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PLATINUM GROUP ELEMENT HIGH-ENERGY PIXE

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Abstract

K X-ray spectra have been obtained from Platinum-Group Element (PGE) minerals using 40 MeV Proton-Induced X-ray Emission. It is possible to resolve all four component X-ray lines for the PGEs. In cases where there is more than one PGE present, some K X-ray lines may overlap, but in all cases, there were single lines available for quantitative analysis.

The spectrum obtained from the sperrylite during exposure to the proton beam beam contained Au X-rays. The presence of the Au can be attributed to (p,xn) reactions with Pt, induced by proton bombardment of the sample. The intensity of Au X-ray lines in the spectrum is proportional to the amount of Pt in the sample and the cross-section for (p,xn) reactions between Pt and Au at 40 MeV.

Keywords : Platinum Group Elements; High-Energy PIXE; Proton Activation Analysis

1. Introduction

Geochemical analysis of minerals for rare and heavy elements has gained new impetus from the application of accelerator-based ion-beam techniques. In particular, the use of PIXE (Proton Induced X-ray Emission) has expanded very rapidly in the past few years, and has contributed to the solution of significant mineralogical problems[1]. Most of the PIXE work on geological materials has been done at low energies[1,2,3] (ca. 2-5 MeV). PIXE analysis of PGE's (Platinum Group Elements) has been done previously using 4 MeV protons. Annegarn et al. used low-energy protons to irradiate PGE's which were preconcentrated from geological specimens using fire-assay techniques[4]. In the resulting spectra, Pt L-lines were obscured by Pb L-lines, and K X-rays for Pt, Ir and Os were not observed. However, it has recently been shown that high-energy PIXE ($E_p > 25$ MeV) can produce well-resolved K X-ray spectra for the rare-earth elements and Au in geological materials[5,6,7], suggesting that high-energy PIXE may provide a solution to problems of X-ray line overlap of geochemically coherent elements at lower energies. In principle, the PGEs should also be susceptible to high-energy PIXE analysis without the attendant complexities of de-convoluting the L X-ray line spectra from geochemically coherent elements. Low-energy protons have insufficient energy to ionize K-shell electrons in PGEs, they can however remove L-shell electrons. L X-ray spectra are significantly more complicated than K X-ray spectra, there being many X-ray lines corresponding to the splitting of energy levels in the L-shells of heavy elements. The relative intensities of L X-ray lines are not well known for heavy elements, this also hinders the interpretation of L X-ray spectra.

From an analytical point of view it is both sensible and advantageous to collect the simplest and most unambiguous raw data. This is especially important when working with geochemically complex materials where geochemically coherent elements are likely to be present. K X-ray spectra can have a maximum of four X-ray lines and the relative intensities of these lines are known. Thus it is more appropriate to do PIXE analysis of heavy elements using K X-ray lines which can only be generated using high-energy protons.

Previous high-energy PIXE and charged particle analysis has shown that there can be additional contributions to the spectrum from nuclear reactions resulting from interactions of the beam with the sample[5,8]. Knowledge of the sample mineralogy, the X-ray and gamma-ray spectral characteristics of elements likely to be in the specimen and the nuclear decay processes that can occur during and after proton irradiation can provide sufficient constraints for such interferences to be identified, at least in the few cases that have been examined so far[5]. Consequently, it seemed worth while to explore the potential of high-energy PIXE for the analysis of PGEs in minerals. Here we examine some platinum group minerals with high levels of PGEs, as it is here that the problems of mutual interference and possible generation of signals from nuclear reactions should be most apparent.

2. Experimental

Samples of sperrylite and rutheniridosmine were prepared as thin mineral fragments, suspended within a mylar envelope 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 to a 40 MeV proton beam 2mm in diameter, with an average beam current on-target of 10 nA, for periods of 15 to 30 minutes. X-rays (and low-energy gamma rays) emitted by the samples were detected with an intrinsic Ge detector; signals were processed using NIM and Camac electronics. A 1.25" paraffin filter, placed between the sample and the detector, was used to suppress the low-energy region (<25 KeV) of the background. The detector and electronics were calibrated using an Am^{241} source. Data were processed offline using the data collection/analysis program XSYS[9].

