A mineralogical application of X-ray absorption microspectroscopy: the hydration of larnite.

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Summary. The technique of X-ray absorption microspectroscopy is described, with particular reference to the determination of calcium in a hydrogel formed in minute amounts in cavities in larnite. The method, which is applicable to other elements, enables chemical data to be obtained from selected small areas in a normal petrological thin section.

IN many mineralogical problems it is desirable to obtain chemical information from extremely limited amounts of material. The technique now to be described is useful in this respect in that chemical data may be obtained from extremely small and precisely defined volumes within normal petrological thin sections. The advantage of studying chemical composition, at high resolution, within the fabric of a thin section will be apparent.

In the present paper the technique of X-ray absorption microspectroscopy is described and its usefulness illustrated in one particular case. This concerns the determination of the calcium content of a hydrogel formed in microscopic amount from the mineral larnite (β-Ca_2SiO_4) in small, sealed hydration cavities in larnite-bearing rocks where the cavities also contain calcium hydroxide (portlandite).

The present paper deals only with the determination of calcium. The technique can in practice be applied to the determination of other elements of higher atomic number.

Theory and method. The measurement of X-ray absorption at selected wavelengths provides an accurate method of determining the mass of an element present in a material of known thickness. A development of this method, using the fine focus X-ray tube devised by Cosslett and Nixon (1953), permits the analysis of small selected areas in a thin section without recourse to photographic recording (Long and Cosslett

1957; Long, 1958). In fig. 1 the transmission of an element is shown plotted against wavelength in the neighbourhood of an absorption edge. The abrupt change in transmission at the wavelength of the edge does not occur in the corresponding transmission curve for other elements that may be present. Hence the ratio of the transmissions of the whole material at λ_1 and λ_2 immediately provides information on the mass of the element present, with only a small error due to the matrix, particularly if λ_1 and λ_2 lie close to the absorption edge.

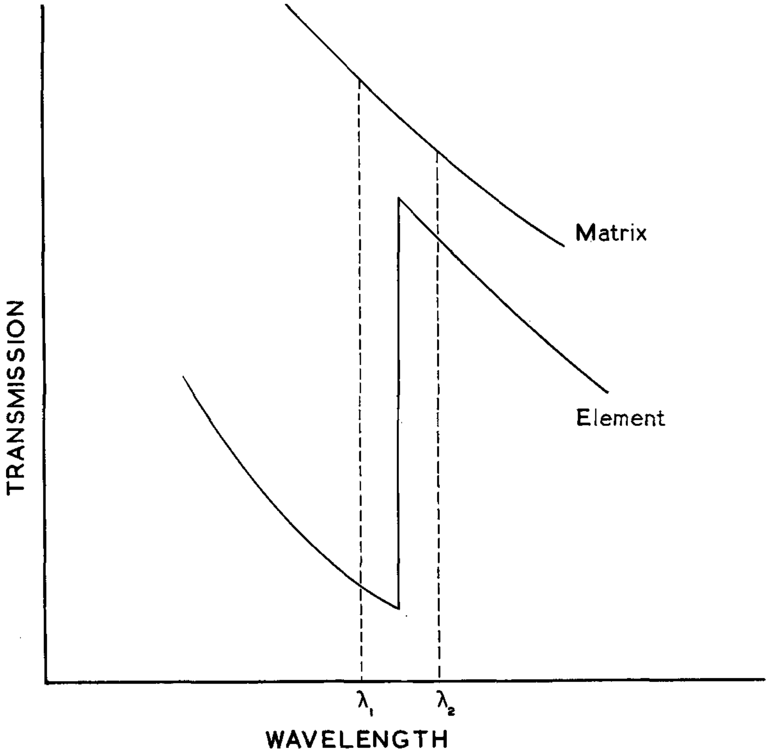

FIG. 1. Transmission of element and matrix in the neighbourhood of the absorption edge.

In the present investigation the composition of the matrix could be estimated approximately, and the error due to its presence reduced to negligible proportions.

