

journal homepage: https://www.irsm.cas.cz/acta



ORIGINAL PAPER

SEQUENTIAL EXTRACTIONS OF LANTHANIDE ELEMENTS AND TOXIC METALS ASSOCIATED WITH RARE EARTH PHOSPHATE-TYPE MINERALS

Francisco PRIETO-GARCÍA¹⁾*, Kinardo FLORES-CASTRO²⁾, Judith PRIETO-MÉNDEZ³⁾ and Eliazar AQUINO-TORRES³⁾

¹⁾ Centro de Investigaciones Químicas ²⁾ Centro de Investigaciones de Ciencias de la Tierra y Materiales ³⁾ Área Académica de Agronomía. Instituto de Ciencias Agropecuarias Universidad Autónoma del Estado de Hidalgo. Carretera Pachuca-Tulancingo km. 4.5, C. P. 42076, Pachuca, Hidalgo, México

*Corresponding author's e-mail: prietog@uaeh.edu.mx

ARTICLE INFO

Article history: Received 7 September 2018 Accepted 8 January 2019 Available online 15 January 2019

Keywords:

Phosphate minerals Rare earth elements Neodymium Praseodymium Cerium Sequential selective extractions

ABSTRACT

The elements of economic interest in coastal sediments are characterized by a relative high concentration in minerals as the ilmenite, rutile, monazite and manganite. The objective of this work has been to carry out a study of selective sequential extractions of lanthanide elements and metals that are toxic. It started with rare earth phosphate-type minerals, using the technology established in the American continent (Tessier), applicable to sludge and sediments. The study is concerned with the outcrops of REE's minerals reported in Mexico as pegmatite, in the settlement "The Dead", Telixtlahuaca, Oaxaca and of "Lagoon Mother" and "Saw of San Carlos", Tamaulipas. There were evaluated in addition samples of Cuarzomonzodiorite, of "The Incarnation", Hidalgo. Two modifications interfere to the above mentioned scheme of extractions and for the reached results it was possible to find the existence of some elements lanthanides as well as of toxic metals, praseodymium, neodymium, ytterbium and lead, associated with these minerals. The procedure of sequential selective extractions according to Tessier's methodology, does not manage to extract significant quantities of these elements, except in the conditions of maximum aggressiveness, of a digestion with HNO₃/HClO₄ concentrates and warming.

INTRODUCTION

The methodologies of sequential chemical extraction are applied in geology with the objective of determining the speciation of trace metals in soils, sediments and rocks, information that cannot be obtained only from a conventional chemical analysis on a total sample. At present, there is a wide variety of different sequential extraction analyses, although one of them has not yet been imposed as a fully accepted standard method (López andt Mandado, 2002). Different digestion and extraction procedures have evaluated to estimate the degree been of environmental contamination by elements such as Zn, Cd, Pb, Co, Ni, Cu and Cr, among others (Tessier et al., 1979; Mahan et al., 1987; Ure et al., 1993; Thomas et al., 1994; Campanela et al., 1995; Ščančar et al., 2000).

The sediments have been used to estimate the magnitude of contamination and the anthropogenic impact (Ščančar et al., 2000) caused by the different elements; to these are added the elements of the rare earths (REE's). The study of coastal sediments has contributed to the knowledge of them in the interpretation of ancient sedimentary environments, as well as for the eventual use of minerals present in

beach sands, especially when it comes to sands rich in metals of economic importance. Among these elements of economic interest are elements of rare earths and they are pointed out that the coastal sediments characterized by a high concentration of black sands, are highlighted by the presence of minerals of economic value, such as ilmenite, rutile, monazite and magnetite (Dawood, 2007).

The REE's are separated into three groups: I. Light REE's: lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium (Nd). II. Intermediate REE's: europium (Eu), samarium (Sa) and gadolinium (Ga). III. Heavy REE's: terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu) (Burkhalter, 2016).

The most common lanthanide deposits are those of monazite in beaches and river sand. It was not until 1883 when their first application was found (Keller and Baldridge, 1999; Kanazawa and Kamitani, 2006). The primary deposits of lanthanides rarely have an economic performance and are the best known. Its most favorable environment is that of alkaline rocks, which in Mexico are found in the regions of Tamaulipas and north of Veracruz and in the southern

Cite this article as: Prieto-García F, Flores-Castro K, Prieto-Méndez J, Aquino-Torres E. Sequential extractions of lanthanide elements and toxic metals associated with rare earth phosphate-type minerals. Acta Geodyn. Geomater., 15, No. 1 (193), 27–37, 2019. DOI: 10.13168/AGG.2019.0003

continuation of the "Rio Grande" (Chihuahua and Coahuila). In Tamaulipas and north of Veracruz there are reports of monazite veins and in the south of the "Rio Grande" there are deposits of iron that are rich in magnetite. It is also reported that the proterozoic lands in which most of the main deposits are located, where the pegmatites of the Telixtlahuaca region in Oaxaca are located, are favorable. In these, the first deposits of lanthanides were discovered in Mexico and their economic use still requires research on profitable metallurgical processes (Gómez, 1990). Precisely; the first mineral deposit in Mexico, in which the lanthanids were considered as of possible commercial interest, was the pegmatites of "Santa Ana" and "La Crisis", in the region of Telixtlahuaca, Oaxaca, where the minerals alanite and fergusonite were identified (González, 1956).

So far the production of lanthanides in the world has been absorbed by three branches of industry: catalysis in oil refining, steel and glass and ceramics. From 1980 the accelerated development of electromagnetic articles began, highlighting the permanent magnets of Sm-Co and Nd-Fe-B and the field of more recent applications has been in the development of superconductors. Studies on mineralogy and petrology of REE's in Mexico are scarce (Gómez, 1990), and even more, those that include the impact of these on the human being.

