Routine quantitative phase analysis of niobium-bearing lateritic ores

Dona Kampata, Jean Naud and Philippe Sonnet

Université Catholique de Louvain
Laboratoire de géologie et minéralogie
3, Place Louis Pasteur
1348 Louvain-la-Neuve, Belgium

ABSTRACT

Routine quantitative analyses by Rietveld full-pattern fitting have been carried out on more than one thousand niobium ore samples originating from four pyrochlore deposits: Lueshe and Bingo (D.R. Congo), Mabounié (Gabon), and Sökli (Finland). The ore samples were characterized by a highly variable mineral content, the presence of mineral phases with a wide range of compositions and a high amorphous content. An analytical procedure was established which addressed several problems: creation of an appropriate crystallographic parameter database, specimen preparation, check for preferred orientation and measurement of the amorphous content by the internal standard method.

INTRODUCTION

X-ray powder diffraction combined with Rietveld full-pattern fitting is now widely accepted as a very promising technique for quantitative phase analysis. The technique, however, requires collecting a large set of input data: the crystal structure of all the different phases must be known, at least approximately, and several other parameters influencing the fit must be determined as well. This restriction makes the method particularly difficult to apply to mixtures involving a large number of phases when, in addition, each phase exhibits a variable chemical composition. This article describes the experience we have gained at analyzing such complex mixtures. Since 1991 on, we have analysed more than one thousand samples of niobium ore. These samples demonstrated considerable mineralogical variability. However, routine quantitative analysis was made possible by carefully defining and testing the analytical conditions. This research was performed as part of a group project performed by the London Natural History Museum (UK), the Ecole des Mines de Saint-Etienne (France) and the GfE Gesellschaft für Elektrometallurgie mbH (Germany). It was partly funded by the European Commission within the framework of the BRITE-EURAM program.
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NIOBium ORE SAMPLES

The analyzed samples originate from four niobium deposits: Lueshe [1, 2] and Bingo [3] located in the Democratic Republic of Congo, Mabounié [4] in Gabon and Sökli [5, 6] in Finland (Figure 1). The deposits are found in rocks which can be qualified as carbonatite, a carbonate-rich rock of volcanic origin. The main niobium-bearing mineral in carbonatite is pyrochlore. In most carbonatite occurrences, the pyrochlore content in carbonatites is too low to be economically recovered. In the four deposits under review, economically mineable ore bodies (>1.5 wt. % Nb₂O₅) formed where the carbonatite rock underwent weathering and dissolution. Pyrochlore, which is moderately resistant to weathering, accumulates in the residual soil formed by the dissolution of the carbonates close to the topographic surface. This process is most efficient in places where the soil was formed under lateritic conditions, i.e. in hot humid conditions similar to present day climates found in humid tropical regions of the world.

The mineralogical composition of the ore is highly variable and complex. Four processes can be invoked to account for this variability. First, carbonatite bodies, even before weathering, are usually quite variable in composition, even at very small scale (down to the centimetric scale). Second, lateritic weathering is a process which produces a pattern of successive layers with different mineral and chemical compositions that is called a weathering profile. In the deposits under investigation, between 3 to 5 zones formed down to a depth of 3 to 100 meters. Each zone is characterized by a definite mineral association or by the disappearance of a mineral which was present in the parent carbonatite rock. Third, weathering considerably modifies the chemical composition of the residual mineral, even if they resist dissolution. Fourth, weathering is a low temperature chemical process. It produces sluggish and incomplete mineral replacement reactions which eventually yield a high proportion of non-diffracting matter.

These four processes explain to a large degree why the ore has a very variable mineral content. The variability makes it extremely difficult to devise an efficient ore treatment process. If the feed of the ore processing plant varies continuously, the setting of the plant must be continuously fine-tuned to keep pyrochlore losses at an acceptable level. One way to keep the feed constant is to blend the ores. In practice, one has to define several ore types and map where the different types occur within the deposit. Several ore blends must also be defined so that each blend corresponds to a particular setting of the plant.

The analyses we performed aimed at defining such ore types and ore blends. Moreover, the analyses had to be performed within a time constraint of two weeks in order to provide a rapid response to on-going pilot plant tests.

