Microbeam Recoil Detection for Hydration of Minerals Studies

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ABSTRACT

The glancing angle geometry is chosen to enable application of the elastic recoil detection micro-analysis on thick geological samples, for hydrogen content determination. Simultaneous PIXE measurements can be used to eliminate the problem of uncertainties in beam charge collection. The method is applied to determine the hydration characteristics of silicates, produced experimentally at high pressure and temperature simulating the lower crust and upper mantle conditions. Preliminary results show that the technique can be applied readily on a microscopic (<100 μm) scale for determination of H at fraction of atomic percent level.

1. Introduction

Solubility of water in minerals is of fundamental importance in understanding the behaviour of melts on quenching, and thus for modelling of magma genesis and evolution. A number of techniques have been used to determine water content on macroscopic samples or as bulk analyser, for example infrared spectroscopy [1] and weight loss on ignition [2]. These methods are prone to errors when bubbles (often microscopic) are present in the sample, and are generally unsuitable when the samples themselves are microscopic, such as monomineralic constituents of natural rocks and most experimental petrological samples. Microbeam techniques such as the ion microprobe and the nuclear microprobe are can be used the water content through H determination [3]. Quantitative analysis is more readily achieved using nuclear microprobes, whereas the matrix effect in ion microprobe can be problematic. The inverse resonant reactions induced by microbeams of F19 or N15 can be used to determine H content, but the shorter range of the beam and high energy imply high energy deposit density which often results in thermal damage to the samples [4]. The forward recoil is an alternative method with generally higher cross section and thus can be carried out with low beam intensities to reduce specimen damage.

In this paper we report preliminary results of application of the forward recoil technique using microbeams of alphas to determine the H content of some experimental petrological samples. The use of simultaneous PIXE helps to eliminate some of potential problem in quantification.

2. Experimental set-up

In an elastic collision, the recoil energy \( E_r \) of the target nucleus is given by

\[
E_r = E_0 \frac{4m_1 m_2}{(m_1 + m_2)^2} \cos^2 \theta
\]

where \( m_1, m_2 \) are the incident and recoiling atomic mass, \( E_0 \) the incident energy and \( \theta \) the laboratory recoil angle. From this equation it is obvious that maximum recoil energy will be obtained for when \( m_1 = m_2 \), decreasing monotonically as with increasing \( m_1 \). For easy discrimination of incident and recoils \( m_1 \neq m_2 \), and thus for hydrogen the first practical beam will be alpha beams since the reactivity of deuterons is not desirable, and He3 is not as readily available. The formula also indicates that the smallest angle \( \theta \) the higher the recoil energy, coinciding with the cross section for Rutherford scattering. Thus the desired geometry is either a transmission geometry \( \theta = 0^\circ \) or a glancing angle as close as possible to 0°. The transmission geometry requires a thin sample to enable the recoils to be detected. For 3-4 MeV alpha beam this requires sample thickness below 20-30 microns which can be a problem if the sample has to be self supporting as well. For limited sample size this can be achieved
readily [5]. The glancing geometry presents a more convenient alternative, in terms of simpler sample preparation, although the effective depth of analysis is shallow at ~0.8-1 μm, to be compared with 2-4 μm (depending on the sample thickness) for transmission geometry for a matrix of silicates. The shallow depth requires the sample to be polished to a good surface finish (<0.1 μm), comparable to that required for electron probe analysis. To minimise the effect of surface roughness, the sample surface should not be too oblique with respect to the beam direction. In the present measurements, 3 MeV alpha beam was used and the incident and exit angle were symmetrically set at 16 deg with respect to the sample surface. This represents an acceptable compromise between the need for larger angle to minimise the effect of surface roughness and to increase effective depth of analysis, and the higher cross section for smaller recoil angles. The recoiling protons were detected in a surface barrier detector, subtending an angle of 1.2 msr at the sample, and covered with a 15 μm thick mylar foil to absorb the scattered alpha beam. The absorber attenuates the proton maximum recoil energy of 1.38 MeV to ~0.92 MeV.