The REE's mineralogy is very coarse and is found mainly in igneous rocks of subalkaline to alkaline tendency (sienites, quartzites, quartz monzonites). The REE's are mostly simple and complex phosphates, associated with Y, Nb, U, Th and platinum group element (PGE), such as Os, Ir, Rh, Pd, Pt (Wilson and Chunnett, 2006). The substitution of calcium by REE's is frequent in apatite, titanite, allanite, feldspars, among others. Other minerals that contain them and that are reported in Mexico are: betaphite, monazite, titanite and xenotime. In igneous rocks on the surface of the earth, the cerium (Ce) is the most abundant element of them. The lanthanides are typically isolated in groups, precipitating their insoluble hydroxides, oxalates or phosphates (Bünzli, 2013).

This study evaluated the potential of lanthanides in the phosphate-type minerals in Mexico. Basic requirements are to know their chemical and mineralogical composition by means of X-ray diffraction (XRD), X-ray fluorescence (XRF), optical and electron microscopy and analysis by atomic absorption spectroscopy (ASS) and XRF techniques of elements such as Y, La, Ce. Pr, Sm, Nd, Gd, Yb, Th, U (Gómez, 1990).

Other metallic elements, such as Cd, Cr, Pb and Hg, that may be associated with these minerals and that due to their degree of toxicity and/or hazard for their contents and forms of association and leaching to the environment, were evaluated.

The objective of this work has been to carry out a study of selective sequential extractions of

lanthanide elements and trace metals that are toxic, from minerals of the rare earth phosphate-type, using the established technique in the american continent (Tessier scheme), applicable to mud and sediments.

EXPERIMENTAL METHODS

The study area corresponds mainly to the state of Oaxaca, where the pegmatites of the Telixtlahuaca region are located, since it is reported that the proterozoic lands are favorable, in which most of the main lanthanide deposits are found. In addition, minerals from other potential areas were evaluated to verify the same criteria for selective extraction of these elements and for similar minerals. The mineral outcrops of REE's reported in Mexico were studied as pegmatite, sample taken from the town "The dead", Telixtlahuaca, Oaxaca (identified as sample vk-102), and "Laguna Madre" and "Sierra de San Carlos", Tamaulipas (identified as sample vk-120). Samples from Cuarzomonzodiorite, from "La Encarnación", Hidalgo (identified as sample vk-122) were evaluated.

A completely random stratified sampling was carried out. Each sample size "n" was taken from a population of approximately 180-200 m³ of selected ore, considering a depth of 10-100 cm. The sample size was calculated from the expression (Münch and Ángeles, 1979):

$$n = [Z^2.p.q.N] / [N.e^2 + Z^2.p.q]$$

where:

- n = sample size to be taken in grams or kilograms (g or kg)
- N = size of the population in grams or kilograms (g or kg)
- p = 0.95 and q = 0.05, as sample probability factors representative
- Z = 1.960 as a statistical value for a 95 % level of reliability
- e = 0.05 as estimation error level.

Its initial mineralogical classification was carried out physically and by observations of the results of the XRD. The samples were reduced in size, first in a jaw mill for which rocks with a maximum size of 8 cm in diameter are required, then the resulting material is fed to a roller mill to refine the size to a value approximate 1.69 mm. If necessary, the particle size can be reduced to approximately 104 µm using a spray mill. They were classified using standard Tyler sieves. The analysis to obtain the distribution of particle sizes and the average size will be done with a LS [™] 13320 Series Laser Diffraction Particle Size equipment brand Beckman Coulter. The morphological characterization was carried out with a JEOL scanning electron microscope. Mod. JSM6300, at 20 kV, and at the same working distance in all the samples (Wd = 39 mm) and with the same number of accounts (approximately 2500) and increases of X350.

The XRD was used to evaluate the present phases and the residues resulting from the final phases

of selective sequential extractions. The solids were pulverized in agate mortars until they reached a particle size of <100 μ m and evaluated in a PHILIPS diffractometer, model PW-1710-BASED, with CuK α radiation source, $\lambda = 0.15406$ nm, nickel filter, aluminum sample holder, generator voltage and current of 40 KV and 30 mA, respectively, with sweeps of angles (2 θ) from 5 to 700 with coupled signal integrator.

The selective leaching of lanthanide elements and other toxic elements was carried out following the Tessier scheme (Tessier, et al., 1979; Toral, 1996; Prieto, 1997; Pérez, 2004; Prieto et al., 2006; Frohne and Rinklebe, 2013). A weighing between 0.5 g and 1.0 g of dry sample will be placed in a 250 ml flask with 20-40 ml of distilled water was added. It is stirred continuously for 1 hr at room temperature in a mechanical stirrer. The sample is filtered with a 0.45 μ m membrane and the solution is brought to a volume of 100 ml with deionized water. In this way a solution is obtained with elements that are simply soluble in these conditions; this fraction is called "zero fraction", which is a modification that is introduced in the sequence of extractions of Tessier. To the solid residue, 20-40 ml of 1 M MgCl₂ is added and stirred continuously for 1 hour at room temperature on a mechanical stirrer, also at the end of this time, the sample is filtered with a membrane of 0.45 microns and the solution is brought to a volume of 100 ml, in this way a solution with easily exchangeable elements (exchangeable fraction) was obtained.

To the residue obtained from the previous extraction is added 20-40 ml of acetic acid/sodium acetate (HOAc/1 M NaOAc), adjusted to a pH of 5, stirred for 5 hrs at room temperature. The sample is filtered with a 0.45 microns membrane and the solution is diluted to 100 ml for further analysis (metal species that leach because they are associated with carbonates will be present here). The residue is again used to perform a third extraction with 20-40 ml of hydroxylamine hydrochloride (NH₂OH·HCl) 0.04 M solution in 25 % HOAc with continuous agitation for 6 hrs and keeping it at a constant temperature of 96 °C. The sample is filtered with a membrane of 0.45 microns and the solution is 100 ml (these will be the elements that leach because they are in the reducible fraction or bound to oxides).

The residual material is subjected to a fourth extraction with 20-40 ml of 30 % hydrogen peroxide (H_2O_2) adjusted to a pH of 2.0 with continuous stirring at a temperature of 85 °C for 5 hrs, then 20-40 ml of ethyl acetate is added. 3.2 M ammonium in 25 % nitric acid (HNO₃), it is kept at room temperature and with stirring for one hour, the obtained solution is filtered through a 0.45 microns membrane and the solution is lowered to 100 ml for its later analysis (here will be the metals of the fraction associated with organic compounds).

