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HIGH-ENERGY PIXE : THE X-RAY SPECTRUM OF URANIUM IN AUTUNITE

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Autunite, a U-bearing mineral ($Ca(UO)_2(PO_4)_2.10\text{-}12H_2O$), has been examined using a high-energy proton beam (E_p = 40 MeV) and Si(Li) and intrinsic Ge solid state detectors. The spectra obtained from the sample show clearly resolved U $K\alpha_1$, $K\alpha_2$ and $K\beta$ X-ray lines (using the Ge detector) and Ca $K\alpha$, $K\beta$ X-rays, Sr $K\alpha$, $K\beta$ and U L X-rays (using the Si(Li) detector), this demonstrates the potential analytical range and flexibility of high energy PIXE analysis.

Keywords : High-energy PIXE; simultaneous multi-element analysis; geological materials

1. Introduction

Simultaneous multi-element analysis of geological materials has been a routine feature of energy-dispersive Electron-Probe Micro-Analysis (EPMA) for many years. More recently, such analysis has also been possible using micro-Proton-Induced X-ray Emission (μ-PIXE), and μ-PIXE analysis has contributed to the solution of a number of significant mineralogical problems[1,2]. Routine EPMA samples with Si(Li) detectors normally provides a working analytical range for X-rays of about 1 - 10 KeV. This energy-region encompasses K X-rays for elements with Z < 33 (As), and includes many of the important major elements (e.g. Na, Mg, Al, Ca, K, Fe) in common silicate minerals. It also includes many of the L X-ray lines for heavy elements such as Au, the Platinum Group Elements (PGEs) and the rare earth elements, and M X-ray lines for elements such as Pb and Bi. Low-energy PIXE (E_p = 2 - 5 MeV) with Si(Li) detectors can extend the X-ray analytical range using characteristic K X-rays to about 25 KeV, which includes such elements as Zr and Ag[1].

Using high-energy protons (E_p = 20 -50 MeV), K X-ray production cross-sections are high, and recent work has shown that it is possible to generate K X-rays from elements with Z = 33 - 80 (As - Hg)[3,4,5]. This capability will be particularly useful when low-energy PIXE and EPMA analysis of heavy elements is hampered by X-ray line overlap or poor sensitivity. Both restrictions are common features of trace heavy element analysis in minerals and rocks, especially in the presence of geochemically coherent elements.

Geochemical coherence of certain elements can lead to significant overlap problems in X-ray spectrometry of geological materials. An important geological example of this involves the mineral zircon, $ZrSiO_4$, which contains extensive minor and trace substitutions of heavy elements (U, Th, Rare Earth Elements, etc) for Zr. This mineral is of particular importance as it is used extensively for the radioactive dating of rocks by the U - Pb method[6,7,8]. As a single crystal of zircon may consist of several overgrowths of different ages and chemical characteristics, detailed microprobe characterization of the minor and trace component chemistry of all overgrowths is essential to correct interpretation of the isotopic results.

Microprobe analysis of trace amounts of U in zircon by low energy PIXE is complicated by the proximity of the U L X-ray lines and the Zr K X-ray lines. A similar example is encountered in the analysis of samples containing both Au and As (by either EPMA or μ-PIXE). As Kα X-rays will overlap with Au L X-ray lines[2], this increases the detection limit when As is present in appreciable amounts, which is often the case in Au-bearing sulphide minerals.

Halden et al. have overcome this problem by using high-energy protons (E_p = 40 MeV) capable of exciting Au K X-rays that occur in an energy range not complicated by X-ray emissions from lighter elements[3]. This suggests that the use of high-energy protons for PIXE may provide an alternative when low-energy methods have problems of line overlap. Recent work has also shown that well-resolved K X-rays for Rare-Earth Elements (REEs) and PGEs can be generated from geological samples using a 40 MeV proton beam[9,10,11].

K-shell ionization cross-sections for heavy elements are high for PIXE analysis when E_p = 40 MeV (e.g. for Z= 80, the cross-section is approximately 8 barns), and the cross-section for K X-ray production from light elements is significantly higher (in the region of 800 barns for light elements)[4]. It might be reasonably anticipated that the cross-section for L X-ray production with 40 MeV protons would also be high; Cohen has shown that the cross-section for L X-ray production increases with increased proton

energy (E_p = 1-3 MeV)[12]. Thus, excitation with 40 MeV protons should provide the widest possible choice of X-ray lines for analysis.

