

X-RAY POWDER DIFFRACTION ANALYSIS AS A TOOL IN MINERAL EXPLORATION FOR AGROMINERAL EVALUATION

RÔMULO SIMÕES ANGÉLICA¹, ALBANO A. DA SILVA LEITE², FLÁVIA CRISTINA SILVEIRA BRAGA³, MARCELO AUGUSTO DE OLIVEIRA⁴, KELLY SILVA OLIVEIRA⁵, EDER DE SOUZA MARTINS⁶

^{1, 5} Instituto de Geociências, Universidade Federal do Pará, 66075-110, Belém, PA, Brasil, (angelica@ufpa.br¹, kesioliveira@gmail.com⁵); ^{2, 3, 4} TERRATIVA MINERAIS SA, Bernardo Guimarães street, 245, 16th floor, Belo Horizonte, 30140-080, BRAZIL (albano.leite@terrativa.com.br², flavia.braga@terrativa.com.br³, marcelo.oliveira@terrativa.com.br⁴); ⁶ EMBRAPA Cerrados, BR 020 Km 8, 73310-970, Panatlna, DF, Brasil (eder.martins@embrapa.br)

Introduction

X-ray diffraction (XRD) analysis is the main tool in the analysis of the crystal structure of solid materials. It has been used since the beginning of the 20th century in the analysis of different kinds of inorganic materials (metals, alloys, soils, minerals, rocks, cements, etc.), besides organic and biological molecules. Since then, a specific scientific discipline has emerged – X-ray Crystallography – which plays a very important role in the development of many scientific fields. Although the theoretical fundamentals of X-ray crystallography are somewhat difficult for non-academic users, the most common application – phase identification – is relatively easy to use in many laboratories in both universities and industry.

Soils scientists have also used XRD analysis very often in order to understand soil mineralogy (e.g., iron and aluminium oxy-hydroxides and clay minerals) and the relationship with its chemical composition and element bioavailability for soil agricultural and environmental quality. With the increasing technology of laboratory equipments and improved software for mineral identification, routine use of XRD analysis in soil mineralogy and also for mineral exploration programs has become more common.

The main objective of this work is to show the power of this tool – X-ray Powder Diffraction Analysis – for soil mineralogy, mainly in mineral exploration for agromineral evaluation. This is part of a major project developed by TERRATIVA MINERAIS. Since 2011, this company screened locations close to agricultural regions in Brazil and with favourable geology & logistics conditions for agrominerals exploration.

Methods

The mineralogical composition of the bulk materials (randomly oriented samples) and the

clay fractions (oriented samples) was carried out by Powder X-ray diffractometry, using a Panalytical X'Pert PRO MPD (PW3040/60) diffractometer with a ceramic X-ray tube (λ CuK α_1 =0.1540598 nm), K β Ni filter and a X'celerator Position-Sensitive Detector. The following analysis conditions were used: a) Randomly oriented samples: scan range from 2 to 52° 2 θ , 40 kV and 30 mA, 0.02° step size and 60s time/step; divergent slit of 1/8° and anti scattering of 1/4°. b) oriented samples: scan range from 3 to 35° 2 θ , 40 kV and 30 mA, 0.02° step size and 30s time/step; divergent slit of 1/8° and anti scattering of 1/4°. XRD patterns were obtained three times: the first was air-dried, the second after treatment with ethylene glycol and a third after heating at 550 °C.

Results and discussions

Different results will be presented related to the several examples applied to soil science and agromineral evaluation.

Phase Identification (PI) and "Crystallinity" Evaluation

Powder diffraction data are commonly used to identify or 'finger print' crystalline materials. Phase identification of a mixture of mineral phases is based in the comparison of the peak position in the obtained X-Ray Diffractogram with patterns from a database. The most common is the PDF (Powder Diffraction File) from the International Centre for Diffraction Data (www.icdd.com).

Crystallinity index is a very general term to describe order-disorder in crystal structures, which can be related to microstrain or crystallite size domains (Jenkins & Snider, 1996). In a very simple way, it is related to "peak broadening" in the diffraction pattern, followed by intensities decreasing. A very interesting example can be given for apatite, the main source of phosphorus for fertilizers (Fig. 1). Mineral deposits of apatite in rocks are of two

main types: igneous (carbonatites) or sedimentary. The first are related to high temperature rock formation and apatite exhibit “high crystallinity”. On the other hand, in sediments and sedimentary rocks, apatite can be related to biogenic origin and low temperature formation, giving rise to “low crystallinity” apatite crystals.

In exploration programs for phosphates, soils samples collected during field work were routinely sent to chemical analysis, mainly for P_2O_5 determination. Nowadays, mineralogical analysis are also been carried out in order to identify the possible origins of the apatite source (igneous or sedimentary) during the early stages of exploration. A good example in Brazil is the National Programa for Phosphates Exploration, that has been carried out by CPRM, the Geological Survey of Brazil (CPRM, 2011).

Finally, XRD can also successfully identify other kinds of phosphate minerals, for instance, Al-phosphates of the Crandallite group, very common in soils from lateritic terrains in northern Brazil (Costa *et al.*, 1980), which may also be suitable for agronomic use after calcination (Francisco *et al.*, 2007).

Very interesting examples of K-feldspar crystallinity in different rocks – and overlying soils – for agromineral use are being studied by our group in several areas in Brazil, and will be presented in another work in this conference.