The residual material is subjected to a fifth extraction with 20-40 ml of conc. HNO₃ mixture and

perchloric acid (HClO₄) conc. (1:1) with continuous stirring for one hour at 110 °C. The obtained solution is also filtered through a 0.45 µm membrane and averaged to 100 ml. Each and every one of the fractions were tested in triplicate. A sixth fraction is introduced to this scheme consisting of an original sample subjected to a total mineralization with additions of HNO₃ and HClO₄ and heat to boiling to near dryness. Subsequently, they are treated to dissolve in distilled water and are diluted to 100 ml; subsequently, it is also filtered through a 0.45 micron membrane. The analysis of the elements in the different leaching fractions was carried out in a sequential inductively coupled plasma (ICP) spectrophotometer with a computer controlled peristaltic pump, with a flow of 0.5-2.0 ml·min⁻¹ and a Grid-type nebulizer. The calibration curves for each element were prepared from unielemental and/or multielemental standards (Cunniff, 1995). For determinations of lanthanide metals (Ce, Gd, Yb, Y, La, Nd, Sm) X-ray fluorescence spectroscopy was also used and ICP spectroscopy was tested for comparative studies.

The XRF for the majority elements (Si, Al, Fe, Mn, Ca, K and P) was made in a Philips PW-1404 with Sc/Mo tube. The samples were prepared by alkaline fusion (0.3 g of sample) with lithium tetraborate (5.5 g) and transformed into beads in a Perlex 3X bead machine. For the minority elements, the samples were prepared in the form of pressed and pelleted tablets with elvacite (Santacreu and Ontiveros, 2017).

RESULTS AND DISCUSSION

The initial diffractograms of the three samples are shown in Figure 1. The presence of quartzite (Qz), biotite (Bt) and monazite (Mnz) are observed as major phases. Almandite (Alm) and hematite (Hem) are identified as minor phases. It can be noted that there are no important differences between the three samples. Only the presence of the plagioclase phase (Pl) in the sample vk-122 at 38° of 20 is appreciated; likewise, the signal of hematite (Hem) close to 22° can be noticed a little more pronounced.

The minerals found are of primary and secondary origin as reported (González, 1961); the main constituents correspond to pegmatites such as quartz (Qz) and feldspar and as constituents called accessories, hematite (Hem). However, in this category, according to González (1961), biotite (Bt) should be considered as a secondary mineral, being observed in the samples as one of the majority phases.

For samples vk-102 and vk-120, they are in fact considered as pegmatitas just from Telixtlahuaca in Oaxaca and from Sierra de San Carlos in Tamaulipas, respectively. However, the sample vk-122, has been considered as Cuarzomonzodiorite of the state of Hidalgo. The Cuarzomonzodiorites are considered as igneous rocks of aphanitic texture, rich in silicon oxides; they are is generally the mineralogical species





Fig. 1 XRD patterns of studied samples. Majority phases, Bt: Biotite; Mnz: monazite, Qtz: quartzite and Pl: plagioclase. Minority phases, Alm: almandite and Hem: hematite

with larger sizes. This corresponds to the point made by Alvero and Cau (2017), who also indicate that the presence of biotite (Bt), which could appear as completely anhedric, always interstitial, can be found bordering crystals of plagioclase and quartz or such as filler of cavities.

From these identified phases, it can be inferred that chemically, there are numerous variations in the formulas, which gives rise to many varieties and very dissimilar compositions. The theoretical average composition that can be estimated for these phases oscillates in their contents between SiO_2 (33-41 %),

Al₂O₃ (12-18 %), MgO (2-20 %) and FeO (5-25 %), mainly. They mainly belong to the silicates class; subclass, phyllosilicates and the group of micas (http://www.uned.es/cristamine/biotita).

The results of the metals analyze for the three evaluated samples (vk-102, vk-120 and vk-122), according to the Tessier scheme, for each extraction fraction, are summarized in Tables 1-3.

As it can be easily seen from Table 1; Fe, Cr, Pb, Nd and Pr can be extracted from sample vk-102. In the case of Fe, in the easily lixiviable fraction, 0.01 % of the total of this element was extracted, in fraction 1

			Metals extracted, mg/kg									
Metals in Rocks		Fe	Cd	Cr	Ph	Ce	La	Sm	Gd	Nd	Pr	Vh
Sample	Fractions	Γt	Cu	CI	10	cı	La	SIII	Gu	INU	11	10
	0	0.52	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""></dl<></th></dl<>	<dl< th=""></dl<>
	1	1.6	<dl< td=""><td><dl< td=""><td><dl< td=""><td><ld< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></ld<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><ld< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></ld<></td></dl<></td></dl<>	<dl< td=""><td><ld< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></ld<></td></dl<>	<ld< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></ld<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	2	14.64	<dl< td=""><td>2.40</td><td>0.67</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2.40	0.67	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
vk-102	3	3.34	<dl< td=""><td>2.54</td><td>1.71</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2.54	1.71	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	4	588.39	<dl< td=""><td>0.81</td><td>3.49</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.81	3.49	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	5	3571.35	<dl< td=""><td>1438.67</td><td>222.74</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>19.54</td><td>223.23</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1438.67	222.74	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>19.54</td><td>223.23</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>19.54</td><td>223.23</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>19.54</td><td>223.23</td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td>19.54</td><td>223.23</td><td><dl< td=""></dl<></td></dl<>	19.54	223.23	<dl< td=""></dl<>
	total	4177.70	<dl< td=""><td>3767.17</td><td>677.73</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>316.80</td><td>1721.78</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	3767.17	677.73	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>316.80</td><td>1721.78</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>316.80</td><td>1721.78</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>316.80</td><td>1721.78</td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td>316.80</td><td>1721.78</td><td><dl< td=""></dl<></td></dl<>	316.80	1721.78	<dl< td=""></dl<>

 Table 1 Results of metals extracted according to the Tessier scheme, by sequential fractions in sample vk-102.

Legend: Fractions 0, simply soluble; fraction 1, interchangeable ions; fraction 2, associated with carbonates; fraction 3, bound to oxides; fraction 4, associated with organic compounds and fraction 5, residual material. DL: detection limit

 Table 2 Results of metals extracted according to Tessier scheme, by sequential fractions in sample vk-120.

