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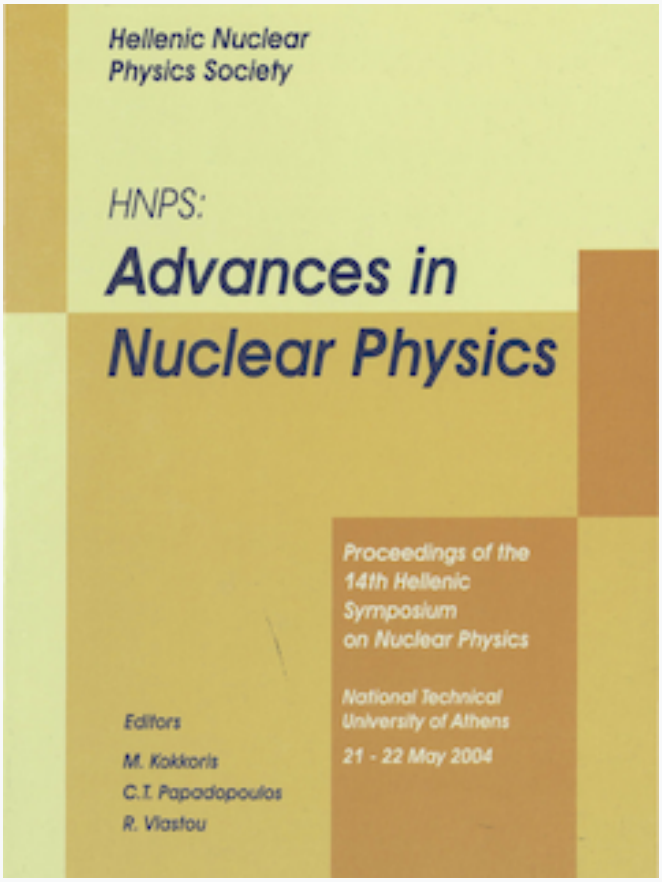

Ion Beam Analysis for the Investigation of Diffusion Processes

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Abstract

The unique advantages of ion beam analysis, such as the depth resolved unambiguous stoichometric information of RBS or the possibility to detect hydrogen with high depth resolution still opens new applications in fundamental as well as applied science. Two examples are presented here.

The diffusion of hydrogen in cement during the formation of cement has been studied with the ^{15}N hydrogen depth profiling. It could be shown, that the known stages of the hydration process are correlated with the diffusion of hydrogen on a nanometer scale.

Diffusion processes play also an important role in geology. The investigation of such processes with RBS will be presented. Prospects of diffusion studies using isotopic tracing with low lying resonances will be discussed.

1 Investigations on the hydration process of Portland cement

Though cement is the mostly used constructive material, the details of the hydration processes and its kinetics are not completely understood. From thermal analysis of the process it is known that the kinetics of the reaction are very non-linear with respect to time. The reaction starts very rapidly for a brief period of some minutes and slows down after that for some hours during which the water-cement mixture remains more or less fluid. After this so called induction period the reaction increases again rapidly and reaches its maximum after about 13 hours, a period during which the cement hardens.

Several models have been proposed to explain this behaviour most of them assuming the formation of a surface layer on the grains of the cement which initially inhibits the diffusion of the water into deeper layers. Either by change of this surface layer or the alteration of the bulk material a break through of the surface layer eventually leads to the complete hydration of the cement.

For the present measurementseveral tricalcium sulphate samples were exposed to a saturated calcium hydroxide solution in order to start the hydration process. The temperature of the hydration bath was kept to 20 ° C. After different hydration times single samples were removed and the hydration stopped by rinsing of the free water with acetone and subsequently drying the samples in vacuum [1].

The hydrogen depth profiling was performed with the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ reaction, which has a distinct, narrow and strong resonance at the ^{15}N-beam energy of 6.4 MeV. Due to the small width of the resonance the resonant reaction can take place with the beam energy set to the resonance energy only in a narrow surface region, by increasing the beam energy the resonance energy is reached after the appropriate energy loss and the region where the reaction takes place is shifted to deeper layers thus probing the hydrogen content there.

The ^{15}N beam is provided by the dynamitron tandem accelerator at the Ruhr-University in Bochum. The ^{15}N beam has an energy resolution better than 4 keV, which implies a depth resolution of better than 2 nm in the surface region, at deeper layers the resolution deteriorates to some extend due to the straggling during the energy loss process.