With a 40 MeV proton beam and an array of appropriate solid state detectors (e.g. Si(Li) and intrinsic Ge), K X-rays for most naturally occurring elements (Na, Z=11 up to and including U, Z=92) are in principle available for quantitative analysis. It is therefore appropriate to examine a mineral that contains light elements and U to see if this is in fact the case. The ability to do such analyses may also be of particular importance in monitoring the complex chemistry of minerals at radioactive waste disposal sites.

2. Experimental

Small single-crystal plates of autunite ($Ca(UO)_2(PO_4)_2.10\text{-}12H_2O$; ca. 20 mm^3) were suspended in mylar envelopes and mounted on an aluminum frame. The Al target frames were mounted in an evacuated chamber on an experimental beam line at the University of Manitoba Accelerator Centre Cyclotron Facility. The samples were exposed for approximately 30 minutes to a 40 MeV proton beam 2mm in diameter, with an average beam current on-target of 10 nA. X-rays emitted by the sample were detected with intrinsic Ge and Si(Li) detectors, signals were processed using NIM and Camac electronics. The detectors and electronics were calibrated using a ^{241}Am source. Data were processed using the data collection/analysis program XSYS[13].

3. Results

The spectrum collected from autunite using the Si(Li) detector is shown in Figure 1. Halden et al. have demonstrated that it is useful to have some prior knowledge of the mineralogy and chemistry of the material to assist in interpreting high-energy PIXE spectra[3]. Autunite would typically contain about 5.5 wt.% CaO and SrO, 58 wt.% UO_3, 14.5 wt.% P_2O_5 and 21 wt.% H_2O[14,15]. The lowest energy peaks visible are the Ca Kα and Kβ X-rays at 3.69 and 4.01 keV respectively. Sr may substitute for Ca in this mineral[15]. The small peaks between the U Lα_1 and U Lβ_2 X-rays (Fig. 1) are the Kα and Kβ X-rays of Sr at 14.14 and 15.84 KeV respectively. As U is the most abundant element, it will show the most intense X-ray peaks. The most prominent X-rays are the L X-rays of U (see figure caption). The relative intensity of the L X-rays and K X-rays (Fig. 2) from U reflects the relative magnitude of the ionization cross-sections for U L and K X-rays.

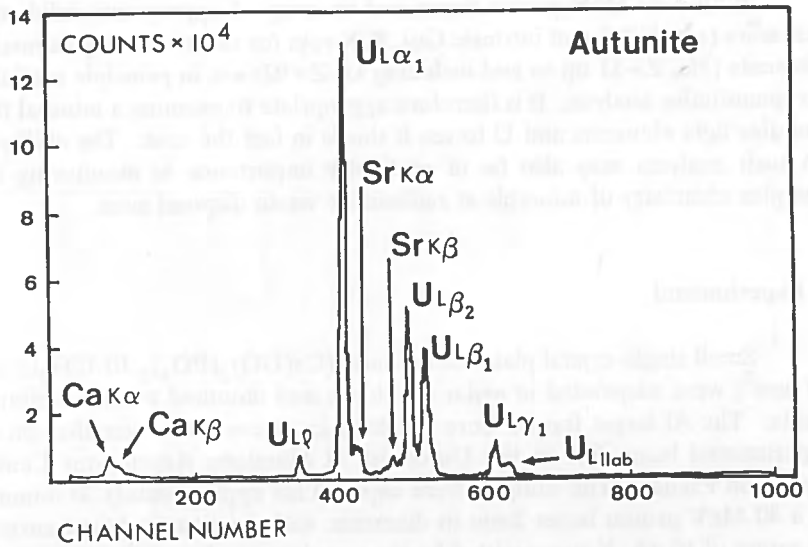

Fig. 1 Spectrum collected using an Si(Li) from autunite during exposure to a 40 MeV proton beam showing the U $L\alpha_1$, $L\beta_1$, $L\beta_2$, $L\gamma_1$ $L\ell$ and L_{IIab} X-rays at 13.61, 17.28, 16.42, 20.16, 11.61 and 21.75 KeV respectively; Ca Kα and Kβ X-rays at 3.69 and 4.01 KeV respectively; and Sr Kα and Kβ X-rays at 14.14 and 15.84 KeV respectively, the intensity scale is linear.

