

PROTON-PROBE ANALYSES OF PLANETARY MATERIALS. D.S.Woolum, Physics,
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We have built a new PIXE (proton-probe) facility at the MIT-Lincoln Lab in collaboration with Lee Grodzins(MIT), Jean Ryan(Lincoln Labs), and Rein Beeuwkes(Harvard Med School). The new features include solely-magnetic focussing of the beam and installation of a cassagrainian,optical-imaging microscope and a wavelength-dispersive Xray spectrometer. The experimental details will be reported elsewhere. Here we report a summary of the results of our preliminary experiments to assess the capabilities of quantitative PIXE analyses for samples of geological interest.

We have attempted conventional analyses { using a Si(Li) detector } of Ca- and Fe-bearing samples. The Ca-rich samples were synthesized from natural diopside, albite-anorthite glass, and reagent grade Ca-phosphate by Benjamin and Burnett in their laboratory, actinide-partitioning studies(1). The starting material was spiked with ~ 200ppm Th-232 and ~ 7 ppm Pu-239. Analyses were performed in vacuum, and 2.0 MeV protons were used. Analysis times were typically ~ 1/2hr, and a ~ 100 μ beam spot was employed. A 2 mil Al absorber was used, and deadtimes were kept to below several percent. The key factor in the use of absorbers is the relative attenuation of the lines of interest versus the major element lines to be eliminated(to minimize deadtime). In this case, the attenuation factors for Si:Ca:Th are ~ 10^{-20} : 10^{-3} :1. Figure 1 shows the $E > 4.5$ KeV portion of the Xray spectrum obtained from the quenched glass in the charge. V, Cr, Mn, Fe, Co, W, Pt, Th and Sr lines are evident, with those at the lower energies riding on the secondary-electron Bremsstrahlung background. Pu-239 was not detected due to the interference from Sr K α . The presence of Co and Pt is due to contamination from the buffer and capsule, and W is an unexpected contaminant, but the rest of the lines are due to the Th spike and the fact that natural diopside was used in the synthesis. None of these elements were detected in the routine electron-probe analyses of the charge, and in particular, upper limits for Fe and Co were 0.03 atomic % were obtained(1). Despite these low levels and the Bremsstrahlung background, their presence with PIXE is clearly detectable. We did not monitor the sample currents in this run, so detailed quantitative analyses are not possible. However, with ~ 150-200 ppm Th in the glass and a peak to background ratio of 5 for the L α _{1,2} peak, these data indicate that analyses for ~ 50 ppm Th in similar Ca-rich samples would be feasible with these running conditions and times. This corresponds to analyzing for the order of 10^{-11} grams of Th. For comparison, Burnett analyzed a duplicate sample on the Caltech electron-probe using 25KeV electrons, a 30 μ beam spot size and the crystal spectrometer to map the Th M α Xray energy region. Analysis time was comparable to the PIXE runs. There was a hint of the presence of the M α ₁ peak, but it was far from being statistically significant. Further, we estimate that for Ca-rich, Fe-poor samples, with a simple Al absorber, and ~ 100 ppm concentrations, K lines from Cr to Mo and L lines from Sm to U should be suitable for analysis, barring overlap of those lines actually obtained in the sample. Lower concentration levels would be possible for the higher energy lines, where self-absorption(by Ca) effects are small.

Fe metal poses the most extreme test of the limitations of conventional PIXE analyses in Fe-bearing systems, so we have analyzed NBS steel samples which are certified for micro-analysis. These analyses were performed in air (2,3) using a 55 μ pinhole collimator and 2 MeV protons. Typical analysis times were ~ 20 minutes. P, Si, Cr and S concentrations of meteoritic metals are of interest because predictions are available for nebular condensates and