3. Results

3.1 *Sperrylite*

The spectrum of sperrylite is shown in Figure 1a. There are four X-ray lines which correspond in energy and relative intensity to the K-line series of Pt (Pt Kα_1, Kα_2, Kβ_1, Kβ_2 : 66.82, 65.11, 75.73 and 77.86 KeV respectively); these are clearly resolved, and are therefore available for analytical purposes. The spectrum also shows the Kα and Kβ X-rays for Pd (21.12 and 23.86 KeV respectively). To the high-energy side of the Pt Kα_1, peak there is a small well-resolved peak at 68.79 KeV. This corresponds in energy to the Au Kα_1 X-ray. As we do not expect Au to occur naturally in this sample, the Au must be in the form of isotopes produced by nuclear reactions involving Pt. Au can be created by (p,xn) reactions involving Pt; K-shell ionization in the resulting Au produces normal Au K X-rays. Whereas the Au Kα_1 X-rays will not interfere with any Pt K X-ray line, there will be a Au Kα_2 X-ray line to the low-energy side of the Au Kα_1 X-ray line which will interfere with the Pt Kα_1 X-ray line. The Pt Kα_1 peak intensity must be corrected for this overlap by subtracting counts associated with the AuKα_2 peak. As the ratio of Kα_1 to Kα_2 peak intensities during proton bombardment will be approximately 1.70[10,11], the intensity (due to Au K X-rays) to be subtracted can be determined by counting on the AuKα_1 peak. As a check on this procedure, the Pt Kα_2 peak is free from any interference, and can also be used for analytical purposes in this particular sample. This ignores for the moment any contribution to the Au K X-rays from electron capture (EC) reactions related to the decay of the Au isotopes. This is a reasonable approximation in this case as the cross-section for proton ionization of K electron-shells in Pt is at least a factor of 8 greater than the (p,xn) cross-section[12] to create excited Au isotopes. With short proton bombardment times (less than the half-lives of the Au isotopes decaying by EC), the contribution from EC related X-rays will be small.

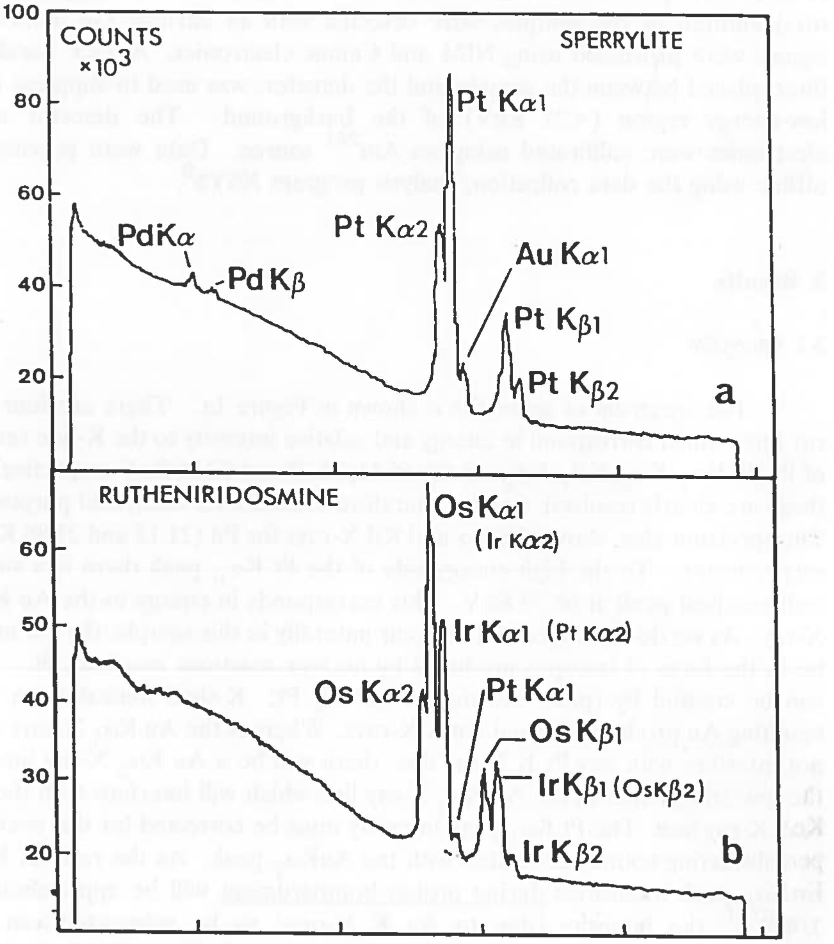

Figure 1a. Spectrum collected from sperrylite showing the four K X-ray lines for platinum. The Au Kα_1 X-ray line is produced from Au created by Pt (p,xn) Au reactions. The low-energy part of the spectrum is suppressed with a 1.25" paraffin filter. Still visible in the low energy part of the spectrum are K X-rays for Pd and escape peaks of Ge caused by proton back-scattering in the detector.

Figure 1b. Spectrum collected from rutheniridosmine, showing Kα X-rays for Os, Ir and Pt, and Kβ X-rays for Os and Ir. The overlapping X-rays are shown in parenthesis after the label corresponding to the principal peak at these positions. The low-energy region is suppressed using the paraffin filter. Just visible are poorly developed peaks that correspond to K X-rays for Ru and Ge, the latter created by scattering in the detector.

