

## **Detection of trace elements in meteorites using PIXE**

Sasha dos-Santos <sup>(a, b)</sup>, Ivan Kravchenko <sup>(b)</sup>, and F.E. Dunnam <sup>(b)</sup>

<sup>a)</sup> University of South Florida, Tampa, Florida 33620

<sup>b)</sup> Department of Physics, University of Florida, Gainesville, Florida 32611

## 1. INTRODUCTION

Particle-Induced X-Ray Emission Spectrometry (PIXE) is a method of determining the chemical composition of a substance (especially those elements present in quantities under 3%). In PIXE analysis, a sample is bombarded by particles, usually protons, and the resulting characteristic X-rays are analyzed. This provides a non-destructive method of determining the abundance of an element that is present in a sample. Since its introduction in the 1970's, PIXE has been used in such diverse fields as medicine, environmental science, archaeology, and astrophysics [1].

In this experiment, we were interested in determining the chemical composition of meteorites using the PIXE method. Meteorites are important to study because they are the only outer space objects that can be directly analyzed in the lab. Representatives of the three major classes of meteorites -- iron, stony, and stony-iron -- were available for study. The expected chemical compositions of the various sub-groups of meteorites have been well documented in the literature; however, each meteorite represents a unique specimen. By studying several meteorites, questions could be answered concerning which elements are the most common in meteorites. The following meteorites were studied (class and group notations [2] are provided in parenthesis): *Allende* (Stone CV3), *Broken Hill* (Stone L5), *Saratov* (Stone L4), *Sahara 99703* (Stone H6), *Sahara 99932* (Stone H6), *Sahara 99754* (Stone H5), *Sahara 00748* (Stone), *Vaca Muerta* (Stony- Iron MES), *Huckitta* (Stony-Iron PAL) , and *Imilac* (Stony-Iron PAL).

## 2. THEORETICAL BACKGROUND

When electrons are freed from an atom by the acquisition of energy, a temporary hole exists in the electron orbital (shell). This hole is filled with an electron from an

outer shell. Each shell has a specific binding energy that depends on the atomic number, Z, of the element. The binding energy represents the energy necessary to dislodge an electron from a shell. An approximation for hydrogen-like atoms is given by the following equation:

$$E = -(ke^2 / 2a_0)(Z^2 / n^2),$$

where k is the Coulomb constant,  $a_0$  is the radius of the H atom, e is the charge of the electron, and n is an integer value [3].

When an electron drops down from an outer shell to fill a vacancy, two competing processes occur--X-ray emission and Auger electron emission. The standard notation for describing X-rays is to state the shell (K, L, M ...etc.) that contained the vacancy, followed by a letter ( $\alpha$ ,  $\beta$ ...etc. ) specifying the shell providing the electron. The characteristic X-rays of each element are unique. Auger electron emission occurs when an electron from an outer shell is emitted. The probability of Auger electron emission is higher for light elements. Both the Auger electron and the characteristic X-ray are of energy equal to the energy difference between the shells involved [1].

### **3. EQUIPMENT**

A vertical Van de Graaff accelerator is used as the ion beam source. The proton source is located inside the Van de Graaff's high voltage terminal; consequently, the hydrogen gas is ionized by an RF (radio frequency) oscillator, resulting in  $H_2^+$  and  $H^+$  ions. The charged particles are pulled out of the terminal by an electrode. Having left the terminal, the ions are repelled by its positive charge and travel down an accelerator tube [4]. An analyzing magnet selects particles based on energy, mass, and charge; it also

bends the beam  $90^\circ$ , to a horizontal position. A quadrupole magnet focuses the beam onto the sample.

An absorber is placed near the sample, suppressing X-rays of low energy. This allows the detector to spend more of its time on X-rays from the elements we are most interested in --- those of higher atomic number and, consequently, higher X-ray energy. The absorber also absorbs some of the bremsstrahlung (continuous background radiation). The primary sources of bremsstrahlung are: 1) electrons ejected from atoms by inelastic collisions with the beam, and 2) nuclear reactions between protons and atoms which result in gamma rays [1].

A Faraday cup lies at the end of the PIXE setup; the cup collects any charge that has not been absorbed by the sample. The Faraday cup is connected to a current integrator. The current integrator integrates current over time to calculate total charge.

