriptions are useful to identify even unexpected variations at the mining faces.

Fluor-hydroxyl-(carbonate) apatite is normally considered the predominant primary phosphorus ore mineral complex. Later processes related to weathering, or sometimes to hydrothermal events, may result in recrystallisation and/or reprecipitation phenomena, originating CO_3^{2-} enriched apatite varieties (fluor-carbonate-apatite up to pure carbonate-apatite). These late apatite, usually with fine prismatic character, are frequently associated with minute grains of dispersed iron oxi-hydroxides. They occur in layer 'c' of the alteration profile usually as granular microcrystalline aggregates as well as in compact phosphate crusts, constituted by primary apatite eluvial grains cemented by secondary carbonate-enriched apatite, which also covers the walls of cavities in the hard crusts.

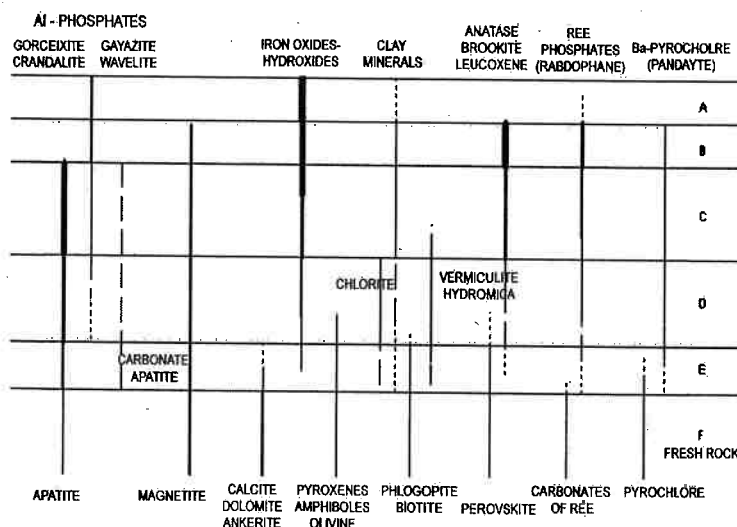


FIG 1 - Behaviour of the main minerals in Weathering Mantle (Born and Kahn, 1990).

APATITE BEHAVIOUR IN MINERAL BENEFICIATION

The froth flotation is the main concentration process applied to phosphate ores from alkaline-carbonatitic complexes, particularly in face of their low grades and complex mineralogy.

As a salt-type mineral, apatite is very susceptible to slight variations on its surface properties, which affect its flotation behaviour (Hanna and Somasundaran, 1976). The usual concentration process involves direct anionic flotation with fatty acids or synthetic collectors in a wide range of pH, allowing high phosphorus recoveries.

The similarity between the surface chemistry of the apatite and some gangue minerals is one of the main factors of the selectivity losses in the flotation process, particularly for those minerals bearing alkaline-earth elements, such as carbonates, iron-magnesium silicates and barite. Additionally, anions interaction and dissolved cations (Ca and Mg) in the pulp may modify the physicochemical surface characteristics of some minerals. Moreover, variations in the intrinsic apatite characteristics, such as composition and surface properties can affect substantially the apatite flotability.

The critical problem is that the flotation process is not selective exclusively for apatite (Born and Kahn, 1990). Then, the maximisation of selectivity and process efficiency can only be achieved with a best knowledge of the ore and the variables that mainly interfere in the concentration process, such as:

- Slime content. The presence of slime in the flotation increases the collector consumption as well as inhibits the flotation ('slime coating'). Such a problem can be overcome by increasing the number of scrubbing and/or desliming stages in order to minimise the slimes content in the conditioning and flotation operations or throughout the addition of dispersants to reduce the slime's coating phenomena.
- Minerals bearing alkaline-earth elements (Ca, Mg and Ba), such as carbonates (calcite and dolomite, mainly), barite, besides iron-magnesium silicates (phlogopite, vermiculite, chlorite, amphibole, Mg-olivine, serpentine, pyroxenes, etc), titanite and perovskite, among others, have some surface chemistry similarities with apatite. These minerals bring in selectivity losses in the flotation process, as well as anions interaction and dissolved cations in the flotation cells, as mentioned earlier, and concentrate dilution by undesirable elements incorporation, per times above the specifications limits.
- Apatite surface coating. In the weathering mantle of the alkaline-carbonatitic complexes apatite particles can be partially to full coat by a thin film of iron oxi-hydroxides. Those higher coating particles do not answer properly to the flotation; an attempt to minimise it by increasing the flotation time or collector amount will result certainly in losses of the flotation selectivity and/or increasing the content of the gangue minerals in the flotation concentrate. This approach, followed by wet high intensity magnetic separation is adopted in several Brazilian plants to improve the phosphate recoveries and to reach the final concentrate specifications.
- Presence of different apatite varieties. Apatite from distinct origin, composition and morphological characteristics are usually present in the same deposit, particularly in those associated to weathering residual process. Habit differences (prismatic, rounded, aggregates), superficial aspects (particle surface smoothness and roughness as well as coating) and mineral composition (fluorapatite, hydroxylapatite, carbonate-apatite and intermediate varieties) bring in different behaviours in the flotation process.
- Presence of non-apatitic phosphates. In the upper levels of the weathering profile, Al-phosphates related to apatite weathering are relatively common. These minerals do not interfere properly in the concentration process since they are not recovered by flotation. When associated to apatite (locked grains or films coating), their presence shall decrease the process selectivity and the global phosphorus recovery.

It must be emphasised that the flotability of the apatite is directly related to its crystallinity degree and weathering surface coating, which are associated to the alteration of the rock. The primary apatite (well crystallised) presents high flotability in opposition of the secondary apatite (lower crystallinity and lower flotability) (Born, Lenharo and Kahn, 1996).

Thus, ore type characterisation and their distribution along the deposit must be such that it effectively orients mining operations to achieve an adequate ore blending system and to allow a good estimation of the ore performance at the concentration plant.

APATITE CHARACTERISATION TECHNIQUES

There are a wide range of techniques applied to apatite characterisation. In this paper the most significant will be presented, which can provide useful information for mineral beneficiation.

Optical microscopy (OM-TL)

The optical microscopy by transmitted polarised light corresponds to a basic and extremely important tool in mineral raw materials characterisation. Its major application is on the identification and quantification of mineral species, as well as definition of mineral associations and evaluation of the liberation degree of valuable minerals. In the phosphate ore studies it allows the obtaining of the following information (Kahn, 1999):

- Textural fabric: mineral associations, liberation degrees and characterisation of apatite inclusions and grain size.
- Morphological features: apatite grains habit – prismatic, round, plate, fibrous, aggregates and others. Aggregates, usually indicative of secondary apatite related to weathering or late metasomatic processes, can be classified as three distinct types according to their morphology: fibro-radiated, microcrystallines and cryptocrystalline.
- Superficial aspects: apatite surfaces smoothness/roughness, as well as surface coatings features that present direct relationship to the apatite flotability (Figure 2).

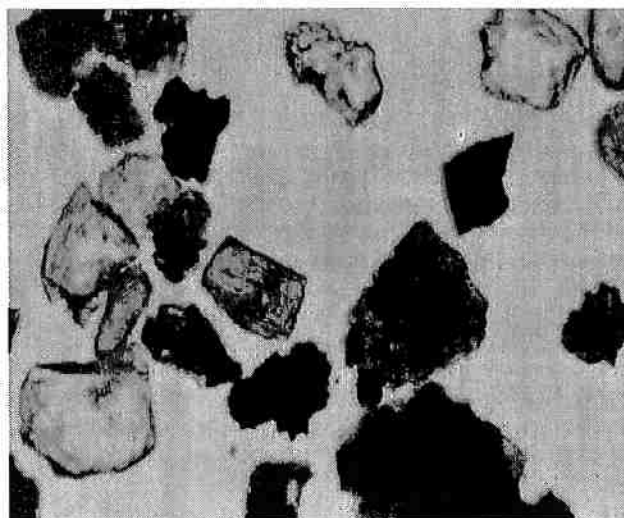


FIG 2 - Apatite grains limpid to median coated by a thin film of iron oxi-hydroxides (darker particles).