3.2 *Rutheniridosmine*

The spectrum of rutheniridosmine (Fig. 1b) is more complex. There is significant K X-ray overlap of three adjacent elements in the periodic table: Ir, Os and Pt. In this situation, the type of data reduction required for quantitative analysis is no more complex than the peak stripping associated with routine energy-dispersive electron microprobe analysis. However, as there are four K X-ray peaks that can potentially interfere, the exact nature of the overlaps must be determined.

A single heavy element (Z=76-80) emitting K X-rays will give a Kα_1 - Kα_2 peak intensity ratio of about 1.70[11]; this is the case for the Pt K X-rays in Figure 1a. In Figure 1b, there are no such obvious Kα_1 - Kα_2 peak pairs with an approximately 1.70 intensity ratio. The most intense peak in Figure 1b has an energy of 62.99 KeV, corresponding in energy to the Kα_1 X-ray peak for Os; the peak to the low-energy side has an energy of 61.47 KeV corresponding to Os Kα_2. These peaks do not have an intensity ratio of approximately 1.70, and consequently there must be significant interference. Halden et al. have emphasised the necessity of prior knowledge of the mineralogy and likely geochemistry of the sample in order to solve such problems[5]. In addition to Os, rutheniridosmine contains Ru, Ir and minor Pt . The peak to the high-energy side of 62.99 KeV has an energy of 64.88 KeV, corresponding to the Ir Kα_1 X-ray peak. There will also be an Ir Kα_2 peak to the low-energy side of the Ir Kα_1 peak; this will interfere with the Os Kα_1 peak to give an anomalously intense peak at this energy. The small peak to the high-energy side of the Ir Kα_1 has an energy of 66.82 KeV; this is the Pt Kα_1 X-ray line. There will also be a Pt Kα_2 peak which will interfere with the Ir Kα_1 X-ray line.

The overlap of X-ray lines from adjacent elements is also seen in the Kβ spectrum. Figure 1a shows the expected relationship between Kβ_1 and Kβ_2 X-ray peaks, in this case for Pt. The Kβ peaks in Figure 1b do not show this relationship. In this case, Os Kβ_1 is free from interference, but Os Kβ_2 overlaps with Ir Kβ_1; this makes the central peak in this region of the spectrum anomalously intense. The smallest peak to the high-energy side of the overlapping Os Kβ_2 and Ir Kβ_1 lines is Ir Kβ_2. There is no evidence of Pt Kβ peaks, probabally because of the relatively low abundance of Pt in rutheniridosmine (ca. 0.0x%[13]).

4. PIXE

Rutheniridosmine contains significant amounts of Os and Ir (about 27-60% Os and 17-42% Ir[13]). Fluorescent yields for Os and Ir will be similar, reflecting the similarity in the K-shell electron-binding energy (and hence the K-shell ionization potentials for these elements)[10]. In a sample containing more Os than Ir, PIXE of Os K X-rays should be more intense than Ir K X-rays during proton bombardment; this is what is observed in Figure 1b, indicating that this particular sample contained more Os than Ir.

High-energy PIXE analysis of platinum group minerals produces K X-ray spectra with a series of well-resolved peaks. In the presence of neighbouring elements in the periodic table, there are significant peak overlaps, but these are quite straight forward, and there are sufficient single K X-ray lines for analytical purposes. In addition, there is no interference from the K X-ray spectra of light elements present in substantial concentrations, as can be the case for L-line spectra of heavy elements (e.g. As Kα X-rays overlap with Au L lines[14]). Conversely, the presence of nuclear peaks is a complicating factor not present in L-line spectra. However, knowledge of the sample mineralogy should allow resolution of such problems. In this study, sperrylite (which does not contain Au) is a case in point, interference resulting from (p,xn) reactions; so also is electrum, a naturally occurring Au-Ag-Hg alloy, where interference stems from a (p,charged particle) reaction[5]. Such geochemical coherence is to be expected in natural materials, and high-energy PIXE provides one means of dealing with the attendent analytical problems.

5. Nuclear Reactions

Recent work has shown that the products of complex nuclear reactions may be observed when a 40 MeV proton beam interacts with a mineralogically and chemically complex sample[5]. In the case of the sperrylite spectrum, some X-rays are characteristic of Au, which was not originally present in the sample. Ideally, sperrylite has the chemical formula $PtAs_2$; consequently, the isotopes of Au must have been created in the sample during exposure to the proton beam via Pt(p,xn)Au reactions. At 40 MeV, (p,xn) and (p,charged particle) type reactions (e.g.(p,α),(p,d), (p,t)) may also result in the creation of isotopes (initially in excited states) which will decay over a period of time, giving off characteristic gamma-rays and X-rays. If, for example,Pt isotopes were the starting point for such reactions, the products would be excited isotopes of Au, Pt and Ir. Similarly, if Ir and Os isotopes were the starting point, excited isotopes of Pt, Os, Ir and Re would be created.