The X-rays are detected by a Si-Li drifted detector. The X-rays lose energy to the detector by pair production, the Compton effect, and the photoelectric effect. (X-rays with energies greater than 30 keV pass right through the detector and are not detected). This energy is imparted to free electrons in the silicon and the lithium. A voltage bias across the detector forces the electrons to move through it [4,5]. A pre-amplifier collects charge and creates voltage pulses and an amplifier amplifies the voltage pulses and converts them into rectangular analog signals. These signals are sent to a computer and analyzed by a multi-channel analyzing program. The program plots channels vs. number of counts. Each channel specifies a certain interval of energy; 1,024 channels were used in our experiment. Peaks in the spectrum occur at energies indicative of characteristic X-rays.

#### **4. EXPERIMENT**

The first item studied was U.S. Geological Survey standard AGV-1, analyzed Andesite. A solution of 2% polystyrene in benzene provided a bonding agent for the powdered sample. An ultrasound cleaner was used to suspend the powder in the polystyrene in benzene. The solution was placed on an aluminized Mylar surface by a process called spin coating. In spin coating, a solution is dropped onto a rapidly spinning substrate, resulting in a very thin film of solution.

The meteorites were placed in sample holders consisting of a square aluminum frame and copper clip. Care was taken to ensure that the beam hit the meteorite without hitting the copper clip (which would result in an excess of copper characteristic X-rays). Because the meteorites were thick targets, a large number of X-rays were produced. The current of the proton beam was adjusted to ensure that an abundance of a certain element (usually Fe) would not produce enough X-rays to overwhelm the detector (this would cause the detector to spend most of its time detecting X-rays of a certain element). The current used for the samples varied between 1.7 and 3 nA. It was not possible to maintain a steady current; the current was read off the current integrator at the end of each trial. To estimate the total charge of the proton beam, the current was multiplied by the time of the trial. Most samples were analyzed for, approximately, 10 minutes.

Several phenomena need to be considered when looking at the chemical spectrum. A phenomenon known as pulse-pileup can lead to mirror images of parts of the spectrum. If there is a large quantity of X-rays arriving at the detector, the detector may mistake two voltage pulses arriving at the same time for one large pulse. For example, two 5V pulses arriving close together may register as one 10 V pulse; if this occurs often enough, a

small peak at a corresponding double energy will appear. While most pulses are interpreted correctly, enough of the pulses are misinterpreted that a repeat of a part of the spectrum is clearly visible. Another false image is called an escape peak; this occurs because the Si-Li detector can absorb 2 keV of energy without registering it in the output. If this absorption occurs, a small peak (resembling a shark's tooth) is visible at 2 keV less than a large peak.

## **5. DATA ANALYSIS**

The chemical spectra were analyzed with RobWin, a software package. RobWin mathematically models the background radiation and identifies possible peaks in the spectrum. While most peaks are identifiable upon visual inspection, RobWin is able to identify peaks that are not easily seen. RobWin can also split what appears to be one large peak into its two or more constituent peaks. By taking into consideration the background radiation, RobWin can also be used to determine the number of counts due to a particular element.

The first step in analyzing the meteorites was to analyze our standard, AGV-1 (figure 1), and compare our results with that of Carlsson and Akselsson [6]. This would give us an idea of how accurately our PIXE setup could detect the presence of elements. It also provided a chance to test our spectrum analyzing software against a known spectrum. Our PIXE setup was not able to detect Al, Si, and Ba because the energy of their characteristic X-rays are not within our limits of detection. The  $K K_{\alpha}$  line, the smallest energy detected, was shorter than expected; this was due to the absorbers in the

PIXE setup. Also, the Pb  $L_{\beta}$  line was larger than expected. Overall, however, our spectrum looked very much like the spectrum of Carlsson and Akselsson [6].

The AGV-1 standard was used to build a sensitivity curve, a measure of the sensitivity of our PIXE setup as a function of atomic number. The y-axis is the log, base ten, of the number of counts of a particular element divided by its concentration in PPM multiplied by the total charge of the proton beam. The concentrations were taken from Carlsson and Akselsson [6]. The total charge of the proton beam during the trial was 100  $\mu\text{C}$ . The relationship between the sensitivity curve and the determination of an element's concentration in PPM is:

$$Y(Z) = s(Z)N_p m_a(Z),$$

where  $Y$  is the yield,  $s$  is the sensitivity curve coefficient,  $N_p$  is the number of protons used in the proton beam, and  $m_a$  is the mass (concentration) of an element present in the sample [1]. This sensitivity curve is only valid for thin targets, and will be used once the meteorites have been made into thin targets.

