APATITES FROM THE JUQUIÁ ALKALINE COMPLEX, SÃO PAULO, BRAZIL

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INTRODUCTION

Chemical, morphological and crystallographic studies were performed on apatites from representative samples of fresh rocks and weathered materials to define apatite characteristics, which affect their behaviour in the flotation process.

Although the presence of several primary and secondary apatite types had already been recognised in surface samples (Walter [5], Alcover Neto [1]), as to their morphological and general composition characteristics, significant new data on the chemical and crystallographic nature of major apatite varieties, in both surface and drill core samples, were obtained in this study. Additionally, the investigation aimed at correlating mineralogical characteristics with modified Hallimond tube microflotation behaviour.

Primary apatites were defined as strontium-hydroxyl-fluor-apatite and hydroxyl-strontium-fluor-apatite. Secondary apatites correspond to sodium-strontium-fluor-carbonate-apatite and sodium-silicon-fluor-carbonate-apatite. Covering primary apatite grains, or filling its fractures, microcrystalline to cryptocrystalline secondary apatites occur as prismatic aggregates with irregular or radial structure and as irregular "snowy" masses.

GEOLOGICAL SETTING

The Juquiá Carbonatitic Complex, São Paulo State, Brazil, covers an area of about 15 Km^2. The circular intrusion is constituted mostly by pyroxenites and alkali-gabbros. Carbonatites occur at the Serrote Hill in the western portion of the intrusion, surrounded by ijolitic and glimmeritic rocks to the north-west and nepheline-syenites at the southern part.

Two different carbonatites, internal and external, are attributed to distinct episodes. The internal carbonatite is formed mainly by calcium-magnesium carbonates enriched in iron, such as ankerite and parankerite, with magnetite, ilmenite, barite, rhabdophane, pyrochlore, stroncianite, pyrite and galena, as accessories. It is surrounded by a ring of external carbonatite, essentially dolomitic, with some magnetite, apatite, barite, pyrochlore and micaceous minerals [2].

Samples representing the most important apatite bearing materials, according to small scale mining experience and geological criteria, were used in this study.

METHODOLOGY

A standard procedure to produce almost pure apatite concentrates involved crushing below 297 μm (48 mesh Tyler), followed by low and high intensity magnetic separations (Frantz) and heavy-liquid methods (TBE and DIM), on the 297 - 105 μm (48-150 mesh Tyler) fraction. Analytical techniques included chemical analyses, optical microscopy, X-ray diffraction, infrared Fourier transform spectroscopy and scanning electron microscopy.

MORPHOLOGICAL AND OPTICAL CHARACTERISTICS

Detailed studies on five samples revealed the following apatite types:

Primary Apatites - Occur as translucent or vitreous grains, of granular or prismatic habit. The grains surfaces are smooth, with no signs of surficial alteration. In some samples, primary apatite contains frequent ovoid to rod-shaped inclusions.

Secondary Apatites - The reprecipitated apatites are divided into sub-groups according to grain morphology:

- **Prismatic Aggregates** - Constitute radial masses of fine hexagonal prisms (0.3 mm length) around an iron oxide nucleus or forming crusts of sub-parallel prisms on primary apatite grains. Extinction is radial-undulating or incomplete, according to the orientation of the aggregates;

- **Crystallite Aggregates** - Fine crystallites forming rugous irregular aggregates, generally associated with iron oxides or criptocrystalline apatite. Optical extinction is incomplete;

- **Criptocrystalline Aggregates** - Criptocrystalline apatite, associated with fine iron oxides, occurs as irregular striated or corrugated masses of 'snowy' aspect, covering primary or secondary apatite grains.

CHEMICAL ANALYSES

According to chemical analyses (Table 1), samples constituted essentially by primary apatites present low CO_2 content, as in MM-5. Samples with predominant secondary apatites (MC-1, MC-4 and MF-2), related to the upper levels of the deposit, have increased CO_2 contents and the CaO/P_2O_5 ratio is higher than the theorical value (1.32) of pure fluor-apatite. This indicates a P_2O_5 deficit due to CO_3 replacing PO_4 in X positions (apatite type B).