The transmission of any material is given by the equation:

$$I/I_0 = T = e^{-m\mu/\rho},$$

where μ/ρ is the mass absorption coefficient, m the mass per sq. cm. of the absorber. If this equation is written for the wavelengths λ_1 and λ_2 both for the element and the matrix the following relationship may be derived:

$$\frac{T_1}{T_2} = e^{-m[(\mu/\rho)_{\lambda_1}-(\mu/\rho)]_{\lambda_2}-m'[(\mu/\rho)'_{\lambda_1}-(\mu/\rho)'_{\lambda_2}]},$$

where T_1 and T_2 are the transmissions at wavelengths λ_1 and λ_2, m is the mass per sq. cm. of the element and m' the mass per sq. cm. of the matrix; $(\mu/\rho)_{\lambda_1}$, and $(\mu/\rho)_{\lambda_2}$ are the mass absorption coefficients of the element at λ_1 and λ_2 and $(\mu/\rho)'_{\lambda_1}$ and $(\mu/\rho)'_{\lambda_2}$ are the corresponding coefficients for the matrix material. In order to determine T_1/T_2 for areas only a few microns in diameter, Engström and others (Engström, 1946; Lindström, 1955) have made contact microradiographs on high resolution film of the Lippmann type, and have measured the density of small selected areas of the developed image with a microphotometer. In the present experiments a point projection method and direct electrical recording have been used.

The geometrical arrangement of the apparatus is shown in figs. 2 and 3. The X-ray tube consists of an electron gun and a magnetic lens, which focuses the electron beam to an area about one micron in diameter on a thin metal foil that forms both the target and the window of the X-ray tube. The X-ray source is thus about 1 μ in diameter, and, since the foil is only a few microns thick, the target to specimen distance t may be made very small in order that a high magnification may be obtained in the image recorded by a fluorescent screen or photographic plate placed a few centimetres from the target. The resolution in the image is equal to the source size, i.e. approximately 1 μ. If a circular aperture of diameter d is placed in a plane at distance D from the target, as indicated in fig. 3, it will pass radiation that has come through a circular area of diameter td/D in the specimen. In the arrangement used for the calcium determination, $d = 3$ mm., $t = 0{\cdot}5$ mm. and $D = 150$ mm. so that the area examined was 10 μ in diameter. The spectrometer crystal, placed above the aperture, selects the appropriate wavelengths from the continuous spectrum generated by the target, and their intensity is measured with a proportional counter.

In order to position the specimen so that the X-rays passing through a particular 10 μ area also pass through the aperture, a fluorescent screen is placed in a plane about 2·5 cm. above the target and accurately located in such a position that a marked point on its surface, the X-ray source, and the centre of the aperture are in the same straight line. Since the X-ray contrast of many thin sections is insufficient to show detail on a fluorescent screen, an electron microscope grid is placed over the section. These grids have accurately formed squares of approximately 90 μ side, so that after locating an area in the specimen by means of an optical microscope, the same area may be identified on the fluorescent screen by reference to the easily visible X-ray image of the grid, which with the screen at a distance of 2·5 cm. from the target is seen at a magnification of 50 times. By moving the specimen stage the required area may be brought on to the marked point on the screen, so that, when the screen is removed, the X-rays passing through this area also pass into the aperture of the spectrometer.