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because, at sufficient levels, their presence can affect cooling-rate estimates. For the cases of P, Si, and S, we were unsuccessful at detecting up to several tenths of a percent of these elements; the K-Xray energies of these elements are very low, so the use of absorbers is severely constrained. The conditions for their detection preclude the use of the Si(Li) because of the high Fe count rates. In an analysis of NBS663 (with 1.3%Cr) using a 1 mil mylar absorber , we obtained a peak-to-background ratio of almost 100 for the Cr K α peak. There is 1.50% Mn and 0.31% V in this sample which elevates the minimum detection limit for Cr, but we estimate that it would be possible to analyze for ~ a few hundred ppm Cr in this sample. Somewhat lower levels would be possible for natural Fe metals. For those elements with Xray lines to the high energy side of the Fe K α peak more favorable Fe absorption can be obtained. We analyzed NBS 663 using a 4 mil Al absorber, for which ~ 5% dead-times was obtained. Here the ability to analyze for the lighter elements is sacrificed, but the situation for the higher energy lines is improved. As opposed to the 1 mil mylar run where deadtime(45%) and pile-up effects were severe, a distinct K α peak from Ni (.32%) is resolved from the Fe K β tail; the presence of Cu(980ppm), W(450 ppm), and Ta(530ppm, uncertified concentration) is also evident, with peak-to-background ratios of order 10, although accurate quantitative work would be difficult, due to overlap. The presence of Ge(100 ppm, uncertified concentration) and As (100ppm) and/or Pb(22ppm) is also indicated. (The latter two are unresolvable; fluorescence yields are comparable for the two, but ionization cross-sections are several times larger for the Pb lines.) Peak to background ratios estimated by extrapolating the high energy background are 2-3 for these lines. Based on these data, we conclude that quantitative analysis of elements in Fe metal with Xray energies $>$ 8KeV can be achieved for levels of roughly a hundred ppm or more, including Cu which suffers strong Fe-absorption. Lower levels should be possible with lower Fe contents and for lengthier analyses. Our estimates do not appear unreasonable in light of the work by the Heidelberg proton-probe group where 40-1600ppm levels of Zr, Y, and Nb in lunar illmentites were determined with somewhat lengthier analyses(4).

These experiments demonstrate some of the advantages and disadvantages of conventional PIXE analyses. The sensitivity is high and simultaneous analysis of all of the elements is possible. However, trace element analysis is precluded in cases where interferences require better than ~ 150eV energy resolution and where high Z major elements are abundant and not well-displaced to the lower energy side of the trace element lines (ie. where good relative absorption cannot be achieved.). For analyses involving these difficulties, a wavelength-dispersive detector is necessary. Analysis of only one element at a time is possible, but deadtime and pileup effects are not a problem, and the energy resolution is significantly better. We have installed a Cameca, curved-crystal, linear-drive spectrometer with LiF and PET crystals, but do not yet have on-line data analysis. Based on sin θ scans of Fe,Ni,Co, and Cu K lines and Ta L lines from meteoritic metal and elemental standards, we obtained 30-60eV FWHM peak widths. Our present energy resolution for full-peak dwell times of ~ 30 sec. is about 50eV. For example, the TaL α_1 and L α_2 (with a 10:1 intensity ratio and 58eV energy separation) were resolved. For the pure elements irradiated with 2 MeV protons at typical beam currents, typical peak intensities with the LiF are ~ 10,000 counts/sec for Fe and Cu K α , ~ 3,000counts/sec for Ta L α ; with the PET, ~ 20,000counts/sec was obtained for V. Increased beam currents or beam energies are feasible and would increase these intensities; for example a factor of ~ 3 increase would be expected with an increase of the beam energy to 2.5-3MeV. Assessing the back-

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ground midway between the $K\alpha$ and $K\beta$ peaks, peak-to-background ratios for Fe and Cu are about 1000. With the PET, we estimate the peak-to-background for V to be ~ 3000 . We are aware of only one other work(5) in which wavelength-dispersive analysis was attempted with PIXE, but no direct comparison with their data is possible. They report Cu $K\alpha$ results using a PET crystal and 2MeV protons, obtaining a peak intensity of 8250 counts/sec and a peak-to-background ratio of 5250. With a peak-to-background ratios of 1000, one would anticipate being able to detect $> 30\text{ppm}$ with 1000 sec analyses, for example, at least in ideal(matrix) circumstances. Although our peak to background ratios are respectable, we believe that we can improve them by better electronic isolation and the addition of collimators.

In summary, our estimates of PIXE sensitivities in the study of planetary materials are significantly better than for the electron probe, particularly with wavelength-dispersive analysis. However, they are less than those claims usually made for PIXE, primarily because these predictions/results are usually based on the assumption/reality of a low Z(organic) matrix. PIXE is a broad-based technique, but clearly, the problems must still be well-chosen, particularly with conventional (Si(Li)) analyses. (1) Benjamin et al.(1980) Geochim.Cosmochim.Acta 44,1251. (2) Horowitz P. & Grodzins L.(1975) Science 189, 795. (3) Horowitz et al.(1976) Science 194,1162. (4) Bosch et al.(1977) A.Physik A280,39. (5) Poole D.M. and Shaw J.L.(1969) In 5th Int. Congr.Xray Optics & Micro-analysis(eds.Mollenstedt & Gaukler; Springer Verlag, Berlin) p.319.

FIGURE 1.