- Apatite variety: optical properties such as birefringence and extinction may allow the differentiation and quantification of distinct apatite varieties.

The major disadvantage of optical microscopy is the operator reliance and the relative low accuracy for quantitative evaluations (low statistics representation).

Scanning electron microscopy (SEM)

It is an important analytical tool usually used in conjunction and/or complementary to the optical microscopy. The SEM has a greater focal depth and space resolution compared to OM since it only focuses on a narrow spot (nm order) that is being scanned at that moment (Evans, Brundle and Wilson, 1992).

In a SEM the electron beam is rastered across the sample and the released resultant signals are detected, building up an image of the sample. These signals bring detailed information of the sample surface topography (secondary electrons – SE), compositional variations related to the average atomic number of each phase (backscattered electrons – BSE) or cathodoluminescence (CL). In addition, characteristic X-rays are also generated when the beam hits the sample; these X-rays can provide qualitative or quantitative chemical elementary data from punctual or selected areas.

In the study of phosphate ores SEM generates images of the apatite grains surface (Figures 3 and 4), coatings (Figure 5) and fabric relations (Figure 5), regardless of chemical data.

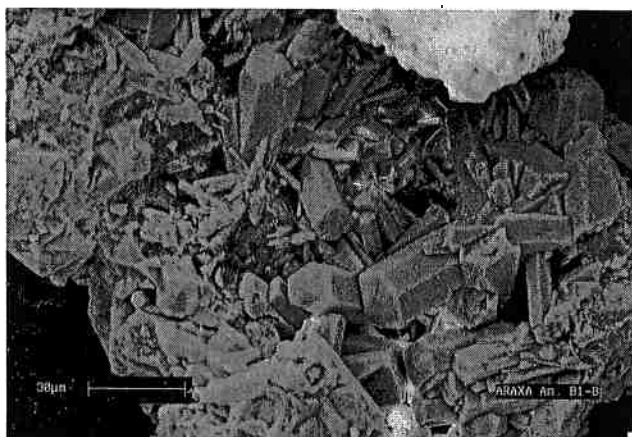


FIG 3 - SEM SE image. Fibro-radiated aggregate of secondary apatite growing over a primary apatite crystal.

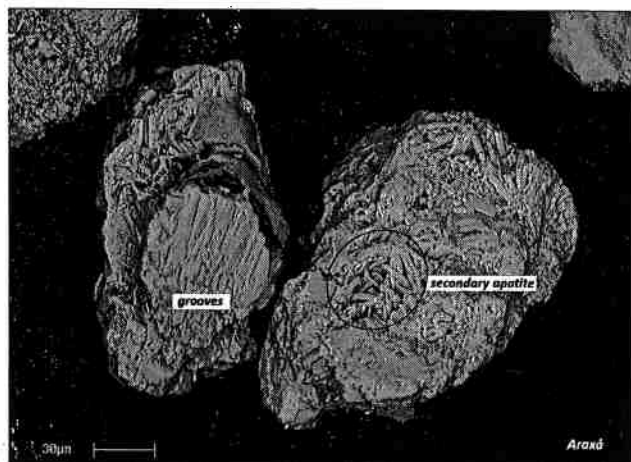


FIG 4 - SEM SE image. Secondary apatite microcrystalline fibro-radiated aggregate growing over a primary apatite and dissolution grooves in a primary apatite.

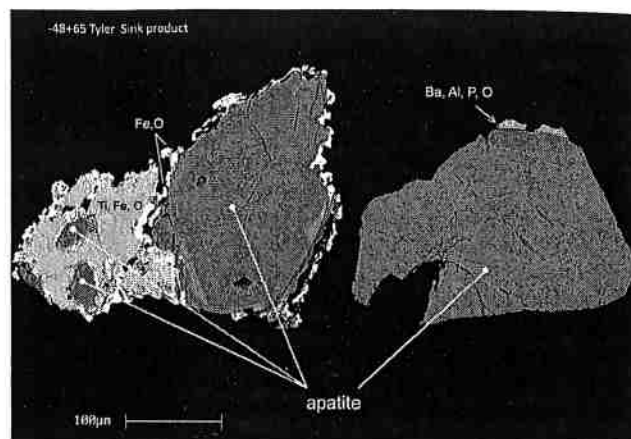


FIG 5 - SEM BSE image. Locked apatite-ilmenite particle with coating by iron oxo-hydroxides (left) and apatite associated with Al-Ba-phosphate (right-side particle).