X-RAY DIFFRACTION

Crystallinity and unit cell dimensions were preferentially determined on almost pure apatite concentrates, but in some cases only a mixture of different apatite varieties was available.

The crystallinity is obtained by the relation between the area and height of the (211) and (112) peaks, according to the methodology proposed by Norman & Murata [4] (Table 2). The highest crystallinity level was verified on samples with largely predominant primary apatite (MM-5 and MF-2), while the lowest levels were obtained for samples constituted mainly by secondary apatites (MC-4, MC-1 and MM-3).

Two types of primary apatite were obtained by correlating unit cell parameters with chemical analysis results, respectively strontium-hydroxyl-fluor-apatite (MF-2) and hydroxyl-strontium-fluor-apatite (MM-5). In the second primary apatite type, the high strontium content explains the distinct unit cell dimensions (Table 1).

Secondary apatites were defined as sodium-strontium-fluor-carbonate-apatite (MC-1) and sodium-silicon-fluor-carbonate-apatite (MC-4), indicating that replacement of the phosphate radical took place, with consequent carbonate enrichment, together with hydroxyl decrease and fluorine increase, as shown by FTIR results.

INFRARED FOURIER TRANSFORM SPECTROSCOPY

Further corroboration of X-ray diffraction results was obtained by infrared analysis, indicating carbonate substitutions for phosphate radicals in the secondary apatite. That kind of replacement characterises the B-type fluor-carbonate-apatite, recognised by bands at 860 cm^{-1} (flexure), and 1430-1460 cm^{-1} doublet (stretch). The spectra also illustrate the hydroxyl absence in the secondary apatites and the low carbonate participation in the primary apatites.

SCANNING ELECTRON MICROSCOPY

The morphological features observed by optical microscopy were confirmed and observed in greater detail by SEM. Additionally, a remarkable sequence of growth lines (Photo 1) was observed in some apatite grains, related to variation in REE, Sr, Si, Al, Fe and Ti contents, detected by EDS analysis.

HALLIMOND TUBE MICROFLOTATION

Microflotation tests indicated that secondary fluor-carbonate-apatites, typically with low cristallinity levels, are less responsive to microflotation with "tall-oil" as collector, than primary hydroxyl-fluor-apatites (Table 2).

RESULTS

Optical microscopy was helpful to identify different, closely associated, morphological varieties of apatite and their relation with weathering processes, but could not furnish any clues about their composition and crystallinity. These were adequately understood only after the simultaneous application of several techniques, as described in this study. However, for future evaluation of phosphate samples from this or other deposits associated with alkaline complexes, optical microscopy can provide valuable preliminary information on the constitution of apatites as the morphology reflects their chemical character, thus serving as an indicator to anticipate the technological behaviour.

XRD and FTIR results indicated strontium-hydroxyl-fluor-apatite and hydroxyl-strontium-fluor-apatite as the primary phases; sodium-strontium-fluor-carbonate-apatite and sodium-silicon-fluor-carbonate-apatite are the main reprecipitated secondary phases, occurring in aggregates or as crusts on primary apatite grains. Significant carbonate substitutions for phosphate and fluorine for hydroxyl occurred in the secondary apatites.

The existence of strontium enriched apatite varieties in Juquiá affected the crystallographic parameters of apatites, which gives them a distinctive character when compared to apatites from other phosphate deposits associated with alkaline complexes from Brazil [3].

The prismatic, microcrystalline and cryptocrystalline secondary apatites present low crystallinity levels and are usually intergrown with iron oxides/hydroxides.

The simultaneous presence of low crystallinity secondary carbonate-apatites, associated with finely dispersed iron oxides/hydroxides, explains the low floatability performance observed for highly weathered materials.