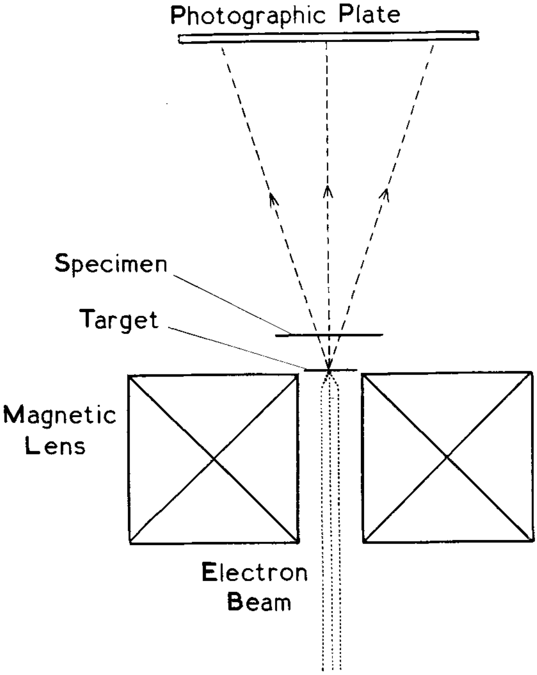

FIG. 2. The geometry of the X-ray projection microscope.

The spectrometer crystal is arranged to alternate, eight times a minute, between two fixed angular positions corresponding to the wavelengths λ_1 and λ_2. A relay, operated synchronously with the solenoid controlling the position of the crystal, transmits the pulses from the proportional counter, through an amplifier and pulse height analyser, to two separate scaling units. Thus at the end of a measurement, two

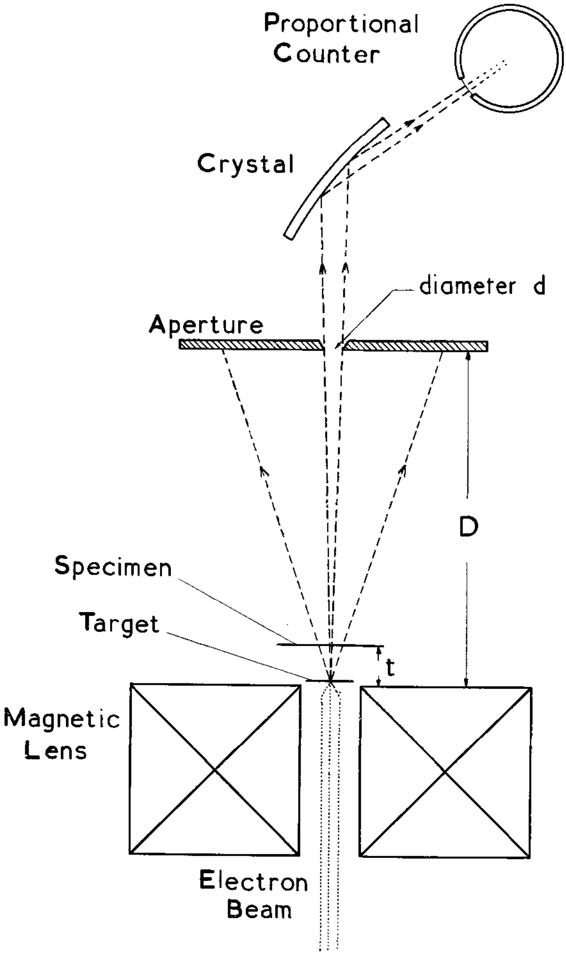

FIG. 3. Arrangement of point focus tube for microanalysis.

totals are obtained which represent the transmitted intensities at λ_1 and λ_2 respectively. In this way it is possible to measure the comparatively low count rates involved for periods of the order of half an hour without introducing errors due to drifts in the primary intensity from the X-ray tube. The ratio of the count rates at the two wavelengths is also measured with no specimen in the beam in order to obtain the final ratio T_1/T_2 for the specimen. The ratio with no absorber present remains constant to about ±1 %. It was always recorded for a short period before and after each measurement on a thin section.