The scattering cross section of alpha on protons deviates from Rutherford scattering, and is accountable in terms of phase shift analysis of the partial waves [6-8]. Extensive compilation of phase shifts for proton-alpha scattering required for cross section calculations for the regime applicable to the present work has been published [8], and tested experimentally. Enhancement over the Rutherford cross section increases with the incident alpha beam energy and decreasing recoil angles. A computer code "RECOIL" has been written, incorporating this cross section parametrised appropriately, that calculates the shape of the recoiling proton spectrum for given experimental conditions, and a uniform hydrogen distribution with depth. The hydrogen depth profile of the sample can be obtained in the first order by comparing the measured data and the calculated shape.

To test the program and calibrate the experimental geometry, polymer foils (polyethylene, kapton) were irradiated with a defocused (diameter 1.0 mm), low intensity (<0.2 nA) beam in order to prevent hydrogen loss from the sample. In addition the sample was continuously translated to further minimise this effect, with dwell time at each new spot of 5 seconds. Doubling the beam density and dwell time produced the same result, and thus it can be assumed that thermal damage and other causes of H loss were averted. Figure 1 shows the data and calculated spectrum, from polyethylene Straggling and multiple scattering effect are included in the calculation, although the effect of the latter is negligible. The dominant contribution to straggling is the absorber in front of the detector. For example the calculated Bohr's estimate for total straggling effect on protons recoiling from a silica (SiO₂) matrix is ~30 keV at the surface, increasing to ~40 keV at the maximum depth analysed (representing ~4% energy spread), which are to be compared with ~16 keV detector resolution. The mean r.m.s. spread in angle at its maximum at this depth is only ~3°, giving a mean spread in energy of <0.1%.

3. Results

The samples consist of experimental petrological trial samples, consisting of a mixture of anorthite and diopside with various amounts of water added. The mixture is sealed, and fused at high pressure (up to 10 kb) and temperature (up to 1200°C) and quenched into glass. Measuring between 0.5 - 1 mm, the samples were set in epoxy and polished. After initial trials where surface charging was found to present a severe problem in beam charge integration, a thin coating of Au (~ 10 nm) was deposited on the samples to conduct the beam charge, and also to provide additional handle on normalisation of the data through the Au X-rays (L and M lines) collected simultaneously in a Si (Li) detector. Measurements were carried out initially with low beam (<0.5 nA) to avoid the possibility of thermal damage, and later increased to 1-2 nA focused to 30 microns. A few initial runs were carried out with the beam defocused to 200 microns, with similar results.

The sample were scanned in discrete steps, starting from outside the perimeter. The PIXE spectra collected simultaneously indicate unambiguously when the beam is on the sample, through the presence of the Ca and Si (including unresolved minor components of Al and Mg) peaks (Fig. 2). Two contrasting spectra of the recoil protons are shown in Fig. 2, showing a sample with a relatively high level of H with uniform bulk distribution, and another with lower H level that enables the observation of the typical surface peak due to adsorption of moisture on the specimen surface. Several spot analyses were carried out on each sample which indicated homogeneity. In the present trial, samples
H content varies from 0.3% to 2.5%. For the higher ranges (>1%, corresponding to >9% water content), the agreement with estimates from electron probe analysis is good.

4. Conclusion
From the present measurements it can be concluded that for uniformly distributed H, a detection limit as low as 10 ppm can be obtained, corresponding to a single count in the range of 0.2-0.9 MeV, for 0.3 mm Coulomb charge, which in turn can be collected in ~5 minutes with a 1 nA beam. There is virtually no background count in this energy range. In contrast, using the inverse resonant reaction F1(p,α) at 6.417 MeV a net yield of ~5 counts is expected for 1% H content, and comparable beam charge using close to 2π sr detection geometry. But more importantly, the limit is set by the cosmic ray background, which defines a lower limit of detection at ~ 50 ppm. The forward recoil technique is thus more suitable for applications for microanalysis, where lower level of beam currents can be used.

References.

Fig.1. H recoil spectrum from polyethylene

Fig.2. PIXE spectra collected simultaneously with the recoil spectra. The microbeam was scanned across the sample. The PIXE spectrum indicates unambiguously when the beam is on sample, and is used to deduce the beam charge from the known sample major element composition (Ca in this case).

Fig.3. Recoil spectra from two of the samples, with contrasting shapes. For the sample with lower H content, the surface peak due to moisture adsorption is evident.