## 6. CONCLUSIONS

The three stony-Iron meteorites studied were *Huckitta* (PAL), *Imilac*(PAL), and *Vaca Muerta* (MES). *Huckitta* (figure 2) and *Vaca Muerta* (figure 3) both contained traces of As. *Vaca Muerta* contained the greatest number of elements of any sample; it was also the only meteorite to contain trace amounts of Ga. *Huckitta* contained the least number of elements of any sample; unlike the similarly grouped *Imilac* (figure 4), *Huckitta* did not contain traces of Cu and Zn.

The stone meteorites studied were: *Allende* (Stone CV3, figure 5), *Broken Hill* (Stone L5), *Saratov* (Stone L4), *Sahara 99703* (Stone H6), *Sahara 99932* (Stone H6),

*Sahara 99754* (Stone H5), and *Sahara 00748* (Stone). *Broken Hill* (figure 6) and *Saratov* (figure 7) contained the exact same elements. Both meteorites contained small amounts of Zn and, unlike the other stone meteorites, did not contain traces of Cu. The three Stone H6 meteorites, *Sahara 99703* (figure 8), *Sahara 99932* (figure 9) and *Sahara 99754* (figure 10) are quite different. *Sahara 99703* is distinct from the other two in that it contains Zn and As; it is also distinct in that it contains more Cu than Ni. *Sahara 00748* (figure 11) is the only meteorite whose Cu  $K_{\alpha}$  and  $K_{\beta}$  lines were higher than the Ni  $K_{\alpha}$  line.

## **7. FUTURE STUDIES**

Thin film samples have many advantages to thick samples. Mirror images are avoided because of the relatively low quantity of X-rays. The proton beam can pass through the target and reach the Faraday cup; the total charge of the beam can then be read directly from a current integrator. Also, thin targets avoid the tendency of absorbing their own X-rays as the X-rays pass through multiple layers of the material. For these reasons, it is a natural next step to develop a method of preparing thin film meteorite samples.

The spin coating process used to create a thin film of AGV-1 will be used for preparing the meteorite samples. Because the aluminized Mylar used as a substrate for AGV-1 is no longer available for purchase, several replacement substrates are currently under consideration. Kimfoil and Polycarbonate films have been analyzed to determine which substrate contains the least amount of impurities. Kimfoil has the least amount of impurities and will most likely be used as the new substrate. The meteorite samples will be prepared using the thin film technique. The meteorites will be placed in a beaker of

acetone and placed in an ultrasound cleaner. The ultrasound cleaner removes impurities, such as polish, that have contaminated the sample since its discovery. Next, the meteorite will be crushed into a fine powder using a mortar and pestle. The powder will be placed in the ultrasound cleaner along with polystyrene in benzene; this solution will then be made into a thin film using the spin coating technique.

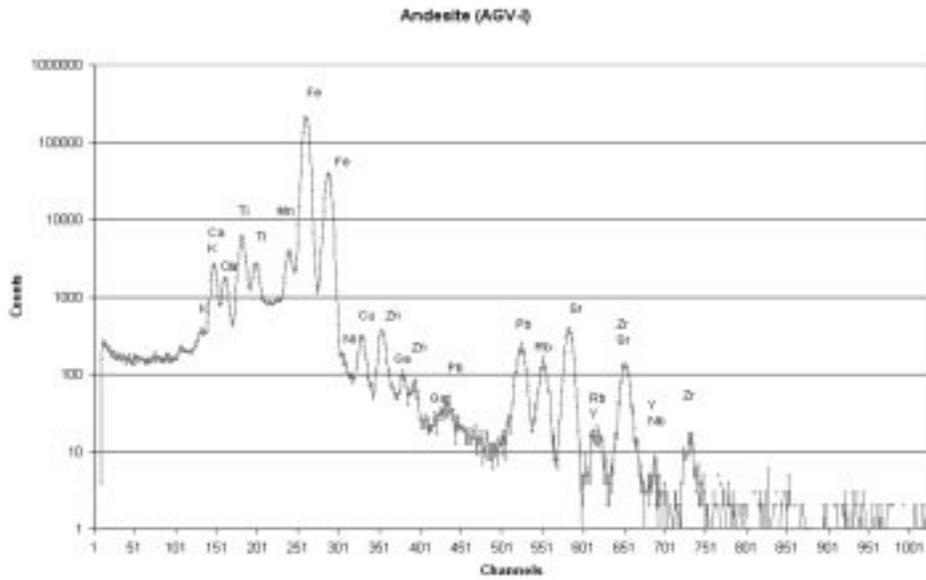
It is important to have the most accurate sensitivity curve possible. In the future, the inclusion of additional standards in the creation of the sensitivity curve will give us an accurate picture of the concentration in PPM. An even better prospect is the purchase of thin film standards which will allow us to measure the concentration in terms of  $\mu\text{g}/\text{cm}^2$ .