		Metals extracted, mg/kg										
Metals in Rocks		Fo	Cd	Cr	Ph	C	La	Sm	Cd	Nd	Dr	Vh
Sample	Sample	- rt	Cu	CI			La			Iu	11	10
	0	16.82	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	1	17.11	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	2	166.39	<dl< td=""><td>0.17</td><td>0.21</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.17	0.21	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
vk-120	3	222.63	<dl< td=""><td>4.65</td><td>8,91</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	4.65	8,91	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	4	172.69	<dl< td=""><td>5.51</td><td>5.83</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	5.51	5.83	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	5	678.28	<dl< td=""><td>1.37</td><td>179.34</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>16.29</td><td>13.57</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1.37	179.34	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>16.29</td><td>13.57</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>16.29</td><td>13.57</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>16.29</td><td>13.57</td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td>16.29</td><td>13.57</td><td><dl< td=""></dl<></td></dl<>	16.29	13.57	<dl< td=""></dl<>
	total	5392.89	<dl< td=""><td>1576.93</td><td>366.55</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>124.12</td><td>1214.85</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1576.93	366.55	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>124.12</td><td>1214.85</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>124.12</td><td>1214.85</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>124.12</td><td>1214.85</td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td>124.12</td><td>1214.85</td><td><dl< td=""></dl<></td></dl<>	124.12	1214.85	<dl< td=""></dl<>

Legend: Fractions 0, simply soluble; fraction 1, interchangeable ions; fraction 2, associated with carbonates; fraction 3, bound to oxides; fraction 4, associated with organic compounds and fraction 5, residual material. DL: detection limit

		Metals extracted, mg/kg										
Metals in Rocks		Fo	Cd	Cr	Ph	Ce	La	Sm	Cd	Nd	Dr	Vb
Sample	Sample	Γt	Cu	CI	10	cı	La	511	Uu	1 u		10
	0	0.78	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""></dl<></th></dl<>	<dl< th=""></dl<>
	1	3.73	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	2	36.49	<dl< td=""><td>1.79</td><td>0.41</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1.79	0.41	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
vk-122	3	123.36	<dl< td=""><td>2.73</td><td>4.69</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2.73	4.69	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	4	554.01	<dl< td=""><td>8.17</td><td>17.66</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	8.17	17.66	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	5	2127.72	<dl< td=""><td>24.2</td><td>191.27</td><td>6.67</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>17.73</td><td>3.69</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	24.2	191.27	6.67	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>17.73</td><td>3.69</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>17.73</td><td>3.69</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>17.73</td><td>3.69</td></dl<></td></dl<>	<dl< td=""><td>17.73</td><td>3.69</td></dl<>	17.73	3.69
	total	50567.78	<dl< td=""><td>2978.23</td><td>2398.87</td><td>368.53</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>12506.25</td><td>407.84</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	2978.23	2398.87	368.53	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>12506.25</td><td>407.84</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>12506.25</td><td>407.84</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>12506.25</td><td>407.84</td></dl<></td></dl<>	<dl< td=""><td>12506.25</td><td>407.84</td></dl<>	12506.25	407.84

 Table 3 Results of metals extracted according to Tessier scheme, by sequential fractions in sample vk-122.

Legend: Fractions 0, simply soluble; fraction 1, interchangeable ions; fraction 2, associated with carbonates; fraction 3, bound to oxides; fraction 4, associated with organic compounds and fraction 5, residual material. DL: detection limit

(easily interchangeable ions) 0.03 %. In "zero" fraction only low concentration was determined (0.52 mg/kg) indicating that, Fe is in the form of easily soluble salts.

From fraction 2, it is possible to extract besides Fe, Cr and Pb. For Fe in this fraction of metals bound to carbonates and bicarbonates, 0.35 % is extracted. In this same fraction; it is possible to extract 0.06 % of Cr and 0.10 % of Pb.

In fraction 3, the metals that are bound to organic matter, it was obtained that for Fe only 0.08 % is extractable while for Cr and for Pb 0.07 % and 0.25 %, respectively. This indicates that the forms of Pb present in this material of phosphate rock, the most

available forms and that are associated mainly with carbonates, bicarbonates and organic matter. Fe and Cr follow in order of importance.

The presence of Fe is associated with the presence of lateritic material; all of this corroborates the point made by Motta de Toledo et Pereira (2003), which could also correspond in terms of the sample (vk-102) to a monazite mineral. For fraction 4 of metals bound to iron and manganese oxyhydroxides, it is reasonable that in the first place appreciable amounts of Fe (14 %) are extractable followed by Cr (0.02 %) and Pb (0.52 %).

Finally, for this sample it can be seen that 15 % of total Fe is strongly associated with parental

material (non-extractable forms), similarly happens for Cr (62 % of the total) and for Pb (67 % of the total). Concerning the REE's, only Pr in relatively high amounts and Nd in smaller quantities (fraction 5) can be obtained. They are badly extractable, since 87 % and 94 % of the total of Pr and Nd, respectively retained in the source material. In both cases, their industrial exploitation in this way does not represent an economic advantage.

Table 2 shows the summary of the concentrations of the metals extracted for each fraction, from the sample vk-120. Fractions of Fe are the most extractable, although to a lesser extent than in the sample vk-102. The presence of iron was obtained from the first extraction, in much higher concentrations than for the sample vk-102, in this case 16.82 mg/kg; that is 30 times greater amounts. Concentration of Fe in "zero" fraction indicated that higher amounts of Fe is in the form of easily soluble salts. In fraction 1, of easily interchangeable ions, it was possible to extract only Fe in concentrations similar to those extracted from the "zero" fraction, that indicates that in this mineral there is presence of soluble Fe salts in proportions with the interchangeable salts. Fraction 2 behaved in a similar way to fraction 1, where it is possible to extract besides Fe, Cr and Pb. For the Fe bound to carbonates and bicarbonates. 3.09 % is extracted, that is, about ten times more than in the sample vk-102. In this same fraction it is possible to extract 0.01 % of Cr and 0.06 % of Pb; but about two to five times lower concentration than in vk-102.