MINERAL VARIABILITY

Pyrochlore is currently the main economic mineral for niobium. Its formula is A₂-xB₂O₆(OH,F)₁₋ₓ.zH₂O. The mineral exhibits a large range of cation substitutions in the A-site: Ca, Na, K, Ba, Sr, REE, U, Th, Mg, Mn, and Sn. The B-site essentially contains Nb but small amounts of Ti, Ta, Si and Zr can be found as well. Due to its high U and Th content (as in the Sökli deposit), pyrochlore is often metamict. In cases of high U and Th content, quantitative X-ray diffraction grossly underestimates the pyrochlore content. Therefore, for pyrochlore essaying, quantitative phase analysis must be complemented by chemical analyses.
Figure 1: Geographical position of the niobium ore deposits of Lueshe, Bingo, Mabounié and Sökli.
Weathering not only increases the niobium content of the rock but it also considerably modifies the chemical composition of the residual pyrochlore. When occurring as weathered residual mineral, pyrochlore mineral is often strongly hydrated and exhibits a large A-cation deficiency [2, 6, 7]. For example, the anhydrous Ca- and Na-rich pyrochlore present in unweathered rock is transformed into hydrated Ba-rich A-cation-depleted baryopyrochlore. Other residual minerals include amphiboles (several varieties often coexisted in the same sample), apatite, magnetite, ilmenite and a wide range of accessory minerals. Most of these minerals are also considerably modified by weathering. For instance, fluorapatite occurring initially transformed into carbonate-apatite (francolite).

New minerals are created by the alteration of silicates: vermiculite, clay minerals, kaolinite, goethite, crandallite (calcium aluminophosphate). At each of the four deposit locations in our study, all these secondary minerals display highly variable composition. Finally, many of these minerals are imperfectly crystalized, some having only a weak diffraction power (crandallite at Sökli, for instance). In addition to having broader and weaker peaks, these minerals contribute to the non-diffracting part of the sample. For instance, comparing chemical analyses of the ore samples with their quantitative mineral compositions reveals that, in the Sökli deposit, crandallite represents a significant part of the amorphous fraction of the samples. As for the Lueshe deposit, goethite probably forms most of the amorphous fraction.

CRYSTAL STRUCTURE DATABASE

A database of crystallographic data for the various phases present in each deposit was established based on the available literature and existing crystal structure databases (ICDD-PDF, ICSD). This database includes minerals typically found in laterite (iron and aluminum oxides and hydroxides, phyllosilicates, ...) and mineral varieties that are specific to each of the deposits (apatite, aluminophosphate, carbonates, pyrochlore, amphiboles, ...). One immediate question arises from the fact that the minerals in the ore sample do not have the same composition as the minerals in the database. Two methods were used to address this problem.

The first method consists in: 1) collecting a range of several structure determinations and 2) choosing the structure model whose calculated diffraction pattern best fits the experimentally measured one. In many instances, the structure model which was chosen had a chemical composition which happened not to be the closest to the composition of the mineral in the sample. These chemical differences, which at first were of concern, proved later not to be an obstacle. The Rietveld method makes it possible to refine the parameters of each phase while performing the quantitative phase and could accommodate for almost all observed discrepancies.

For some minerals, no published structure models provided calculated spectra which reasonably matched the measured ones even after several refinement attempts. A second method was then used. It consists in 1) performing chemical analyses by electron microprobe on the mineral causing the problem, 2) obtaining a purified concentrate of the mineral and, 3) refining the crystallographic parameters using the Rietveld method on the concentrate. This procedure was used, for instance, for kalipyrochlore, which is one of the pyrochlore varieties present at the Lueshe deposit [8].
MEASUREMENTS

Specimen preparation first involved pulverizing using a swing mill with a hardened steel grinding container to a particle size < 50 μm. As will be discussed below, two types of specimens were prepared for each ore sample: raw specimens and specimens mixed with an internal standard. Front-loading sample holders were loaded with special care to avoid preferred orientation. This loading was done by using sample holders with grooves on the bottom surface (Siemens standard sample holder), by gently pressing the raw powder in the holder and, finally, by scraping off the excess powder with a razor blade to remove the surface layer which was oriented.

XRD measurements were taken under the following conditions: Siemens D-500 diffractometer, Cu Kα mean radiation, curved graphite monochromator on diffracted beam, variable aperture slit, scan range of 4-90° 2θ step size of 0.02°, 2.4 sec/step counting time and scintillation detector. The possible presence of preferred orientation was investigated on several specimens using the DOSOPHATEX stage [9]. This stage was mounted at the center of a θ-2θ CGR goniometer. In addition to spinning the specimen, it allows to tilt the specimen along the ψ angle. Defocalisation which necessarily occurs when ψ-tilting the specimen is corrected using an appropriate software. The measurement procedure involved 1° 2θ step scan and, at each scan step, ψ-tilting of the specimen from -60° to +60°, with 50 steps and 3" counting time per step. The total counting time per degree 2θ step amounted to 15', which precluded using the DOSOPHATEX stage routinely. Preferential orientations proved to be moderate to negligible for most specimens. They were well within the range of preferred orientation which could easily be corrected by the Rietveld refinement method.