Mineral chemical composition

Microanalyses techniques by EDS or WDS coupled to a SEM generate punctual chemical data (Figure 6) or element distributions images of selected areas (Figure 7) or lines. The attained quantitative chemical composition of particulate grains presents low significance information for mineral dressing applications, being more widely used with specific purposes such as chemical characterisation of different apatite or gangue species.

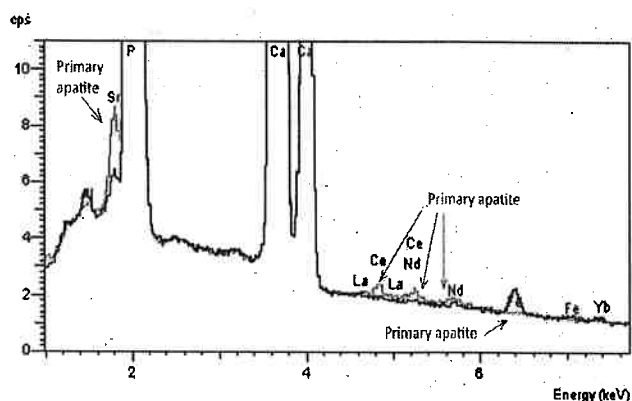


FIG 6 - Comparative EDS spectra from punctual analysis of primary and secondary apatite.

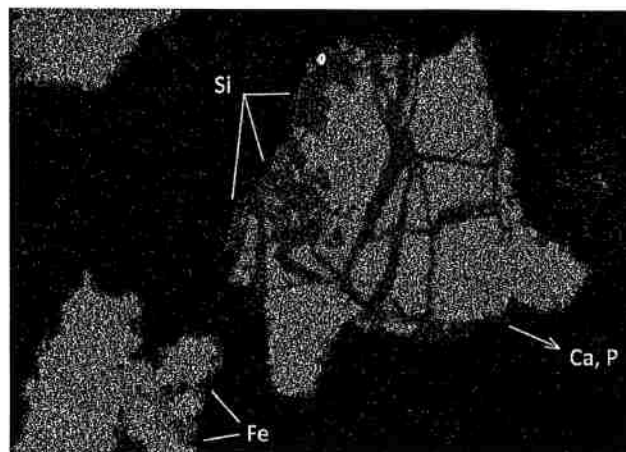


FIG 7 - SEM-EDS element map distribution for Si, P and Fe.

However, mineral separations techniques, working with more representative sample volume, allow the selective concentration of a given variety or mineral specie based on their physical properties, such as magnetic susceptibility or specific gravity. The average chemical composition of these purified mineral concentrates can be determined by different techniques, depending on the target elements and the amount of available material, such as X-ray fluorescence (XRF), ICP-OES, atomic absorption, FTIR, REE by neutron activation and classical methods, among others.

Cathodoluminescence microscopy (CL)

Cathodoluminescence (CL) is an optical and electrical phenomenon whereby a beam of electrons impacts on a sample that may emit visible light. When a high energy electron beam hits onto a semiconductor phase in the sample, electrons from the valence band are promoted into the conduction band, leaving behind a hole. When an electron and a hole recombine, it is possible for a photon to be emitted depending on the material, its purity and its defect state. Cathodoluminescence microscopy finds important and particular application in the study of compositional variation in apatite grains, although it is still very little used. The different apatite varieties can be easily and quickly individualised due to the distinct CL colours, which are related to the presence of trace elements in its structure (Table 1; Marshall, 1988; Götze, 2000).

TABLE 1
Cathodoluminescence colour in apatites (Marshall, 1988; Götze, 2000).