### **Acknowledgements**

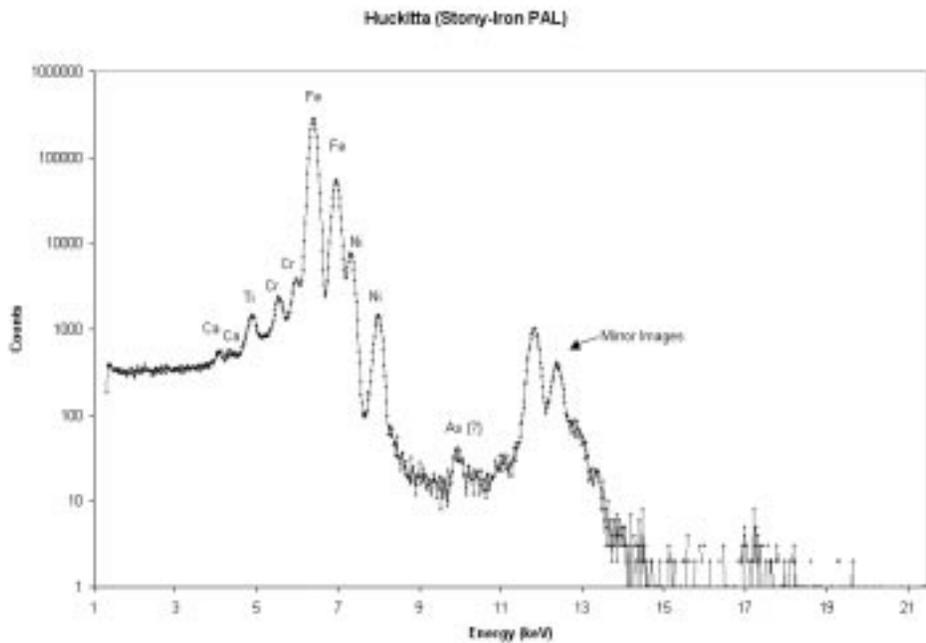
I would like to thank Drs. Ivan Kravchenko and F.E. Dunnam for assisting me in this project. Thanks also goes to Drs. Kevin Ingersent and Alan Dorsey for heading the research experiences for undergraduates (REU) program at UF. Acknowledgement is also made to the National Science Foundation for sponsoring the REU program.