The beam intensities were typically 15 nA for an $^{15}N^{2+}$ beam. The reaction is observed by the 4.4 MeV γ-rays from the first excited state in ^{12}C, which were detected in a 12x12 inch NaJ(Tl) detector. This detector has a bore hole such that the samples can be placed in the centre providing a 4π geometry and a photopeak efficiency of (49 ± 3) %.

The method is illustrated in Fig 1, where for three samples the yield is plotted against the beam energy (lower axis) or the depth in the sample (upper axis). It is shown that the content can be probed to a depth of more than 2 μm, the depth resolution at the surface is in the order of a few nanometer.

In Fig 2 results are shown for one hydration process, each curve corresponding to a different duration of the hydration. It is found that during the first time of the hydration, the hydrogen is peaked mainly at the surface in a region of a few nanometer followed by a slowly decreasing diffusion tail reaching into the depth of the grains. After the induction period (here after about 1.5 h) the break down can be seen as a decreasing hydrogen content at the surface together with a changing diffusion behaviour in the depth of the material. Details of the shape of the depth profile are still under discussion; however, the data show the relation between the reaction kinetics on the macroscopic scale and the diffusion of the water on a nanometer scale.

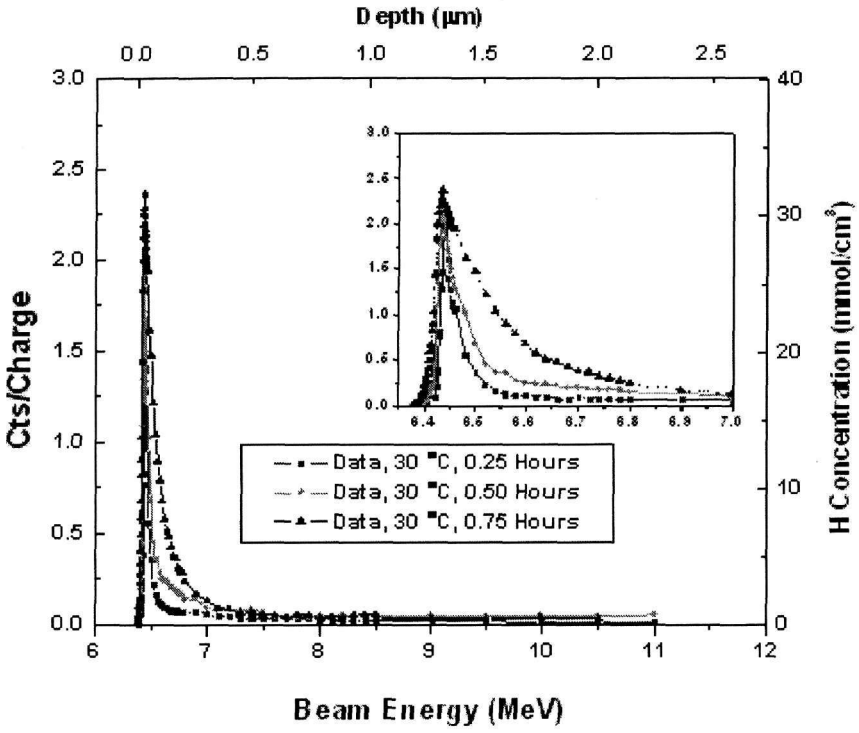

Fig. 1. Examples of hydrogen depth profiles in cement

The method employed here for the first time in the field of cement chemistry, will allow studying this processes under different conditions such as different temperatures, with technical cement mixtures and with the use of accelerators or retarders.

2 Investigation of diffusion processes in geological samples

The understanding of diffusion processes in minerals is important in geology for mainly two reasons. First diffusion can be observed in geological samples from the field, where different phases such as inclusions are present. If the kinetics of the diffusion is understood, one can obtain from those data information about the history of the sample, i.e. the age and which pressure and temperature it has been exposed to. Secondly diffusion and the plastic flow in the mantle of the earth are related [2], thus activation energies obtained from diffusion experiments are important for the creep mechanism as well.

