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Uranium in surface soils: An easy-and-quick assay combining X-ray diffraction and X-ray fluorescence qualitative data

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ABSTRACT

An environmental concern for uranium-producing countries is the possible dissemination of this radionuclide in soils nearby mineral deposits, even non-exploited ones. This is the case of the Nisa uranium deposit in Alto-Alentejo, East-central Portugal, considered economically impracticable after prospecting efforts that left behind masses of accumulated debris.

A first step towards the assessment of uranium retention through adsorption by soil clay minerals was a test study of a topsoils profile close to the Nisa deposit. With the aim of quickly appraising the presence of this element in a large set of as-collected soil samples, a combination of laboratory X-ray techniques was applied: X-ray diffraction to identify the main mineral phases and X-ray fluorescence spectrometry in wavelength dispersive mode to certify the presence of uranium and roughly estimate its comparative content. A description of the so-implemented "easy-and-quick uranium assay" is presented and critically evaluated. Obtained results compare well to the chemical data from certified analytical tests of uranium performed over a set of eleven test soil samples.

1. Introduction

Uranium is one of the most widespread radionuclide contaminants in soils and groundwater close to former mining areas and non-exploited deposits, configuring an environmental concern.

Portugal was a uranium producer since the first decade of last century for about five decades through the exploitation of deposits situated in the northern part of the country. The uranium-rich area of Alto-Alentejo, central eastern Portugal (Fig. 1), was identified later on about fifty years ago. The uranium-bearing mineralization occurs mostly in schistose rocks at the contact metamorphic aureole produced by intrusion of the Hercynian monzonitic granite of Alto-Alentejo into the pre-Ordovician schist–greywacke complex forming deposits of vein and dissemination types (Pilar, 1966).

The Nisa uranium deposit (Fig. 2) is situated at the sharp border of a large and arch-shaped granite pluton and was discovered in 1957 through preliminary prospection by scintimetry (Gonçalves, 1966; Gonçalves and Teixeira Lopes, 1971). After a decade of prospection and reserves evaluation that started in 1961, the Nisa deposit was considered economically uninteresting until recently, when bulk energy resources were re-evaluated.

Meanwhile, the existence of this uranium deposit and the remnants of preceding prospect efforts have become an environmental concern for the local population.

A characterization of topsoils and stream sediments in the uranium-rich area of Alto-Alentejo was recently undertaken taking the Nisa region as a testing objective. Such study had the dual purpose of assessing the possible uranium retention by adsorption on argillaceous soil components and of ascertaining the eventual release of this hazardous metal into the aquifer groundwater. For this specific purpose, a detailed study was carried out on the quality of available water points, particularly in what concerns the uranium content but the results are still under appraisal.

An alternative to the time-consuming chemical analysis methods – particularly in what concerns sample preparation/digestion – was developed as a first approach to the assessment of uranium spreading in soils and stream sediments. A description is presented of the implemented prompt methodology, based on a combination of common X-ray laboratory techniques, diffraction and fluorescence spectrometry. The results so-obtained for a test soil profile are described and evaluated, proving the adequacy of this easy-and-quick test as a first assay to unveil the presence of uranium in soils, prior to the selection of critical areas to perform a detailed geochemical mapping.

2. Uranium mineralogy

2.1. Uranium minerals in the Nisa area

Previous studies on the Nisa deposit (Lencastre, 1965; Limpo-de-Faria, 1966; Pilar, 1969) have shown that the dominant uranium minerals belong to the Autunite group with the general