5.1 *Pt(p,xn)Au reactions*

At 40 MeV, the cross-section for (p,4n) reactions with heavy elements is high, (p,2n) and (p,3n) reactions may also occur, but with lower probabilities[12]. Au isotopes will be the product of (p,xn) reactions with Pt isotopes. A number of Au isotopes (e.g. ^{191}Au, ^{192}Au, ^{193}Au and ^{194}Au) will decay by EC to Pt isotopes: ^{191}Au, ^{192}Au, ^{193}Au and ^{194}Au will decay with half-lives of 3.2, 5.0, 17.6 and 39.5 hours respectively.

^{194}Pt, ^{195}Pt, and ^{196}Pt are the most abundant naturally occurring isotopes of Pt. Using these isotopes as the most likely starting point for nuclear reactions involving Pt, the following reactions will be of interest:

^{194}Pt(p,4n)^{191}Au; ^{194}Pt(p,3n)^{192}Au; ^{194}Pt(p,2n)^{193}Au
^{195}Pt(p,4n)^{192}Au; ^{195}Pt(p,3n)^{193}Au; ^{195}Pt(p,2n)^{194}Au
^{196}Pt(p,4n)^{193}Au; ^{196}Pt(p,3n)^{194}Au; ^{196}Pt(p,2n)^{195}Au

The probabilties of ^{191}Au, ^{193}Au and ^{195}Au decaying by EC are extremely small whereas the probabilities of ^{192}Au and ^{194}Au decaying by EC are extremely high: ca. 99% and 97% respectively.

For the Au isotopes, the process of EC is most likely to involve the capture of a K-shell electron. The filling of the resulting K-shell vacancy will produce Au X-rays. In a case where Pt(p,xn) Au reactions have occurred, Au X-ray lines in a spectrum collected <u>after</u> proton bombardment will be due almost entirely to X-rays created by the EC decay of ^{192}Au and ^{194}Au, and the intensities of the Au X-ray lines will reflect the initial abundance of Pt. The Au X-ray intensity v. Pt concentration relationship will be a function of the cross-sections for the proton reactions and the probabilities for electron capture from the K electron-shell for the various isotopes.

6. Proton Activation Analysis

The intensities of gamma-rays and X-rays from excited isotopes in an off-line proton activated spectrum will be a function of the following:

(i) the abundance of the initial isotope,
(ii) the cross-section for the nuclear reaction ((p,xn) and/or (p, charged particle)) and the time of exposure of the sample to the proton beam; both these factors will determine the abundance of the product isotope;
(iii) the branching ratio for the various decay schemes available to the product isotope;
(iv) the half-lives of the isotopes;
(v) the amount of time spent counting off-line on the product isotopes.

Using this as a general framework within which geochemical analyses may be done using proton beams, it would be better (especially in cases where the excited product isotopes have half-lives of a few hours) to analyze gamma-rays and X-rays after bombardment. The time spent counting on gamma and X-rays will be a function of the half-lives of the product isotopes, detector efficiency and the amount of the product isotope created. Geochemical analyses done in this way will be the result of proton activation of the sample. Proton activation is analogous to neutron activation analysis. The particular advantage, however, of this form of analysis is that it is done with a milli- or micro-beam offering 'pin-point' analysis as opposed to bulk sample irradiation. If the decay scheme of an excited product nucleus includes EC, this will place an additional constraint on high-energy PIXE. If exposure times (to proton bombardment) significantly exceed the half-life of the EC branch of an isotope's decay scheme, the K X-rays from EC could contribute to PIXE X-rays in a satellite peak. In cases where this might be possible, PIXE analytical times should be kept short.

7. Discussion

Proton activation offers a number of potential analytical advantages, especially as it can be done in conjunction with PIXE analysis. An EC K X-ray spectrum can be collected off-line releasing the proton beam for other on-line experiments. Proton Activation Analysis may be of use when Pt X-rays generated on-line are swamped either by Ir- (which is geochemically coherent) X-rays or by Au X-rays. An example of this might be the analysis of rutheniridosmine, where Pt is normally present in abundances around 0.0x% and the resulting on-line Pt K X-ray peaks are nearly obscured by the more prominent Ir K X-rays. An off-line spectrum is also likely to have lower bremsstrahlung, compton scatter of prompt gamma rays generated during on-line proton bombardment will not exist, and there will be no contribution from matrix effects stemming from the beam interaction with the specimen. This may make the technique more sensitive for trace element analysis.

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