In fraction 3, metals bound to organic matter, Fe is only extractable at 4.13 % while on the other hand for Cr and for Pb 0.29 % and 0.49 %, respectively, higher than the quantities that were extraced from the sample vk-102. This indicates that the forms of Fe and Pb present in this sample are the most available forms and that they are mainly associated with carbonates, bicarbonates and organic matter. In fraction 4, the case of metals bound to iron and manganese oxyhydroxides, 3.20 % of Fe, 0.35 % of Cr and 0.49 % of Pb were extracted. In fraction 5, it was possible to extract similarly to the sample vk-102, Pr and Nd, as well as Fe, Cr and Pb. For Fe a 12.58 % was reached; 76.4% is retained in the source material without being extracted. For the Cr decrease of the extractable percentage (0.09 %) was achieved; 99 % is retained and does not appear as removable forms. For the Pb a greater extraction of a 48 % was obtained and for that reason they only remain in retained forms a 51 % of the total Pb.

Table 3 shows the concentrations of the metals extracted from each fraction in the case of the sample vk-122. With similar results, it was found that the fractions of Fe were the most extractable. However, the fractions "zero" and 1, as the most available or leachable, turned out to be of intermediate values in proportions, if the three samples are compared to each other. From fraction 2, it was possible to extract Fe, Cr and Pb, which is repeated in the three samples; this corroborates when these elements are united with carbonates and bicarbonates; it was possible to extract 0.01 % of the total Fe, 0.06. % Cr and 0.02 % of Pb. Fraction 3 increases to 0.07 %, 0.09 % and 0.20 % for Fe, Cr and Pb, respectively. It also happens for fractions 4 and 5. Unlike the two previous samples (defined as pragmatites), for this sample vk-122 (defined as quarcomeriorite), Nd was neither found nor extracted. In fraction 5 it was possible to extract quantities that, although relatively small, are quantifiable of cerium (Ce) and ytterbium (Yb).

In general, 28 % of the total Fe is extracted from this sample vk-122, while 72 % remains nonextractable together with the original mineral. Next in order of importance are Pb, Cr, Pr, Ce and Yb from which 2 %, 0.4 %, 0.2 %, 0.07 % and 0.04 %, respectively, can be extracted, relating to their total contents.

The XRD carried out in the samples at the end of the sequential extractions to the resulting solid waste, showed mainly the quartzite phase (Qz), which was not attacked by the different extractants. In Figure 2 this is appreciated. Only for sample vk-122, the 45° signal that could be associated with the cristobalite phase, differentiate it from samples vk-102 and vk-120. Similarly, the weakest signals observed approximately at 25° (possible anorthoclase, A), 45° (cristobalite, Crs) and 58° (unidentified), respectively, mark the difference between this sample and the previous ones: It can be seen in the diffractogram of the center of Figure 2.

The three samples were also analyzed by SEM. For the sample vk-102, the presence of elements such as Si, Al, O, P and K were observed as main or major elements. This sample has been classified as pegmatite, as well as the sample vk-12. Due to its biotite content, it can be considered that they obey an approximate chemical composition of K (Mg, Fe)₃(AlSi₃)O₁₀(OH)₂, a brown form of mica consisting of hydrous silicate of potassium, magnesium and aluminum.

As indicated in the consulted bibliography, because they are micas, they are presented in tabular crystals of hexagonal contour or in flexible and elastic sheets (Valderrama et al., 2005).

On the other hand, monazite is, in geology, a reddish-brown phosphate that includes rare earth elements in its composition. It appears normally in the form of small isolated crystals. Actually, there are at least four different types of monazite, depending on the composition of the same:

- monazite-Ce (Ce, La, Pr, Nd, Th, Y) PO₄
- monazite-La (La, Ce, Nd, Pr) PO₄
- monazite-Nd (Nd, La, Ce, Pr) PO₄
- monazite-Pr (Pr, Nd, Ce, La) PO₄

The identified elements are indicated in bold in Tables 4-6. In these same tables, the presence of Nd



Fig. 2 XRD patterns of non-attacked residues after the sequential extractions of the Tessier schneme.

was observed, which was identified in the metal analysis. In the same way, the microphotograph taken in the sample can be observed initially and before being sent to the sequential extractions. You can notice the cuts and edges of this mineral (Fig. 3).

Tables 4-6 show the values obtained from semiquantitative analysis performed by SEM (from the EDS spectra). Table 4 shows the percentage values by weight of the elements found in sample vk-102. The rare earth elements that were found are indicated in red and the presence of potentially toxic elements such as lead or chromium is highlighted in blue. The values in table 5 were similar to those in Table 4, which corroborates the same type of material (pegmatite).

Figures 4 and 5 show the microphotographs corresponding to samples vk-120 and vk-122 and Tables 5 and 6 show the semi quantitatively results of the EDS spectra of the same samples.

The sample vk-120, also classified as a pegmatite, shows the similarity of morphology with the vk-102 (Figs. 3 and 4). For the case of sample vk-122, which was identified as a quartzomonzodiorite, one can see the presence of Si, O, Al, Fe, Mg and Ca as major elements. The presence of K was extremely low (<0.5 %), that is about 13 times lower than in the sample vk-120 and about 45 times less than in the sample vk-102. This apparently marks the difference between the two previous ones defined as pragmatites and this sample. Likewise, in this sample, relatively high Mg proportions appear, as do the contents of Ca and Fe. A certain morphological difference of this sample (Fig. 5) can also be observed with respect to the two previous ones (Figs. 3 and 4); you can clearly see a laminar form more accentuated than in the previous ones.



Fig. 3 Microphotograph of the sample vk-102 initially (PROZA Correction Acc.Volt.= 30 kV Take-off Angle=30.00 deg, Number of Iterations = 6).



Fig. 4 Microphotograph of the sample vk-120 initially (PROZA Correction Acc.Volt. = 30 kV Take-off Angle = 30.00 deg, Number of Iterations = 16).



Fig. 5 Microphotograph of sample vk-122 initially (PROZA Correction Acc.Volt. = 30 kV Takeoff Angle = 30.00 deg, Number of Iterations = 15).

