

A COMBINATION OF CHEMICAL, PHYSICO-CHEMICAL AND DXRD METHODS FOR THE RECOGNITION OF METAL-BEARING PHASES ASSOCIATED WITH IRON OXIDES/HYDROXIDES IN LATERITES

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The main goal of the experimental procedure presented here is to break up, very selectively, the iron oxides and hydroxides of natural samples in order to localize and determine the quantities of included trace-elements.

It combines the results of (1) chemical extractions by citrate-bicarbonate (CB) and dithionite-citrate-bicarbonate reagents associated with a kinetic control of the reactions, (2) X-ray diffraction (DXR) and differential X-ray diffraction (DXRD) which enable the determination of the substituted ratios in hematites and goethites, and (3) physico-chemical analysis which enable characterization of the textures as well as the solid-reagent contacts.

The deferrification obtained with this new procedure is as efficient as the classical hot DCB and is more specific, especially in the presence of aluminous oxides/hydroxides. Furthermore, because of the longer reaction time, the kinetic study can be achieved more easily.

Samples were obtained from a lateritic core, which had been extracted for evaluating the potential of a

Burundian nickeliferous deposit. They belong to the following units: yellow laterite, red saprolite, dismantled duricrust and red soil.

In this way, differential behaviour of some iron oxides/hydroxides has been shown by measuring together the evolution of the residue and the associated amounts of other elements such as aluminum, chromium, manganese... all throughout the reduction. The existence of chromium substitution ratios in goethites, which perverts significantly the DXR interpretation, the preferential association of titane phases with hematites, and the non-correlative relationships between extracted iron with copper and manganese have been pointed out. The absence of correlation in the case of copper can be explained by inclusions of this element in a residual mineral having a spinel structure. In the case of manganese, which can be partially reduced by dithionite, no clear conclusion can be yielded. This shows one limit of the methodology presented in this communication.

Based on these few examples, it may be concluded that despite the complex nature of lateritic environments it is possible to carry out metal-bearing phase identification in the case of ferruginous minerals.

DETERMINATION OF RARE EARTH ELEMENTS IN GEOLOGICAL SAMPLES BY ISOTOPE DILUTION MASS SPECTROMETRY

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Among the many raw materials that are being used in modern industry, rare earth elements are playing an increasingly important role. Since their early commercial exploration, great changes have taken place in the type of deposits explored, as well as their industrial application.

New advances in the development of analytical techniques, established by geochemists, are helping in the characterization and quality control in the fields of rare earth element application, permitting the precise and accurate determination of these elements, even at very

low concentrations.

Considering the importance of precision (and accuracy) in the analytical data, the objective of the present study was to establish the mass spectrometric isotope dilution technique for the analysis of the rare earth elements, as this technique possesses high sensitivity, precision (and accuracy). Within this general objective, chemical separation methods involving ion exchange chromatography were established for the group and individual separation of the rare earth elements.

The method was established for the international rock standards AGV-1, GSP-1, G-2 and PCC-1 and the results obtained compared with the literature values. The analytical procedure established involved the preparation and calibration of the tracers by isotope dilution mass spectrometry, sample digestion, chemical separation and isotope analyses using a fully automated thermoionic mass spectrometer micromass VG isotope model 354. The sample dissolution was carried out in a teflon vessel under pressure. The material (samples + tracer) was digested using a mixture of concentrated HNO₃ and 40% HF in the pressure vessel at 160°C for a period of 18 hours. The sample solution was evaporated and, later, a mixture of concentrated HClO₄ and HNO₃ was added and evaporated again. Finally, the residue was dissolved in 2N HCl and taken for chemical separa-

tion. The elaborate dissolution procedure was necessary as the rare earth elements are generally present in the accessory, resistant minerals.

The chemical separation was carried out in two steps in cationic resin columns. In the first column, the total rare earth elements were separated from other elements using 2N HCl and 8N HNO₃ as eluting agents. In the second column, using 0,25N α -HIBA (pH=4.6) as an eluting agent, rare earth elements were separated into individual fractions (La, Ce and Nd) and sub groups (Sm-Eu-Gd and Yb-Er-Dy). Nine elements (La, Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb), with concentrations in the range 0.5ppm to 400ppm, were determined with a total precision of 1 to 2% and an accuracy of 5%. The rare earth element concentrations, determined in the rock standard PCC-1, demonstrated the low blank levels in our analysis.

The results obtained in the present study have shown that the analytical procedures developed and employed are satisfactory, as indicated by the high precision and accuracy obtained for the elemental concentrations values. Further, the great advantage of the technique, as shown by the present study, is the non-dependence of the precision and accuracy on the concentration levels of the elements in the samples. The study has also shown that α -HIBA is an efficient eluting agent for the separation of individual rare earth elements.

DETERMINATION OF URANIUM AT THE PPT LEVEL BY TIME-RESOLVED LASER-INDUCED SPECTROFLUOROMETRY: APPLICATIONS IN THE ENVIRONMENT AND IN GEOLOGICAL SURVEY

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Analytical control of uranium at a very low level required in several fields, such as, nuclear geology medicine and prospection. Due to its high sensitivity and selectivity, time-Resolved Laser-Induced Spectrofluorometry (TRLIS) is the method chosen for such applications. The principle of TRLIS is based on the fact that uranium is known to exhibit visible fluorescence in solution when excited by a UV pulsed source. In phosphoric medium, the uranium fluorescence is characterized by a long lifetime (> 100 us). Measurement of the fluorescence a few microseconds after the laser pulse permits the elimination of the short lifetime fluorescence (<1 us) of organic matter. This temporal resolution leads to very selective and sensitive measurements.

Besides a nitrogen laser used as the excitation source, the new apparatus "FLUO 2001", specially designed for such applications, consists of a cell-holder for receiving

the solution to be analysed, a monochromator, a multi-channel detection (intensified photodiodes array), a control unit that assures both the pulsed functioning of the intensifier and the photodiodes array and, finally, an IBM-AT computer that plots the whole system with specially adapted hardware. Analytical software is used for both concentration determinations and lifetime measurements. For the moment, the most interesting results have been obtained for uranium, with a limit of detection of 1 ppt 5×10^{-12} M in a phosphoric medium. Some lanthanides and actinides have also been determined by TRLIS with good sensitivity (ppb level and lower). Furthermore, remote sensing measurements can be carried out with fiber optics and optodes. This adaptation has the advantage of allowing measurements in

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