RIETVELD COMPUTATIONS

First, the specimens from the raw samples (without addition of an internal standard) were measured. The entire measured diffraction patterns were fitted by synthetic patterns using the Rietveld least squares refinement method. Our study was performed using the Siroquant program from Sietronics Analytical X-ray Systems running on a 486 or a Pentium generation PC. In most samples, 3 to 12 phases had to be considered simultaneously. After allowing for instrumental zero correction, parameters were successively refined for each mineral according to the following sequence: 1) unit cell dimensions, 2) shape of the lines, 3) line asymmetry, 4) line halfwidth and 5) preferred orientation factor. Typical global χ² values ranged from 6 for clay-rich samples with high background level down to 2 in more favorable cases. Detection limit was around 1 wt. % (provided the mineral had a negligible proportion of amorphous content). Not withstanding the fact that statistical error is, by definition, dependent upon the counting rate and thus upon proportion of the phase, our rough estimate for the overall relative precision for the weight percentages is around 5%.
AMORPHOUS MATTER MEASUREMENT

Several sources contribute to the overall amorphous content of the specimens: the amorphous matter (essentially iron hydroxides), the non-diffracting proportion of the minerals due to the poorly crystallized state (phyllosilicates, crandallite) and the metamict proportion of U- and Th-bearing minerals.

The overall amorphous content was measured by running a second Rietveld quantitative analysis after adding an internal standard. A fixed proportion (10 wt.%) of zincite (ZnO with wurtzite structure, < 40 μm, Union Minière Oxyde, Neige B, ref 522601) was incorporated into the samples. Zincite was chosen because it did not produce diffraction lines which coincide with the diagnostic lines or with the most intense lines of the minerals present in the sample.

The crystallinity of the added zincite was checked beforehand by the following procedure. First, amorphous-free quartz was prepared by sifting commercial quartz (Merck, pro analysi, 1.07536.) through a 40 μm mesh screen. It was then washed repeatedly with a 1 M NaOH solution during 1 hour at 75°C until the weight of the solid residue remained unchanged. Next, zinc oxide was mixed in known proportions to the amorphous-free quartz. Finally, the mixture was analyzed by X-ray diffraction quantitative phase analysis using the Rietveld method. We were able to show, using this procedure, that the zincite powder we were using had a crystallinity of close to 98%.

Mixing the internal standard with the samples required particular care. The samples displayed very variable textures (depending on the position in their weathering profile), high water and clay contents and a variable tendency to agglomerate or to stick. A routine method had to be devised to be able to homogeneously incorporate the zincite internal standard into the samples. We decided not to homogenize the mixture by milling, in order to avoid overgrinding. We tested four different methods for mixing the same test mixture (quartz50-zincite50). The first method involved desegregation of the mixture in acetone using ultrasonic agitation (Sanyo Soniprep 150). The mix was then allowed to dry by evaporating the acetone. Unfortunately, the differential sedimentation rates of the particles and the evaporation of the liquid out of the mix provoked mineral segregation. The second method used the Rotovapor mixer (Buchi RE 120) which performs simultaneous rotation of the sample and solvent extraction by pumping (heptane was used here). This method also caused segregation by selective adhesion of the phases on the wall of the glass container, which proved difficult to scrape off. The third method involved dry mechanical mixing of the mixture. To avoid overgrinding, we used a slow rotating mixer. The mixer consisted of a 20 cc cylindrical glass vial of 2.5 cm diameter containing around 1 gram of powder which is placed in an oblique position in respect to a horizontal rotation axis (60 rpm). This method created a slow rotating and rocking movement which enabled us to obtain a fairly homogeneous mixture in a few minutes. However, this method occasionally produced lumps. The fourth method was designed to avoid the lumping. First, the sample is mixed with the standard during 10 to 15 minutes using the dry mechanical mixing device outlined above. Second, the mixture is desegregated by gentle grinding in a hand mortar to eliminate possible lumps. Finally, mechanical mixing is used again during 10 minutes. This last method yielded highly reproducible results and was finally chosen for routine analysis.
DISCUSSION OF RESULTS AND CONCLUSION

As an example, we present the results we obtained for one drill core in one of the four deposits we studied. Sixty three samples were taken along the core. The graph in Figure 2 depicts the weight percents of each mineral in the samples as a function of depth. Eleven different minerals were measured as well as the amorphous content. The graph clearly shows that the mineral composition of the ore is highly variable depending on its position in the weathering profile. Amorphous contents around 40 wt. % are not uncommon and values up to 60 wt. % are found in several samples. The abundance of carbonates, at the bottom of the drill hole, indicates that the unweathered bedrock has been reached.

Our results suggest that quantitative phase analysis can be routinely applied to complex ores. It provides fast and accurate results which, in the case of pyrochlore deposits, proved to be an extremely useful method of assessing the economic potential of niobium deposits.

Figure 2: Mineralogical composition of 63 ore samples taken along a drill core in one of the four studied deposits. Sample #1 is situated at the top of the core.
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