Nature	Luminescence colour	CL activators elements
Primary apatite	Blue to violet	$\text{Sm}^{+3} > \text{Dy}^{+3} \text{ e } \text{Eu}^{+2}$
Secondary apatite	Yellowish-white, yellow, salmon-pink	$\text{Sm}^{+3} \gg, \text{Dy}^{+3}$ $\text{Mn}^{+2} \text{ e } \text{Dy}^{+3} > \text{Sm}^{+3}$
Hydrothermal	Yellow to green	Mn (broad band)

In MO-CL, primary apatite presents blue-violet luminescence and it occurs as euhedral to subeuhedral grains. Secondary apatite presents a weak or no luminescence (depleted in REE) and sometimes yellowish-green colour due to Mn presence (Figure 8). It is common to observe the secondary apatite growing from the primary crystals, sometimes with optical continuity and as an interstitial cement phase.

SEM-CL presents the same fabric image as OM-CL but in grey levels (Figure 9) unless the CL spectrometer is coupled to the SEM. CL images are also a useful tool for quantitative evaluation of distinct apatite phases and forecast the ore behaviour in industrial processes (Santos, 1998).

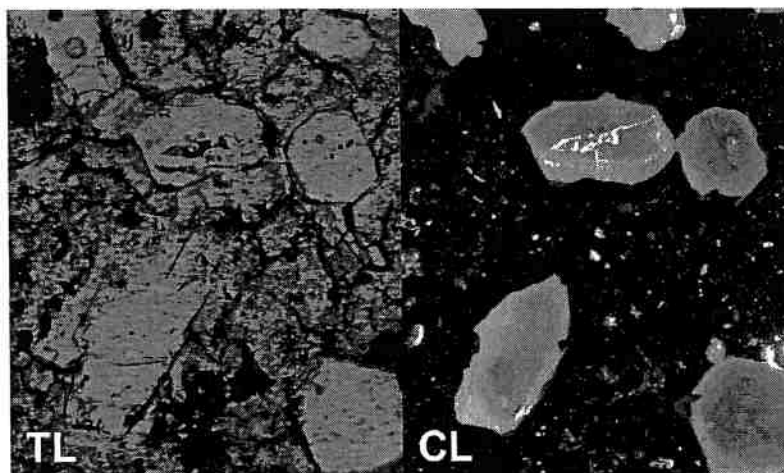


FIG 8 - OM-TL and CL images from a primary apatite cemented by secondary apatite.

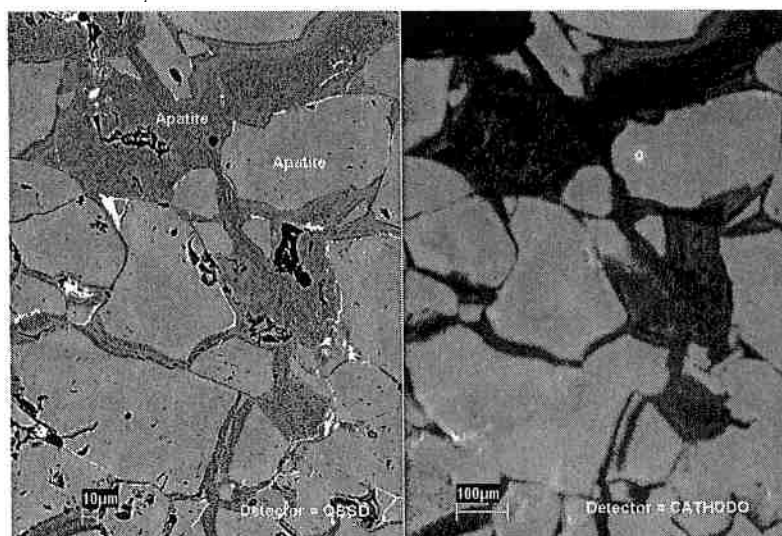


FIG 9 - SEM-BSE and CL images from a primary apatite (brighter) cemented by secondary apatite (darker).

X-ray diffraction (XRD)

X-ray diffraction (XRD) is a large spread technique basically applied in minerals characterisation with a major focus in the identification and quantification of mineral species.

Specifically on apatite studies, XRD allows the identification and the differentiation of distinct varieties, through the evaluation of unit cell parameters ('a' and 'c') and crystallinity degree; the first ones are indicative of the substitutions in the apatite crystalline structure. The behaviour of these parameters as a function of the most usual crystalline structure substitutions is presented in Table 2.