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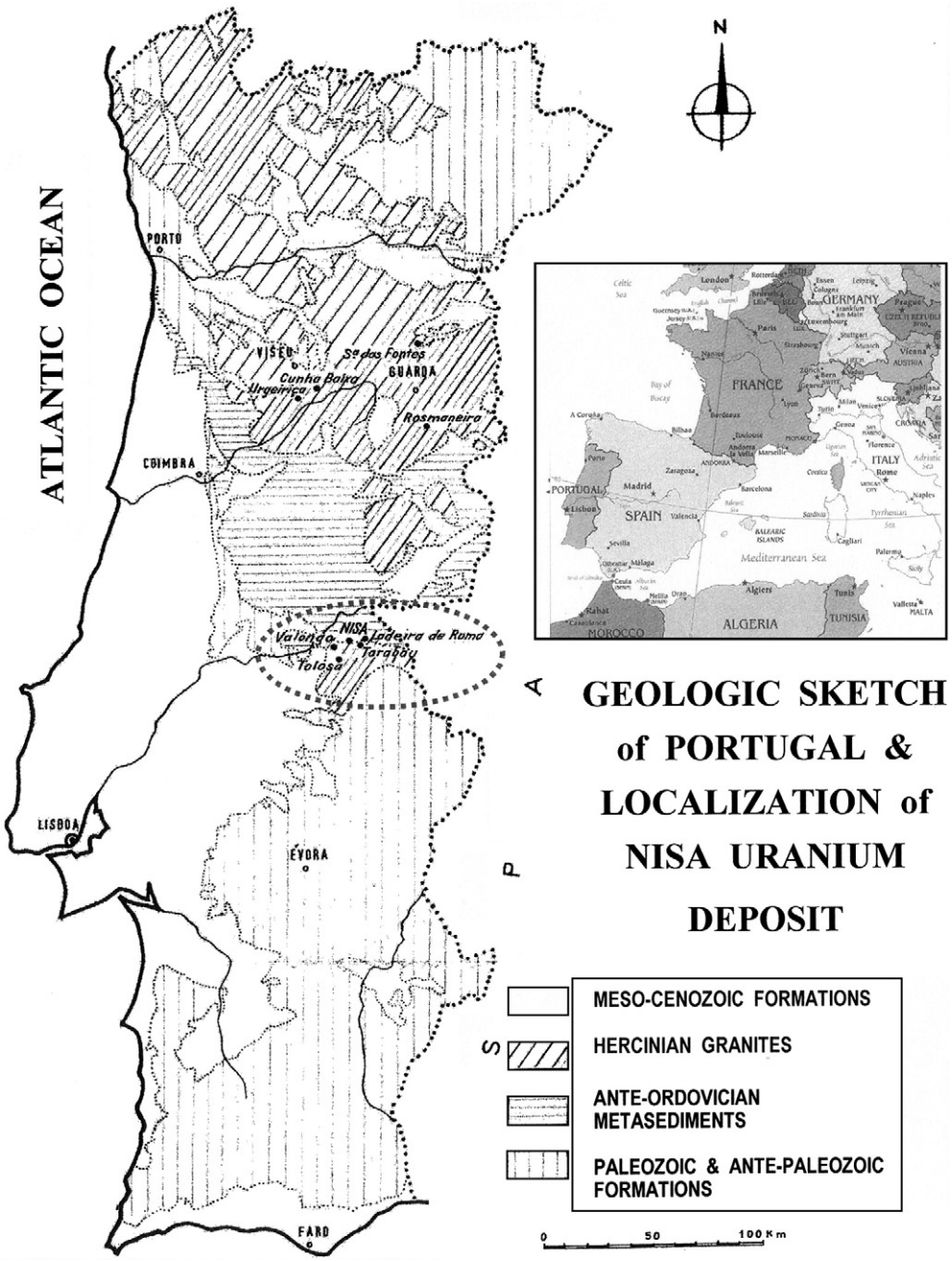

Fig. 1. Sketch of the geologic map of Portugal. The uranium-rich area of Alto-Alentejo is assigned.

formula $A(UO_2)_2(XO_4)_2$. 8–12 H_2O, where A = Ba, Ca, Cu, Fe^{2+}, Mg, Mn, Na, and X = P, As, V.

Along with pitchblende (~$UO_{2+\delta}$, amorphous, with dominant U^{4+} but displaying a significant content of U^{6+}), various uranyl phosphate secondary minerals have been assigned:

Autunite s.s., $Ca(UO_2)_2(PO_4)_2$.10–12 H_2O
Phosphuranylite, $Ca(UO_2)_3(PO_4)_2(OH)_2$.6 H_2O
Nisaite/phurcalite, $Ca_2(UO_2)_3(PO_4)_2(OH)_4$.4 H_2O
Torbernite, $Cu(UO_2)_2(PO_4)_2$.8–12 H_2O
Saleeite, $Mg(UO_2)_2(PO_4)_2$.10 H_2O
Uranocircite, $Ba(UO_2)_2(PO_4)_2$.12 H_2O
Sabugalite, $HAl(UO_2)_4(PO_4)_4$.16 H_2O

The calcium uranyl hydroxyl-phosphate hydrate named nisaite/phurcalite in the above list of Nisa uranium minerals deserves a comment. The mineral species nisaite is widespread at the Nisa area and was described for the first time as resembling phosphuranylite, despite presenting distinctive optical characteristics combined with a unique X-ray diffraction powder pattern (Lencastre and Vairinho, 1970). Conversely phurcalite was assigned a few years later on single specimens from Bergen, Saxony (Deliens and Piret, 1978) and Shinkolobwe, Zaire (Deliens and Comblain, 1978) but the crystal structure of the mineral was determined and described at the same time (Piret and Declercq, 1978). A decade after an arsenate-rich variety of phurcalite was assigned at Dartmoor, southwest England and the identity of nisaite and phurcalite was then claimed (Braithwaite et al., 1989) but no further structural characterization has yet been undertaken on the Nisa mineral to certify such identity.

The hydrated acid aluminium-uranyl phosphate in the list of Nisa minerals is also worthy of a remark. Sabugalite was first described fifty years ago by Frondel (1951), owing its name to Sabugal, in Beira-Alta,