The spectrum collected from the autunite using the intrinsic Ge detector is shown in Figure 2. Three peaks are apparent at the high-energy end of the spectrum. The two 'lower-energy' peaks correspond in energy and relative intensity to the U $K\alpha_1$ and U $K\alpha_2$ X-ray lines (98.42 and 94.64 KeV respectively). To the high-energy side of the U Kα X-rays, the third peak coincides approximately with the position of U Kβ X-ray line (approximately 111.78 KeV). The tails on the low-energy side of the peaks, and the unresolved nature of the U Kβ X-rays, are artifacts of an extreme gain setting on the detector preamplifier.

The background in this spectrum is relatively high compared to other high-energy PIXE spectra[3,9]; two characteristics of the sample are likely to have contributed this background scattering:

(i) The samples were irregular, comparatively thick fragments (as opposed to thin target 30 μm wafers used in the study of Au[3]);
(ii) U is present in significant amounts in autunite; it is dense, and the

mineral has appreciable 'stopping power',leading to high bremsstrahlung.

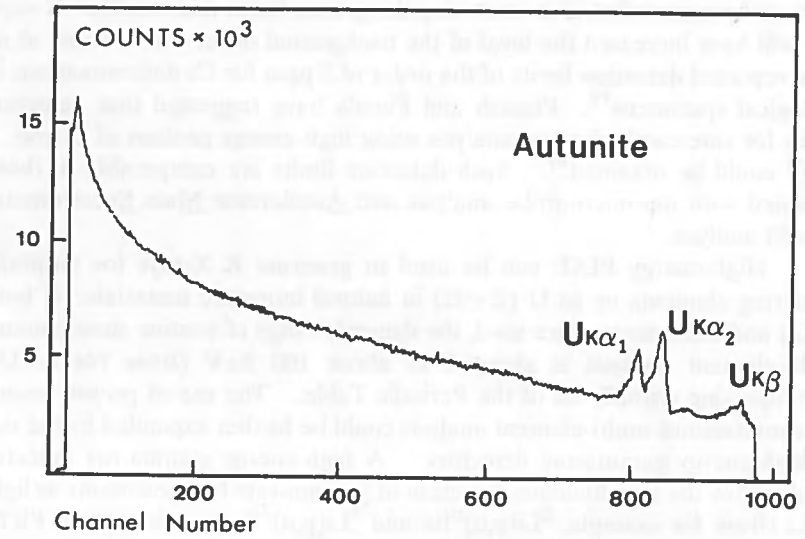

Fig. 2 Spectrum collected from autunite using an intrinsic Ge detector during exposure to a 40 MeV proton beam showing the U $K\alpha_1$, $K\alpha_2$ and $K\beta$ X-rays at 98.42, 94.64 and 111.78 KeV respectively; the intensity scale is linear.

4. Discussion

The ability to generate both the K and the L X-rays presents the analyst with a number of choices. Although in this example, U is clearly a major element, the sensitivity of analyzing trace amounts of U using L X-rays (in the absence of a geochemically coherent element) would be significantly better using high-energy protons as opposed to low-energy protons. If a problem of geochemical coherence were to occur where it was necessary to analyze minor or trace amounts of U in the presence of an major element (e.g. Zr, Sr and Mo) whose K X-rays were likely to obscure the U L X-rays, then the U K X-rays would be available for analysis in the intrinsic Ge detector spectrum.

The absolute sensitivity of high-energy PIXE will depend upon sample preparation, the detector used, proton flux, and the volume of material

examined. The samples used in this study were not prepared as polished thin wafers as in other studies[3]; and the mineral plates used in this experiment are likely to have contributed to scattering the proton beam and resultant X-rays; this will have increased the level of the background observed. Mckee et al. have reported detection limits of the order of 5 ppm for Cs determinations in biological specimens[16]. Piesach and Pineda have suggested that detection limits for rare earth element analysis using high-energy protons of below μgg^{-1} could be obtained[11]. Such detection limits are comparable to those obtained with ion-microprobe analysis and Accelerator Mass Spectrometry (AMS) analysis.

High-energy PIXE can be used to generate K X-rays for naturally occurring elements up to U (Z=92) in natural inorganic materials. If both Si(Li) and Ge detectors are used, the dynamic range of routine simultaneous multi-element analysis is about 1 to about 100 KeV (from Na to U), encompassing virtually all of the Periodic Table. The use of proton beams for simultaneous multi-element analysis could be further expanded by the use of high-energy gamma-ray detectors. A high-energy gamma-ray detector would allow the simultaneous detection of gamma-rays from elements as light as Li (from for example, $^{6}Li(p,n)^{6}Be$ and $^{7}Li(p,n)^{7}Be$ reactions) in a PIGE experiment running concurrently with PIXE. This would expand the potential analytical range to Li - U.

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