TABLE 2

Variation of the apatite unit cell parameters ('a' and 'c') according to usual atomic substitutions.

	Substituted by	'a'	'c'
Ca ²⁺	Sr ²⁺ , Ba ²⁺ , Ce ²⁺ , La ²⁺	Increase	Increase
PO ₄ ³⁻	CO ₃ ²⁻	Decrease (2 × 'c')	Increase
F ⁻	OH ⁻	Increase >	Decrease

Nowadays apatite unit cell parameters can be easily determined by Rietveld refinement. If the apatite and the gangue minerals crystalline structures are well known this technique may also give quantitative mineralogical composition and the content of the distinct apatite varieties.

XRD may also provide information about the apatite crystallinity, which shall be determined by area or height intensities ratio between the diffracted peaks of the hkl planes (211) and (112) (Born, Lenharo and Kahn, 1996).

For Brazilian apatites the correlation between the crystallinity data, optical microscopy, chemical analysis and unit cell dimensions show, as general tendency, that secondary apatites usually present lower crystallinity indexes and higher contents of Fe₂O₃ as indicated in Figure 10.

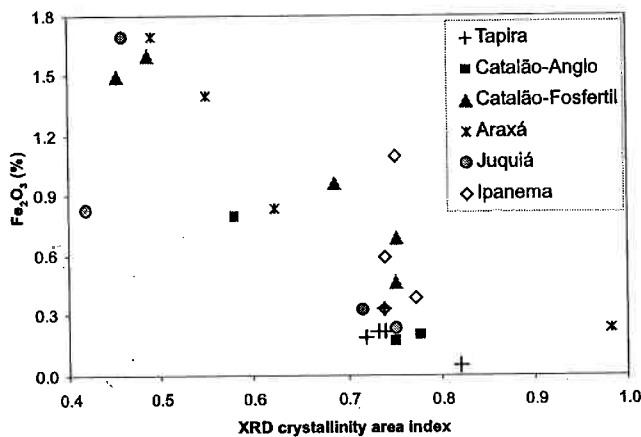


FIG 10 - Correlation between apatite Fe₂O₃ grades and XRD crystallinity for Brazilian deposits.

Fourier-transform infrared spectrometry (FTIR)

Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate (stretching, scissoring, rocking, wagging and twisting), corresponding to discrete energy levels. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and by the associated vibronic coupling. The frequency of the vibrations can be associated with a particular atom bond type. The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample.

Examination of the transmitted light reveals how much energy was absorbed at each wavelength; the observed absorption bands can be associated with a particular bond type or chemical groups (Marcott, 1986).

The main purpose of infrared spectroscopy in apatite studies is to confirm the hydroxyl and carbonate groups, which may already have been suggested by XRD and/or chemical data, as a complementary technique. The groups OH⁻ and CO₃²⁻ of hydroxyl and carbonate-apatite present characteristic IR absorption groups, which allow an easy identification of these varieties, as illustrated in Figure 11.

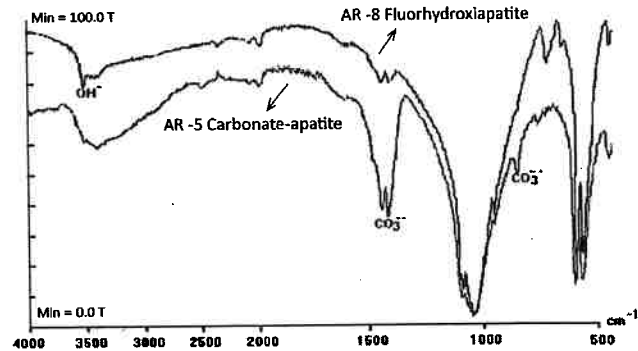


FIG 11 - IR spectra of primary and secondary apatite from Araxá.

Quantification of distinct apatite varieties can be done through the area intensity measurements of OH⁻ and CO₃²⁻ groups or by reflected FTIR microscopy coupled to image analysis.

Microflotation in Hallimond tube

Microflotation in Hallimond modified tube is a test conducted with pure minerals under controlled conditions. It aims to estimate the flotation behaviour of apatite and/or associated to gangue minerals in relation to the pH, collector type, depressants and ionic species in solution. A comparison between fluorapatite, francolite, dolomite and quartz flotation recovery versus the collector dosage is shown in Figure 12.