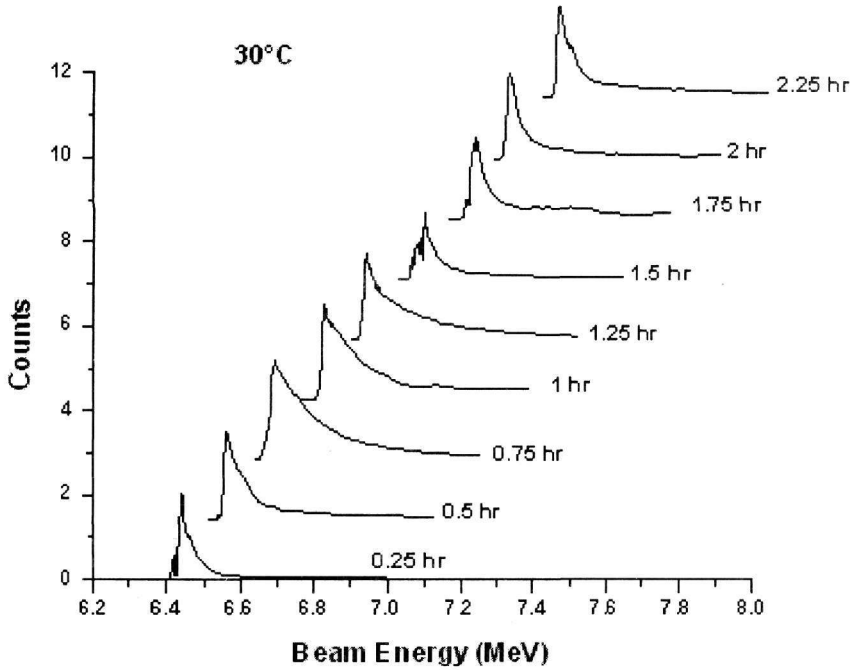

Fig. 2. Hydrogen depth profiles in different phases of the hydration process

Diffusion processes in the mantle of the earth may take place on the scale of some 100 μm in 100000 years under geological conditions, it can be observed in laboratory in reasonable time only on the scale of nanometers. Therefore a method for the preparation of thin films with the complex stoichometry of e.g. minerals is required to prepare thin samples for diffusion studies [3]. Amongst various methods the Pulsed Laser Deposition (PLD) has been proven favourable, since it conserves the stoichiometry of material to be deposited. Such a system dedicated to geological studies has been set up in Bochum.

Rutherford Backscattering Spectroscopy (RBS) has been employed to control the stoichiometry of the layers as well as to investigate the diffusion after a specific time and temperature. A He beam of 2 MeV was used and the backscattered particles are observed at an angle of 170°. Since the samples proved to be very stable, beam currents up to 50 nA could be employed to obtain good statistics in short time.

Fig. 3 shows a RBS spectrum of a 40 nm thick olivine layer ($Fe_{0,43}Mg_{1,57}SiO_4$))

deposited for test purposes onto a graphite backing. The different components of the layer can be seen clearly and their relative abundance determined in this spectrum easily.

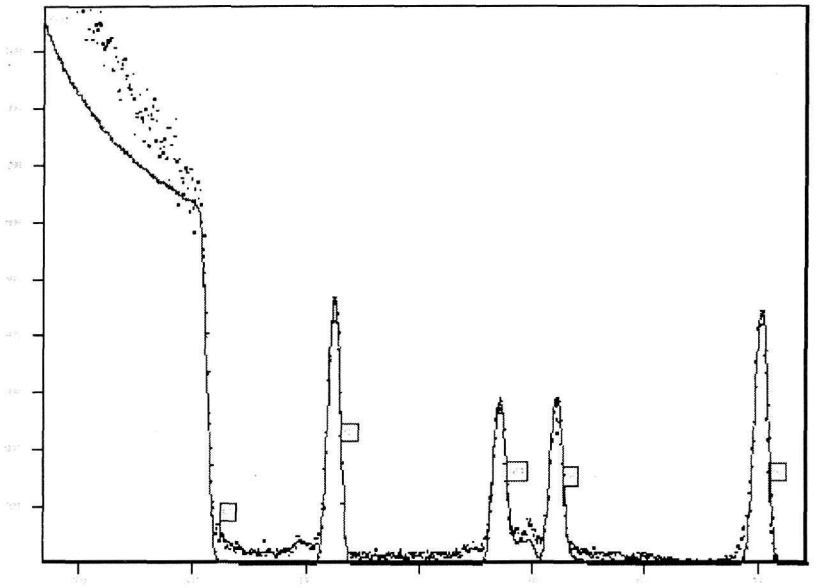

Fig. 3. RBS spectrum of an olivine layer on graphite

An analysis of a diffusion experiment is illustrated in Fig. 4. It shows the RBS spectra of an olivine layer on a bulk olivine, where the layer is enriched in Fe compared to the natural backing. The two spectra have been measured before and after an exposure to 900 ° C for 67 hours. In both spectra the edges of the O, Si, Mg and Fe can bee seen. The iron edge shows clearly the higher concentration at the surface, which is smeared out after the heat treatment. From a fit to this data and measurements at different temperatures the activation energy for the diffusion (here the Fe-Mg exchange) can be obtained.