## References

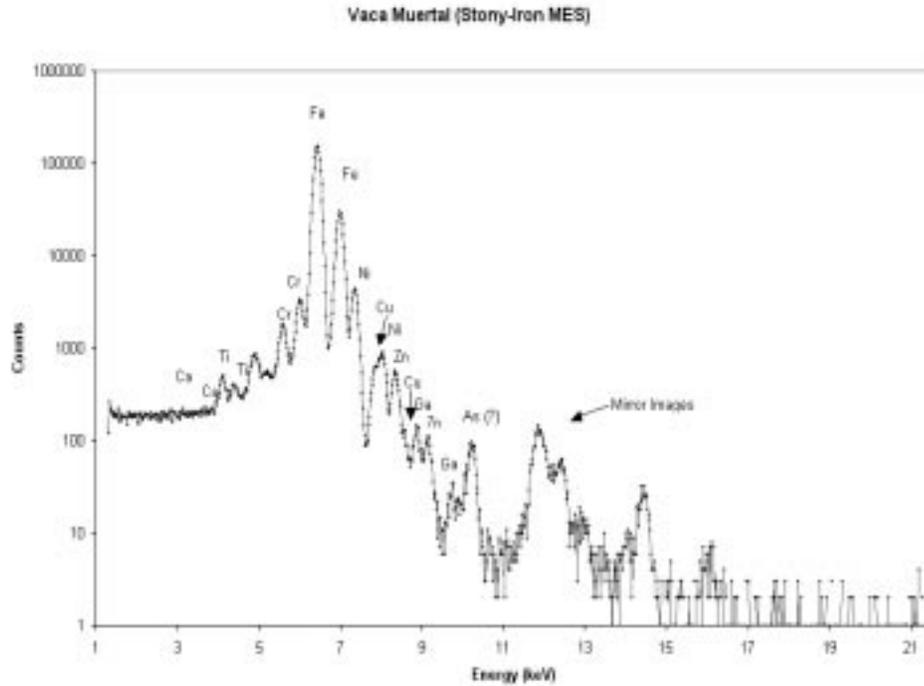
- [1] J.L. Campbell, S.A.E. Johansson, and K.G. Malmqvist, *Particle Induced X-Ray Emission Spectrometry (PIXE)*, (John Wiley & Sons Inc., New York, 1995).
- [2] F. Heide and F. Wlotzka, *Meteorites: Messengers From Space*, (Springer-Verlag, Berlin, 1995).
- [3] R.S. Shankland, *Atomic and Nuclear Physics*, (Macmillan Company New York, 1960).
- [4] R.A. Weller in *Handbook of Modern Ion Beam Materials Analysis*, edited by J.R. Tesmer and M. Nasati, (Materials Research Society Pittsburgh, 1995).
- [5] G.F. Knoll, *Radiation Detection and Measurement*, (Wiley New York, 1989).
- [6] K.R. Akselsson and L.E. Carlsson, "Major and trace elements in geological material," *Nuclear Instruments and Methods* **181**, 531-537 (1981).



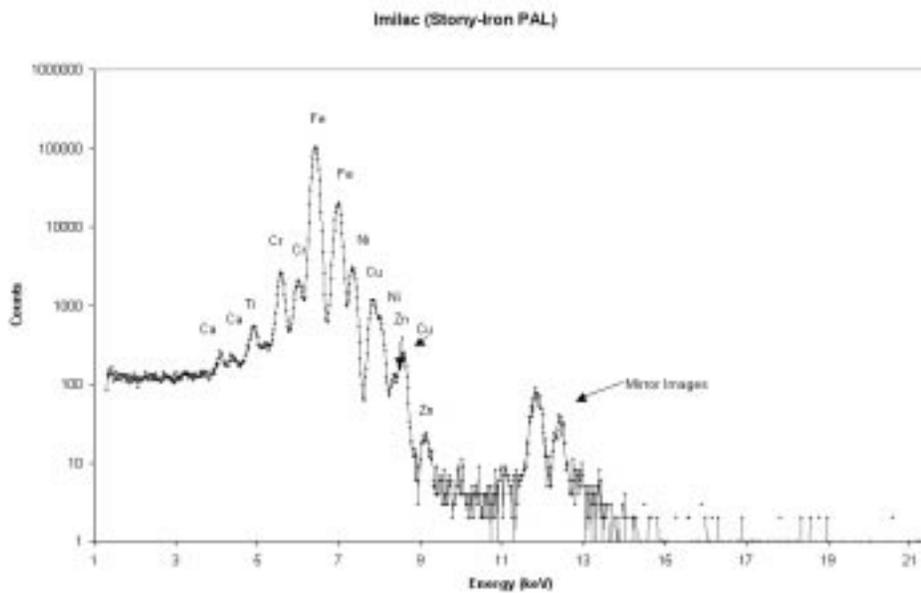
**Figure 1.** PIXE spectrum of a terrestrial sample: United States Geological Survey Standard AGV-1.