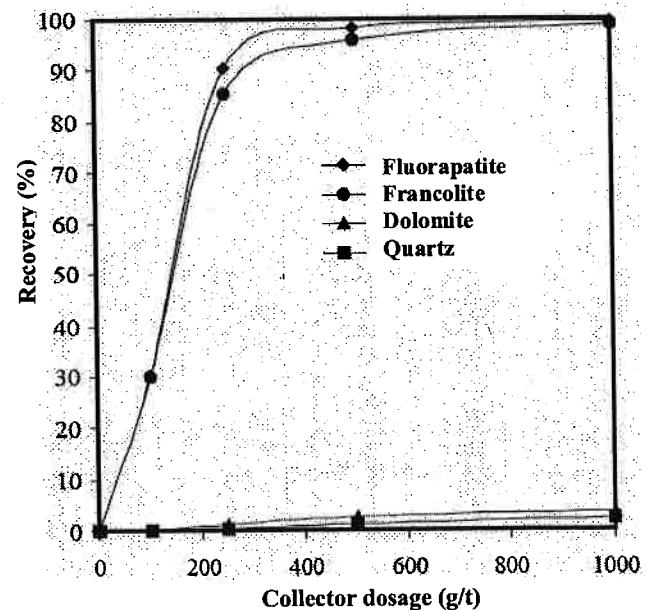


FIG 12 - Microflotation recovery of fluorapatite, francolite, dolomite and quartz as a function of AERO 6493 addition at natural pH of 6.5, with DI water (Miller, Wang and Li, 2002).

The application of this technique and correlation with froth flotation practice is still questionable. However, it is entirely applicable to evaluate the correlation between the crystallo-chemical characteristics and the flotability of a given mineral, as well as indicate flotation parameters (pH, reagents, ...) that should be evaluated in bench scale flotation tests.

According to Born, Lenharo and Kahn (1996) hydroxylapatite and fluorapatite present higher flotability indices when compared to carbonate-fluorapatite. Secondary apatite are usually CO_3^{2-} enriched and strongly associated to weathering processes; other features are also identified such as overgrowth and intergrowth with very fine impurities that significantly interferes on its flotation behaviour.

Magnetic separation

Apatite surface coatings by iron oxi-hydroxides not only decrease its effective own surface area (area available to interact with the flotation collector) as change the average particle magnetic susceptibility. The amount of highly coated particles that does not respond properly to the flotation process can be easily and quickly estimated by Frantz magnetic separators or by wet high intensity magnetic separator (WHIMS). This procedure has been widely used to evaluate the apatite potential recovery in Brazilian phosphate plants for more than 15 years and came to substitute the tedious and slow optical microscopy procedure for evaluating particles intensity coating.

Surface characterisation techniques

The apatite flotation behaviour is directly affected by variations on its surface properties. In the upper levels of the weathering profile where apatite is the main Ca-bearing mineral; the intensity of the surface coating by iron oxi-hydroxides plays a major role on its flotation behaviour. Although in the lower weathering profile levels and in fresh rocks it might be present several minerals bearing alkaline-earth elements (Ca, Mg and Ba) that bring in selectivity losses in the flotation, due to some surface chemistry similarities with apatite as well as may present anions interaction with dissolved cations in the flotation pulp. For this purpose, the use of X-ray photoelectron spectroscopy (XPS), contact angle, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and atomic force microscopy (AFM) is able to provide information about the surface (<5 - 10 nm) composition of the apatite and gangue minerals such as morphology, wettability and the adsorbed ions and/or collectors. This information is particularly helpful to understand the collector-mineral interactions and for the development of more selective reagents.

Wettability

Wettability of minerals particles is a fundamental characteristic for the flotation process. There are two common methods to measure the contact angle of a liquid on a solid surface: tensiometry and goniometry. On the goniometry the shape of a liquid drop on a solid surface is observed from the side; the contact angle is then measured and corresponds to the angle between the tangent of the drop surface at the contact line and the surface. If the liquid is very strongly attracted to the solid surface the droplet will be completely spread out on the solid surface and the contact angle will be close to 0° (hydrophilic solid); less strongly hydrophilic and hydrophobic solids will have a contact angle up to 90° .