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TABLE 1: Typical unit cell dimensions (Å) and chemical composition

Sample/Specie	*Ore type*	*"a"*	*"c"*	*$\%P_2O_5$*	*%F*	*$\%CO_2$*	*%CaO*	*%SrO*
MF-2 /Primary	friable	9.39502	6.88814	*40.4*	*1.9*	*1.30*	*55.0*	*0.59*
MM-5 /Primary	micaceous	9.38448	6.88946	*42.2*	*2.5*	*0.38*	*53.5*	*0.84*
MC-1/Secondary	cemented	9.35929	6.90060	*37.5*	*2.1*	*3.70*	*53.1*	*1.00*
MC-4/Secondary	cemented	9.34802	6.89401	*35.7*	*3.4*	*3.80*	*53.4*	*0.48*

TABLE 2: Crystallinity and Floatability Results

		Crystallinity		*Microflotation*		
Sample	*Ore type*	*Area*	*Height*	*Tests*	*Floatability(%)*	*S.Deviation*
MC-1	Carbonatite-Weathered	0.419	0.423	5	24.81	5.28
MF-2	Carbonatite-Weathered	0.717	0.772	3	22.47	5.21
MM-3	Carbon./Glimm.-Weathered	0.559	0.583	2	18.50	2.36
MC-4	Carbonatite-Weathered	0.460	0.334	3	12.02	3.40
MM-5	Carb./Glim-Semi-weathered	0.751	0.793	3	31.94	6.31

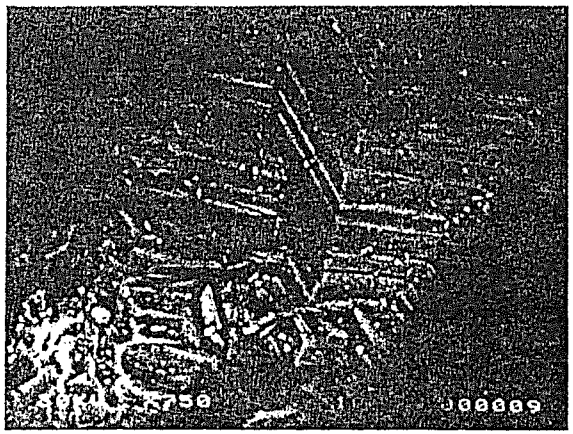

PHOTO 1: Sequence of growth lines in apatite grain related to variation in REE, Sr, Si, Al, Fe and Ti contents

TRENDS AND PROBLEMS IN APPLIED CLAY SCIENCE

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ABSTRACT

Utilization of clays changes with time. In different periods, various qualities and quantities of different clays have been demanded. Trends (direction of further development) in clay consumption and utilization reflect: (1) availability of clays, (2) state of understanding of clays (3) innovation in clay technology and (4) demand for new products made of clays and/or large scale operations. Consumption of clays generally increases; however, there are certain periods of greater interest in specific types of clays. Also stagnation occurs which is caused by economic recession or imbalance between clay science, clay technology and clay resources. Lack of novelty and repeated re-discoveries in clay science and clay technology indicate such stagnant periods. In such cases it is worthwhile to speculate about future developments.

CLAYS AND CLAY MINERALS

Clays were popular from the early prehistory of mankind. Reasons for this popularity were the common availability of clays, extraordinary properties and easy workability (Kühnel 1990). Nothing was known about composition and structure of clays and only useful and artistic products were manufactured by curious and skilled men with inventive and artistic minds. For millennia empirism ruled that clay utilization and archaeology reconstruct the long and complicated way to the formulation of clay science in the second half of the 20th century.

TREND IN CLAY UTILIZATION

Trends in clay utilization result from an interaction between three basic fields: (1) Clay Science, (2) Clay Technology and (3) Clay resources. Each of these drives clay utilization in a certain direction. While Clay Science has its objectives in comprehensive characterization, modification of clays for required applications, synthesis and new clay applications, clay technology follows improvement of product quality, new and "hitech" products and more efficient technologies. Exploration of clay resources looks for new reserves, more efficient processing, blending and tailoring of "ready to use mixes" and recycling. Parallel with such a complex interaction, new, sensitive and selective analytical techniques and instruments are being developed.

CLAY HELPS AND CLAY THREAT

Mass and properties of clays are two major features which are exploited by man. Till now, we consider only the positive man-helping actions of clays. In a previous paper (Kühnel 1992) the positive and negative, direct and indirect working of clays was summarized as follows.