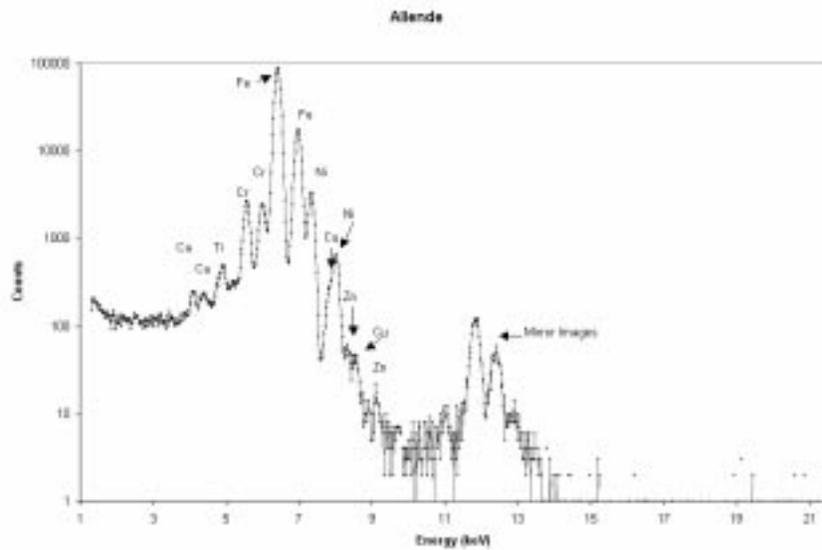
**Figure 2.** PIXE spectrum of *Huckitta* (Stony-Iron PAL) meteorite. The irradiation time was 15 min. The total charge of the proton beam was 1.62  $\mu\text{C}$ .



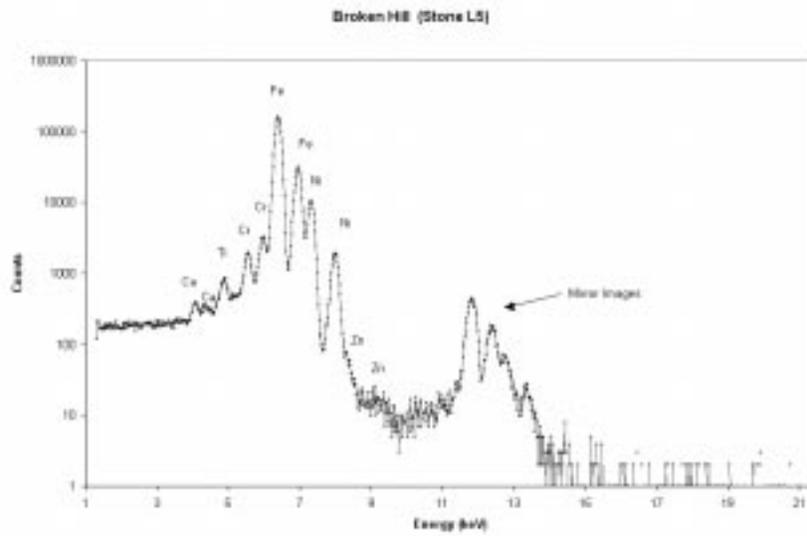
**Figure 3.** PIXE spectrum of *Vaca Muerta* (Stony-Iron MES) meteorite. The irradiation time was 35 min. The total charge of the proton beam was 3.78  $\mu\text{C}$ .



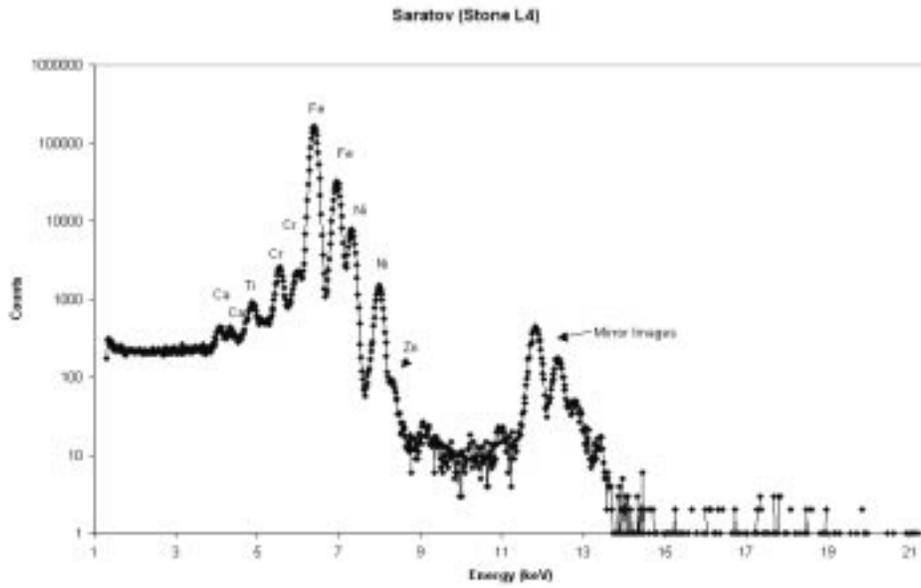
**Figure 4.** PIXE spectrum of *Imilac* (Stony-Iron PAL) meteorite. The irradiation time was 20 min. The total charge of the proton beam was 1.02  $\mu\text{C}$ .