Elements	k-relation (calculated)	ZAF	Atoms % by weight	Elements % by weight	mistake
0 K	0.0627	0.707	11.70	10.00	±/ 0.01
0-K	0.0037	9.191	11.70	10.00	+/- 0.01
Si-K	0.3810	1.660	56.45	53.22	+/- 0.54
Al-K	0.0995	1.358	14.31	13.50	+/- 0.17
K-K	0.1265	1.659	16.5	20.91	+/- 0.42
Ca-K	0.0079	1.749	1.3	1.36	+/- 0.16
Fe-K	0.0039	1.237	0.26	0.47	+/- 0.16
Ti-K	0.0014	1.535	0.13	0.21	+/- 0.11
Pr-L	0.0015	1.355	0.04	0.21	+/- 0.23
Nd-L	0.0000	1.337	0.01	0.03	+/- 0.00
Pb-L	0.0000	1.407	0.02	0.09	+/- 0.00
Total			100.00	100.00	

Table 4 Percentages of the elements present in the sample vk-102 according to the K or L lines.

The number of cation results are based upon 24 Oxygen atoms

Table 5 Percentages of the elements present in the sample vk-120 according to the K or L lines.

Elements	k-relation	ZAF	Atoms % by weight	Elements % by weight	mistake
	(calculateu)			70 Dy weight	
O-K	0.0984	5.168	65.54	50.86	+/- 0.87
Si-K	0.1451	2.082	22.19	30.22	+/- 0.21
Al-K	0.0496	2.109	7.99	10.45	+/- 0.10
Mg-K	0.0003	2.867	0.07	0.08	+/- 0.06
K-K	0.0425	1.441	3.23	6.13	+/- 0.11
Ca-K	0.0114	1.385	0.81	1.58	+/- 0.05
Fe-K	0.0022	1.209	0.10	0.27	+/- 0.06
Ti-k	0.0005	1.350	0.03	0.06	+/- 0.04
Pr-L	0.0014	1.241	0.03	0.18	+/- 0.09
Nd-L	0.0014	1.244	0.03	0.18	+/- 0.10
Pb-L	0.0000	1.407	0.02	0.09	+/- 0.00
Total			100.00	100.00	

The number of cation results are based upon 24 Oxygen atoms

Table 6 Percentages of the elements present in the sample vk-122 according to the K or L lines.

Elements	k-relation (calculated)	ZAF	Atoms % by weight	Elements % by weight	mistake
О-К	0.1071	4.668	65.38	50.00	+/- 0.63
Si-K	0.1075	2.288	18.33	24.56	+/- 0.16
Al-K	0.0148	2.894	3.32	4.28	+/- 0.09
Mg-K	0.0262	3.267	7.37	8.55	+/- 0.12
K-K	0.0033	1.400	0.25	0.46	+/- 0.03
Ca-K	0.0442	1.272	2.93	5.60	+/- 0.07
Fe-K	0.0503	1.196	2.24	6.01	+/- 0.18
Ti-k	0.0025	1.311	0.13	0.31	+/- 0.04
Pr-L	0.0015	1.242	0.03	0.16	+/- 0.07
Ce-L	0.0000	1.260	0.01	0.04	+/- 0.00
Yb-L	0.0000	1.359	0.02	0.06	+/- 0.00
Pb-L	0.0010	1.465	0.01	0.13	+/- 0.29
Total			100.00	100.00	

The number of cation results are based upon 24 Oxygen atoms

Sample	% SiO ₂	% Al ₂ O ₃	% MgO	% CaO	% TiO	% Fe ₂ O ₃	% K ₂ O	Totals
vk-102	56.06	14.82	ND	4.16	0.17	0.40	17.15	92.76
vk-120	56.86	16.73	1.12	4.48	0.04	0.52	7.14	86.89
vk-122	42.78	8.95	8.74	6.35	0.52	7.45	4.75	79.54

 Table 7 Analysis by XRF of major elements (% of oxides).

 Table 8 Analysis by XRF of trace elements (mg/kg).

Sample	Cd	Cr	Pb	Ce	La	Sm	Gd	Nd	Pr	Yb	Totals
vk-102	0.105	4177.79	609.89	0.083	<dl< td=""><td><dl< td=""><td><dl< td=""><td>354.82</td><td>1148.43</td><td><dl< td=""><td>62.91.11</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>354.82</td><td>1148.43</td><td><dl< td=""><td>62.91.11</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>354.82</td><td>1148.43</td><td><dl< td=""><td>62.91.11</td></dl<></td></dl<>	354.82	1148.43	<dl< td=""><td>62.91.11</td></dl<>	62.91.11
vk-120	<dl< td=""><td>1947.51</td><td>478.35</td><td><dl< td=""><td>0.040</td><td><dl< td=""><td><dl< td=""><td>168.31</td><td>1462.68</td><td><dl< td=""><td>4056.88</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1947.51	478.35	<dl< td=""><td>0.040</td><td><dl< td=""><td><dl< td=""><td>168.31</td><td>1462.68</td><td><dl< td=""><td>4056.88</td></dl<></td></dl<></td></dl<></td></dl<>	0.040	<dl< td=""><td><dl< td=""><td>168.31</td><td>1462.68</td><td><dl< td=""><td>4056.88</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>168.31</td><td>1462.68</td><td><dl< td=""><td>4056.88</td></dl<></td></dl<>	168.31	1462.68	<dl< td=""><td>4056.88</td></dl<>	4056.88
vk-122	<dl< td=""><td>2400.45</td><td>1540.07</td><td>66.34</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.160</td><td>7478.74</td><td>108.77</td><td>11594.53</td></dl<></td></dl<></td></dl<></td></dl<>	2400.45	1540.07	66.34	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.160</td><td>7478.74</td><td>108.77</td><td>11594.53</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.160</td><td>7478.74</td><td>108.77</td><td>11594.53</td></dl<></td></dl<>	<dl< td=""><td>0.160</td><td>7478.74</td><td>108.77</td><td>11594.53</td></dl<>	0.160	7478.74	108.77	11594.53

DL: detection limit

The results of XRF can be seen in Tables 7 and 8, expressed as a percentage of their respective oxides and for the trace elements in mg/kg.