Clay Minerals Analysis

Clays and clay minerals are important constituents of most sediments and soils on the Earth's surface and are of great importance for agricultural purposes. Because clay particles (< 2mm) can not be investigated under macro or microscopic methods, XRD Analysis has become the primary method for analyzing those minerals. Figure 2 shows the XRD patterns of the clay fraction from a siltstone of the Pedra de Fogo Formation (Parnaíba Basin, northern Brazil), which exhibits $K_2O > 7\%$, mainly related to the interlayer space of the crystal structure from the clay minerals present in the sample (smectite and illite). The air-dried diffractogram shows the typical shift of the $d_{(001)}$ peak of smectite from 15.3 to 17.3 Å in the ethyleneglycol state. After heating, one observes the typical collapse to 10 Å,

overlapping with the illite peak.

Quantification: The Rietveld Method

Since the beginning of XRD analysis, quantitative estimation of the mineral phases has been a challenge due to different factors that influence peak intensities. The Rietveld Method is a powerful tool for the refinement of crystal structures based in the fitting of the entire profile of the diffraction pattern to a calculated profile using a least-squares approach. Many commercial and free softwares are available for this purpose.

Conclusions

X-Ray Powder Diffraction Analysis is a powerful tool in the analysis of mineral phases for agricultural purposes. New equipments are more efficient and relatively easy to use, associated to new, friendly-user softwares data evaluation. Phase identification is the main result obtained but several other kinds of analysis and informations can be obtained from a diffraction pattern, including: crystallinity evaluation, quantitative analysis, isomorphic substitutions (e.g., Al-goethite, Mg in the calcite structure), among others.

Keywords: X-ray Diffraction, Agrominerals, Clay Minerals, Soils

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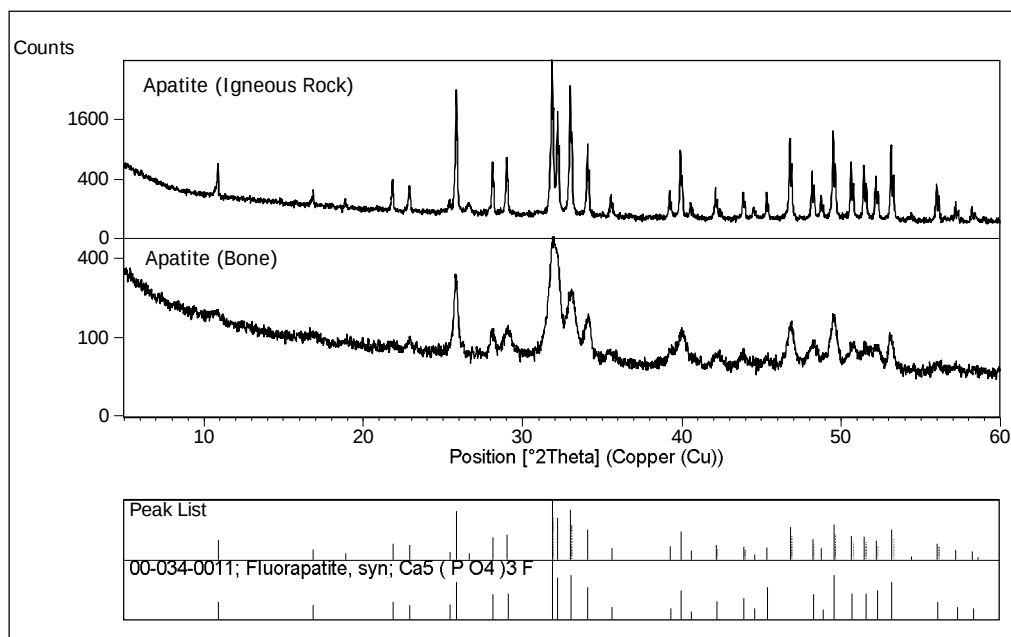


Figure 1. X-Ray Diffractograms of two different apatites, related to igneous rocks (top) and a bone (base), exhibiting different crystallinity related to distinct peak broadening.

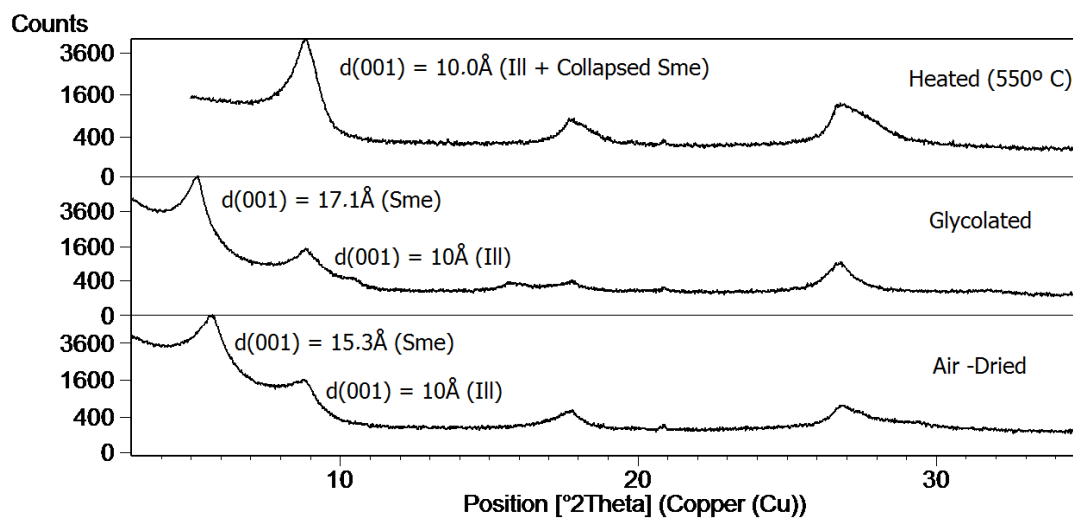


Figure 2. X-Ray Diffractograms of oriented slides (clay fraction) of a siltstone from the Paranaíba Basin, Northern Brazil: airdried, glycolated, and heated at 550 °C. Sme (Smectite) and Ill (Illite).