Dynamic wetting, which comprises the formation, spreading and coalescence of water droplets over the mineral particles, can be achieved by measuring the contact angle against time through goniometry or by an environmental scanning electron microscope (ESEM) (Jenkins and Donald, 1999).

In the ESEM the sample chamber relative humidity is raised to 100 per cent by controlling the specimen's temperature and the chamber pressure to produce water condensation over the mineral particles. Dynamic wetting is then observed and the images are recorded in real time. The great advantage of the ESEM is the possibility of measuring the contact angle in real systems without any previous mineral separation, even for few micron particles.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as ESCA, is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation, providing surface chemistry composition (Evan, Brundle and Wilson, 1992).

The sample is irradiated with mono-energetic X-rays and then photoelectrons are emitted from the sample surface. An electron energy analyser determines the binding energy of the photoelectrons. The elemental identity, chemical state and quantity of an element are determined from the binding energy and intensity of a photoelectron peak.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS)

TOF-SIMS provides spectroscopy data for surface chemical composition characterisation and imaging for determining the distribution of chemical species (<5 - 10 nm), such as adsorbed collectors and/or depressants on the mineral surfaces (Evans, Brundle and Wilson, 1992).

It uses a pulsed primary ion beam to desorb and ionise species from the sample surface. The resulting secondary ions are accelerated into a mass spectrometer, where they are analysed by measuring their time-of-flight from the sample surface to the detector, providing chemical composition, imaging maps of chemical species and depth profiling of thin films. Chemical information are usually not quantitative despite the detection limits being very low (ppm) for most species.

Atomic force microscopy (AFM)

AFM operating in dynamic mode can build up a true three-dimensional surface profile image of a mineral since the sample topography is related to the presence of materials with distinct mechanical properties (hardness, wettability ...).

AFM uses a sharp tip of Si or SiN attached to a cantilever to scan the surface of a sample. When the tip is brought near a sample, the sample and the tip interact, causing the bending of the cantilever, which can be detected by measuring the deflection of a laser beam. The interaction between the tip and the sample results from several forces, such mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces, solvation forces, etc.

DISCUSSION AND CONCLUSIONS

In phosphate deposits from alkaline-carbonatitic complexes the distribution of the primary alkaline rocks is responsible for the main lateral variations, while the weathering process promotes a remarkably vertical zoning, particularly under tropic and subtropical regions. Therefore, there are significant mineralogical, textural and grain size variations that characterise ore types with distinct technological behaviour.

Ore type characterisation and distribution must be adequately and continuously monitored by its mineral, geological and chemical characteristics combined with operational and technological parameters, focusing the industrial performance.

optimisation to be really effective. The main parameters to be considered are the slime content, the apatite liberation degree and the surface coating by iron oxi-hydroxides, the amount of gangue minerals bearing alkaline-earth elements and the presence of different apatite varieties as well as non-apatitic phosphates. It is emphasised that many of these parameters can be determined only by systematic laboratory determinations on numerous ore samples involving time and labour of laboratory work.

As a salt-type mineral the apatite behaviour in froth flotation concentration is very susceptible to slight variations on its surface properties. The intensity of the apatite surface coating by iron oxi-hydroxides plays a major role on its flotation behaviour for the upper levels of the weathering profile in the residual phosphate deposits; the amount of highly coated particles that do not respond to the flotation process can be easily and quickly estimated by laboratory magnetic separation.

For the lower levels of weathering profile (saprolitic ore) and in the fresh alkaline-carbonatitic rocks the presence of other minerals-bearing alkaline-earth elements brings in selectivity losses in the flotation process since their surface chemistry presents some similarities with apatite as well as anions interaction with dissolved cations in the flotation pulp. For this purpose, modern surface characterisation techniques, such as XPS, TOF-SIMS and AFM, which are able to provide information about the surface composition of the apatite and the gangue minerals (less than 25 nm depth) coupled to contact angle measurements are particularly useful to understand the collector-mineral interactions and helpful in the development of more selective reagents.

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