As can be seen from Table 7, the compositions obtained for SiO₂, Al₂O₃, CaO and Fe₂O₃ in samples vk-102 and vk-120, did not show significant differences, which suggests that it corresponds to similar samples, both they have been identified as pegmatites. They only differ in their contents of K₂O and TiO, as well as that, in the vk-102 no presence of MgO was proved, while in the second a value close to 1% was detected. This marks the difference between both samples because in the totals of evaluated oxides, that there is about 7 % and 13 % of other components (not valued in this study) in the samples vk-102 and vk -120, respectively.

In the case of trace elements, the significant differences were observed among all studied samples (Table 8). The main characteristic is the presence of Cr and Pb in all of them, as well as Nd and Pr. Regarding the latter, it should be noted that the Nd in the sample vk-122 (identified as quartzomonzodiorite), was detected in very small concentrations by XRF (those that were not detected by ICP or by SEM-EDS) and as for the Pr, it was detected in concentrations about 6-7 times higher than the two previous samples. Also for this sample vk-122, appreciable Yb and Ce were identified as in ICP and SEM, which corroborates their presence. It should also be noted that in sample vk-102, traces of Ce were found

The correspondence between the results determined quantitatively by ICP and XRF together with the semi quantitative values given by SEM for samples vk-102, vk-120 and vk-122 can be seen in Tables 9-11, respectively. Sample vk-102 (Table 9) embodies correlations higher than 0.70 in case of ICP/SEM, highlighting that by ICP and XRF the Cr was detected however not by SEM. The concentrations of Si, Al, Ca, K and Ti are not reported, since they were not determined in ICP. It is very interesting that the correlations ICP/SEM and XRF/SEM are very similar in magnitudes. Results ICP/SEM and XRF/SEM determined for sample vk-

120 (Table 10) were much lower than for the previous sample vk-102.

The best levels of correspondence between ICP and SEM results exhibits sample vk-122, however, the lack of correlation between XRF and SEM should be highlighted.

CONCLUSIONS

The scanning electron microscopy (SEM) allowed to corroborate the presence of some elements of the lantanoid type: praseodymium (Pr), neodymium (Nd), cerium (Ce), ytterbium (Yb), as well as toxic metals, lead (Pb), associated to minerals of the rare earth phosphate-type. The X-ray fluorescence (XRF) allowed to verify the existence of the same lanthanide elements and toxic metals mentioned above, in the studied samples.

The procedure of selective sequential extractions according to the Tessier methodology, does not manage to extract significant amounts of the REE's (lanthanoids) that are present in these samples, except in the conditions of maximum aggressiveness, i.e. digestion with concentrated $HNO_3/HClO_4$ and warming.

The REE could only be extracted, and at very low levels of concentration, in the fifth fraction of the sequential extraction. In the case of sample vk-102, 94 % and 88 % of the total contents of Nd and Pr, respectively, still retained in sample and they are not possible to extract them. However, significant amounts of Cr (38 %) and Pb (34 %), metals that are potentially toxic, were extracted. Sample vk-120 exhibited extractive efficiency 13 % and 1 % of the total contents of Nd and Pr, respectively. Its behavior concerning the non-extractable amount of Pr, differed from that of the sample vk-102. However, it is practically possible to extract 53 % of the total Pb. The extractive efficiencies in the case of sample vk-122, with respect to the elements Ce (2 %), Yb (1 %), Pr (0.1 %) and Pb (8 %), are the lowest in comparison with other samples. This can be explained by difficult extraction from quartzomondiorite, when compared to a pragmatite. It can be said that most of them are practically conserved in the original sample vk-122.

Sample vk-102	% (ICP)	% (SEM)	% (XRF)	ICP/SEM	XRF/SEM
Fe	0.418	0.470	0.400	0.89	0.85
Cd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Cr	0.144	<dl< th=""><th>0.42</th><th>**</th><th>**</th></dl<>	0.42	**	**
Pb	0.063	0.09	0.061	0.70	0.68
Ce	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
La	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Sm	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Gd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Nd	0.03	0.03	0.04	1.06	1.18
Pr	0.172	0.21	0.11	0.82	0.55
Yb	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**

Table 9 Correlation of the percentage contents of the elements found in the sample vk-102 by ICP and SEM.

* Small amounts were detected (0.105 mg/kg)

** It can not be calculated

DL: detection limit

 Table 10
 Correlation of the percentage contents of the elements found in the sample vk-120 by ICP and SEM.

Sample vk-12(% (ICP)	% (SEM)	% (XRF)	ICP/SEM	XRF/SEM
Fe	0.13	0.27	0.400	0.47	1.48
Cd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Cr	0.001	<dl< th=""><th>0.42</th><th>**</th><th>**</th></dl<>	0.42	**	**
Pb	0.05	0.09	0.061	0.60	0.68
Ce	<dl< th=""><th>0.04</th><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	0.04	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
La	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Sm	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Gd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Nd	0.02	0.18	0.04	0.09	0.20
Pr	0.01	0.18	0.11	0.08	0.64
Yb	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**

* Small amounts were detected (0.083 mg/kg)

** It can not be calculated

DL: detection limit

Table 11 Correlation of the percentage contents of the elements found in the sample vk-122 by ICP and SEM.

Sample vk-122	% (ICP)	% (SEM)	% (XRF)	ICP/SEM	XRF/SEM
Fe	5.34	6.01	7.45	0.89	1.24
Cd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Cr	0.301	<dl< th=""><th>0.20</th><th>**</th><th>**</th></dl<>	0.20	**	**
Pb	0.09	0.13	0.139	0.67	1.07
Ce	0.038	0.04	0.007	0.94	0.17
La	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Sm	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Gd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Nd	<dl< th=""><th><dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th>**</th><th>**</th></dl<></th></dl<>	<dl< th=""><th>**</th><th>**</th></dl<>	**	**
Pr	0.13	0.16	0.50	0.78	3.12
Yb	0.041	0.06	0.011	0.69	0.18

* Small amounts were detected (0.16 mg/kg) ** It can not be calculated

DL: detection limit

From the obtained results it can be concluded that the Tessier sequential extractions technique is not sufficiently efficient for the recovery of REE's from minerals studied in this work.