3 Prospects for isotopic tracing experiments with resonances

In order to study the mobility of an element, which concentration can not be changed in a given compound (such as O and Si in Olivine), the self diffusion

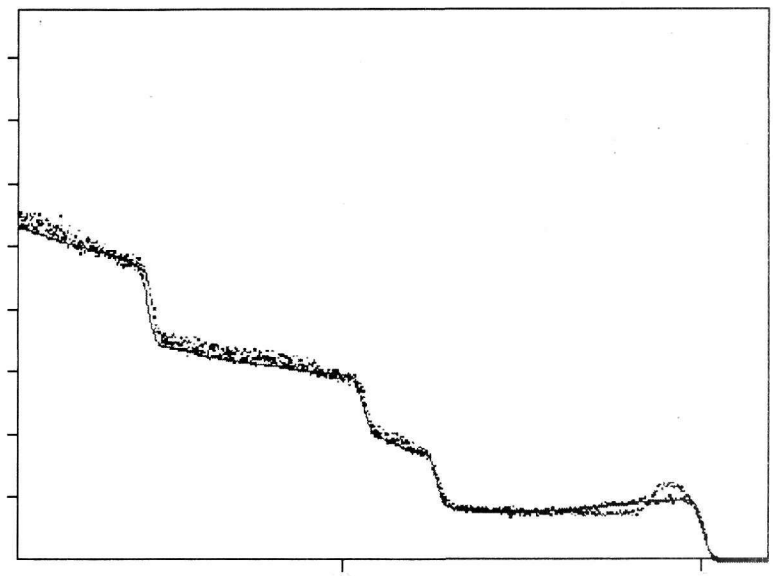

Fig. 4. RBS spectra of an olivine layer enriched in Fe on bulk olivine before and after a heat treatment

has to be studied using an isotopic tracer in the layer. The depth profiling can be done by a nuclear reaction being sensitive to the tracer isotope, similar to the hydrogen profiling described above. Several light isotopes exhibit narrow and isolated proton induced resonances in the proton energy range between 150 keV to 500 keV. The depth resolution is here large due to the high stopping power and limited by the width of the resonance, the energy resolution of the beam and the Doppler broadening due to the thermal motion of the target atoms only[4], all contributions adding quadratically to the overall energy resolution. From the experimental point of view a beam resolution of better than 50 eV is crucial for the application in geological diffusion studies.

The proton beam of the 500 keV accelerator at Bochum has been tuned to an energy spread less than 50 eV. This was checked with the E_P = 417 keV resonance in $^{29}Si(p,\gamma)^{30}P$. The beam intensity during this test was about 10 μA, a commercial Si-Wafer used as a target and the γ-rays observed with a Ge detector. Fig 5 shows an excitation curve of the resonance as a typical thick target shape superimposed by the well known Lewis-peak, which appears with this high beam energy resolution and reflects the quantised nature of the energy loss process (see references in [4]). From the leading edge, the overall resolution is estimated to be 70 eV, which is mainly due to the thermal Doppler broadening. The conversion of the energy scale into a depth scale can be

calculated by the stopping power and is indicated in Fig 3 to be about 1nm. With this excellent depth resolution diffusion experiments for several species such as O, Si and Mg will be pursued in the near future.

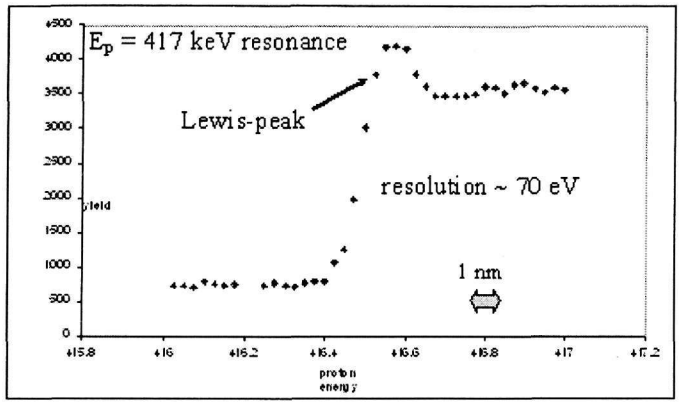

Fig. 5. Demonstration of the depth resolution with a thick target yield curve of the $^{29}Si(p,\gamma)^{30}P$ resonance

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