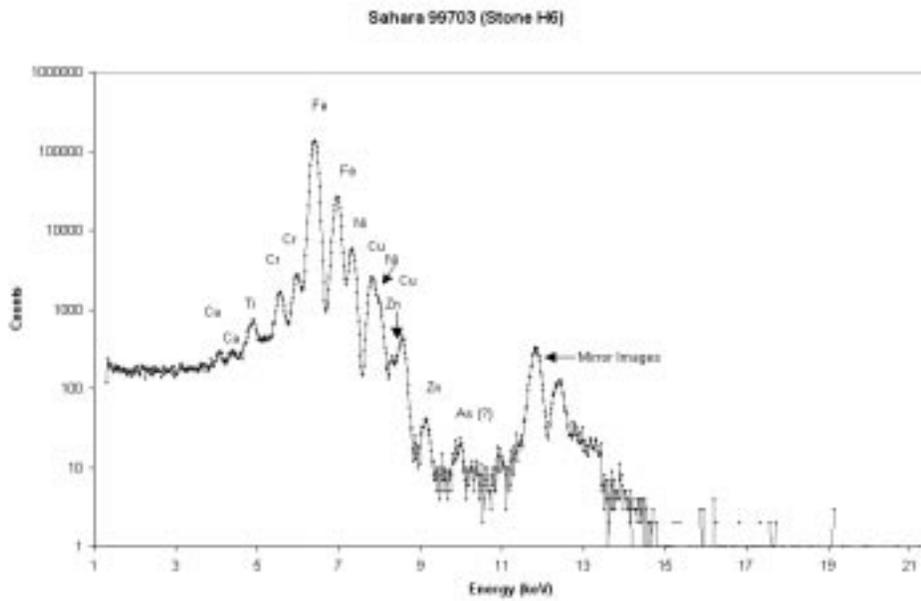
**Figure 5.** PIXE spectrum of *Allende* (Stone CV3) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.05 $\mu$ C.



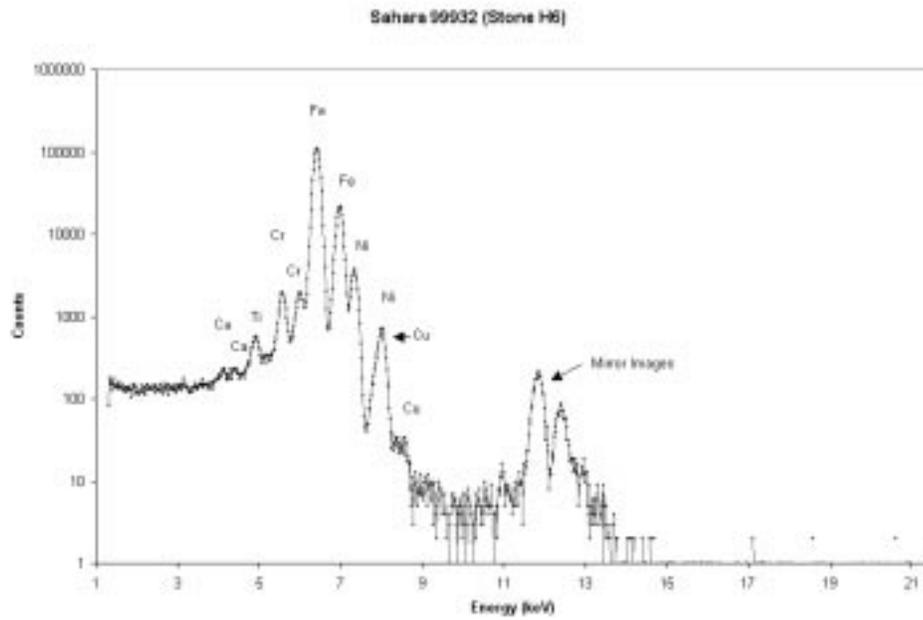
**Figure 6.** PIXE spectrum of *Broken Hill* (Stone L5) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.80  $\mu$ C.