REFERENCES

- Bünzli, J.C.G.: 2013, In: Lanthanides. In book: Kirk-Othmer Encyclopedia of Chemical Technology Publisher: Wiley Online Library, 1–43.
- Burkhalter Thiebaut, E. and Vergara Espuelas, R.: 2016, Rare Earth Project of Matamulas: "The First Deposit in Europe". Quantum Minería – España, (in Spanish).
- Campanella, L., D'Orazio, D., Petronio, B.M. and Pietrantonio, E.: 1995, Proposal for a metal speciation study in sediments. Analytica Chimica Acta, 309, 387–393. DOI: 10.1016/0003-2670(95)00025-U
- Cunniff, P.: 1995, Official methods of analysis of AOAC International. 16th edition, AOAC International, Arlington.
- Dawood, Y.H., El-Naby, H. and Abd, H.: 2007. Mineral chemistry of monazite from the black sand deposits, northern Sinai, Egypt: a provenance perspective. Mineralogical Magazine, 71(4), 389–406. DOI: 10.1180/minmag.2007.071.4.389
- Frohne, T. and Rinklebe, J.: 2013, Biogeochemical fractions of mercury in soil profiles of two different floodplain ecosystems in Germany. Water Air Soil Pollut, 224(6), 1591. DOI 10.1007/s11270-013-1591-4
- Gómez, A.: 1990, Studies on rare earths in Mexico. Part I. The resources of lanthanids in Mexico. UNAM. Instituto de Geología Bolestín, 108, México, 3–23, (in Spanish).
- González, G.: 1956, Mineral wealth and mineral deposits in Mexico. 3rd edition, México, D.F. Cong. Geol. Internal., 20, 497, (in Spanish).
- González, J.: 1961. The granitic pegmatites of Santa Ana, Telixtlahuaca, Oaxaca. Estudios Geol., 38, 39–51, (in Spanish).
- Kanazawa, Y. and Kamitani, M.: 2006, Rare earth minerals and resources in the World. Journal of Alloys and Compounds, 408–412, 1339–1343. DOI: 10.1016/j.jallcom.2005.04.033
- Keller, G.R. and Baldridge, W.S.: 1999, The Rio Grande rift: A geological and geophysical overview: Rocky Mountain Geology, 34, 121–130. DOI:10.2113/34.1.121
- López, P.L. and Mandado, J.M.: 2002, Sequential chemical extractions of heavy metals. Applications in Geological Sciences. Estudios Geol., 58, 133–144, ((in Spanish with English abstract).
- Mahan, K.I., Foderato, T.A., Garza, T.L., Martinez, R.M., Maroney, G.A., Trivisonno M.R. and Willging E.M.: 1987, Microwave digestion techniques in the sequential extraction of calcium, iron, chromium, manganese, lead and zinc in sediments. Anal. Chem., 59, 938–945. DOI: 10.1021/ac00134a003
- Motta De Toledo, M.C. and Pereira, V.P.: 2003, Occurrence and variability of composition of monazite group phosphates in carbonatites. Pesquisas em Geociências, 30(1), 83–98.
- Münch, L. and Ángeles, E.: 1997, Methods and techniques of investigation. Edit. Trillas. México. 99–114, (in Spanish).
- Pérez, F.: 2004, Arsenic dynamics in sludge and well water

in the general distributor of Zimapán, Hidalgo. Tesis Doctoral, Universidad Autónoma del Estado de Hidalgo, 36–48, (in Spanish).

- Prieto, F.: 1997, Wastewater treatment through the formation of ferrites "in situ". Design and optimization of a pilot scale reactor. Ferrite evaluation. Tesis Doctoral, Universidad de Valladolid. Facultad de Ciencias. España, 24–25, (in Spanish).
- Prieto, F.; Pérez, F. and Barrado, E.: 2006. Selective leaching of arsenic and other elements of sedimentary material carried by groundwater in Zimapán, Hidalgo, Mexico. Interciencia, 31(1), 50–56, (in Spanish).
- Santacreu, D.A. and Ontiveros, M.A.C.: 2017, Technological choices in hand-made indigenous pottery from western Mallorca (Balearic Islands, Spain) (C.1200-75 BC): an archaeometric approach. Archaeometry, 59, 4, 642–666. DOI: 10.1111/arcm.12273
- Ščančar, J., Milačič, R. and Horvat, M.: 2000, Comparison of various digestion and extraction procedures in analysis of heavy metals in sediments. Water Air and Soil Pollution, 118, 87–99. DOI: 10.1023/A:1005187602820
- Tessier, A., Campbel, P.G.C. and Bisson, M.: 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51(7), 844–851. DOI: 10.1021/ac50043a017
- Thomas, R.P., Ure, A.M., Davidson, C.M., Littlejohn, D., Rauret, G., Rubio, R. and López-Sánchez, J.F.: 1994, Three stage sequential extraction procedure for the determination of metals in river sediments. Analytica Chimica Acta, 286, 423–429.

DOI: 10.1016/0003-2670(94)85088-7

- Toral Ferrero, Y.: 1996. Comparative study of speciation schemes of solid samples of environmental interest. Trabajo de Licenciatura. Universidad de Valladolid. Facultad de Ciencias, 32–33, (in Spanish).
- Ure, A.M., Quevauviller, Ph., Muntau, H. and Griepink, B.: 1993, Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the European communities. Intern. J. Environ. Anal. Chem., 51, 135–151. DOI: 10.1080/03067319308027619
- Valderrama, L.; Poblete, R. and Contreras, C.: 2005, Characterization and concentration of sands samples from Caldera, Atacama Region. Magazine of the Faculty of Engineering. Universidad de Atacama, 19, 1, 38–44, (in Spanish).
- Wilson, A. and Chunnet, G.: 2006, Trace element and platinum group element distributions and the Genesis of the Merensky Reef, Western Bushveld Complex, South Africa. Journal of Petrology, 47, 12, 2369– 2403. DOI: 10.1093/petrology/egl048