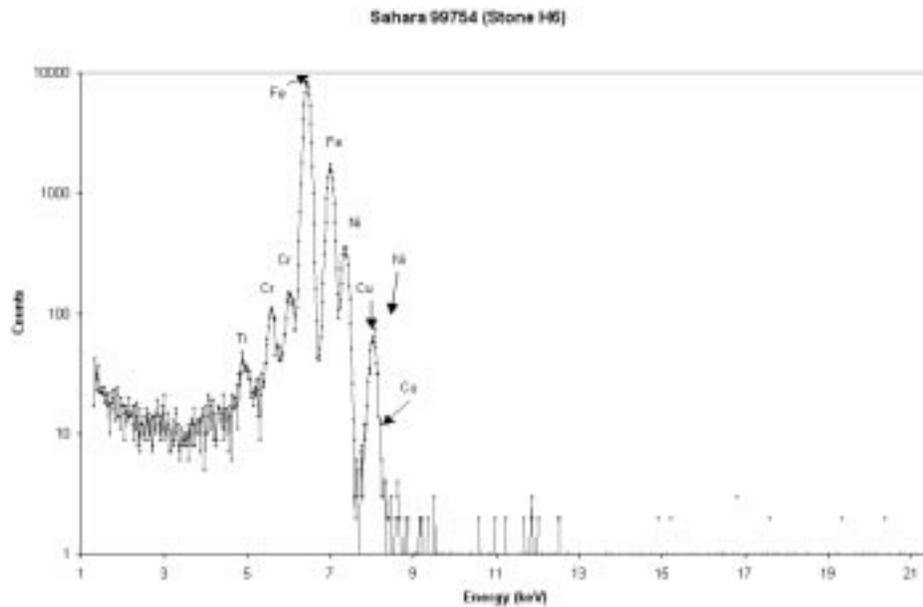
**Figure 7.** PIXE spectrum of *Saratov* (Stone L4) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.50  $\mu\text{C}$ .



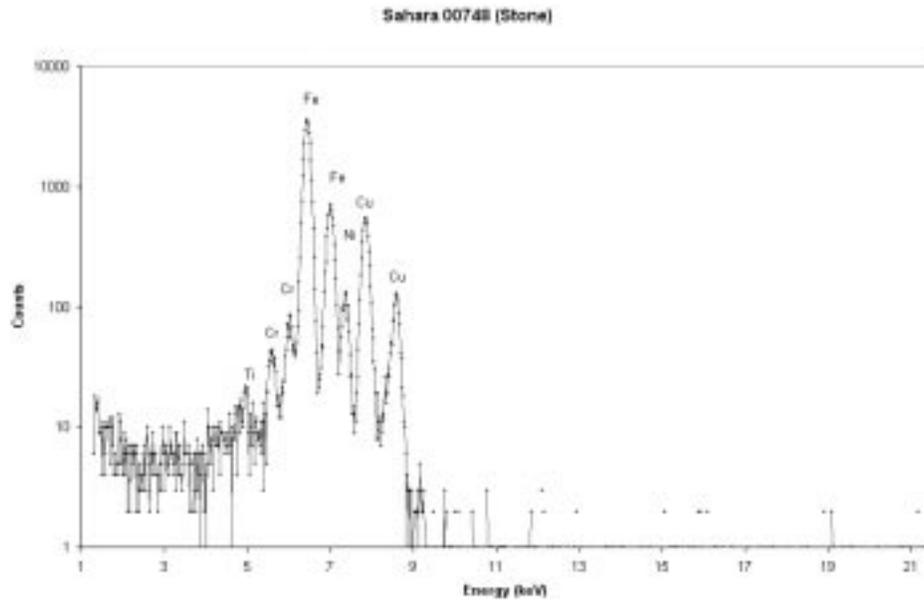
**Figure 8.** PIXE spectrum of *Sahara 99703* (Stone H6) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.08  $\mu\text{C}$ .



**Figure 9.** PIXE spectrum of *Sahara 99932* (Stone H6) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.20  $\mu\text{C}$ .



**Figure 10.** PIXE spectrum of *Sahara 99754* (Stone H6) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.05  $\mu\text{C}$ .



**Figure 11.** PIXE spectrum of *Sahara 00748* (Stone) meteorite. The irradiation time was 10 min. The total charge of the proton beam was 1.20  $\mu\text{C}$ .