For calcium the wavelength of the absorption edge is 3·07 Å., and 3·14 and 3·00 Å. were chosen for λ_1 and λ_2. In order to generate sufficient intensity in this part of the continuous spectrum, the X-ray tube was run at 25 kV with a target current of 10 microamps. For a 2 μ spot this gives a specific loading of 80 kW per sq. mm. Under these conditions the spectrum from the target (12 μ aluminium foil) contains a considerable intensity of continuous radiation whose wavelength is much shorter than 3 Å. It was found that the spectrometer crystal did not completely monochromatize the beam transmitted through the specimen. As a result of reflection of harmonics of the 3 Å. band, and of a small amount of Compton scattering that occurred at the monochromator, the measured calcium thickness was always slightly lower than the true value. The extent of the deficiency was determined by measuring the apparent thickness of calcium in the steps at the edge of a cleavage flake of gypsum, the true thickness of each step being measured subsequently on a polarizing microscope with the aid of a Berek compensator.

When monochromatization is incomplete the transmission ratio may be derived from an equation of the form:

$$(T_1/T_2)' = (T_{3\cdot 14}+f.T_\lambda)/(T_{3\cdot 00}+f.T_\lambda),$$

where $T_{3\cdot 14}$ and $T_{3\cdot 00}$ are the transmissions of a calcium compound at 3·14 and 3·00 Å. respectively. The intensity of the impurity radiation is expressed as f, the number of impurity quanta per 3 Å. quantum. Its effective wavelength is λ and T_λ is the transmission of the specimen for this wavelength. In the present experiments λ was found to be 1·56 Å. and f was 0·0139.

The values of T_1/T_2 calculated from the above equation were then found to agree with the measured values to within about ±2 % for thicknesses of gypsum up to 50 μ. In the case of thick specimens of gypsum the effects of imperfect monochromatization are much greater than is the case for the thin sections of the natural calcium silicate minerals studied, since these contain a higher proportion of calcium, which in turn is associated with a matrix of lower absorption coefficient than the sulphate of the gypsum molecule.

The transmission ratio $(T_1/T_2)'$ may thus be calculated for any calcium compound and the curves for different compounds may be plotted on the same graph if the thickness is expressed in terms of the mass of calcium per unit area. The calculated X-ray transmission relationships for the two minerals afwillite ($3CaO.2SiO_2.3H_2O$) and larnite are shown in fig. 4; this illustrates the very small effect of the matrix on the transmission ratio since the afwillite and larnite curves are almost coincident despite the very different calcium to silicon ratios. In practice the afwillite curve was used for the calcium silicate hydrogel studied. This is reasonable in view of the very small divergence of the larnite and afwillite curves.

Study of the natural hydrogel. The thin section was prepared for examination in the following manner: A suitable area was photographed and the areas to be analysed were carefully marked on the photograph. The coverslip was then removed and the section transferred from the slide to a thin aluminium disk provided with a central hole about 4 mm. in diameter, over which the area of interest was located. An electron microscope grid was then stuck over this area and the precise co-ordinates of the points to be examined determined with respect to the grid squares. It was necessary, at this stage, to refer back to the original photomicrograph. As already noted the positioning of the specimen in the X-ray beam was accomplished by observing the magnified image of the electron microscope grid on a fluorescent screen.

A photomicrograph of the hydration cavity studied in the present series of experiments is illustrated in fig. 5. The infilled cavity contains afwillite and portlandite and is surrounded by a narrow zone in which the larnite has been hydrated. The width of this narrow sheath is of the order of 150 μ. The determinations of the calcium content in the sheath of hydrogel and the larnite were carried out at specific points within the grid square whose position has been illustrated in the photomicrograph. Each single determination was carried out on an area of approximately one-hundredth of the figured grid square involving in the case of the hydrogel a mass of approximately 10^{-9} g. of calcium in the individual determinations.

Previous work has shown that the calcium oxide : silica ratio of calcium silicate hydrogels prepared in the laboratory at ordinary temperatures varies systematically with the calcium hydroxide content of the solutions involved. The effective limits of variation in the range where the hydrogels yield X-ray powder data indicating structural affinity with the calcium silicate hydrate mineral tobermorite are 0·8:1 and 1·5:1. The latter ratio is obtained in solutions saturated with calcium hydroxide.

In an earlier communication (McConnell, 1955) an account was presented of the hydration of natural β-Ca_2SiO_4 and the formation of a

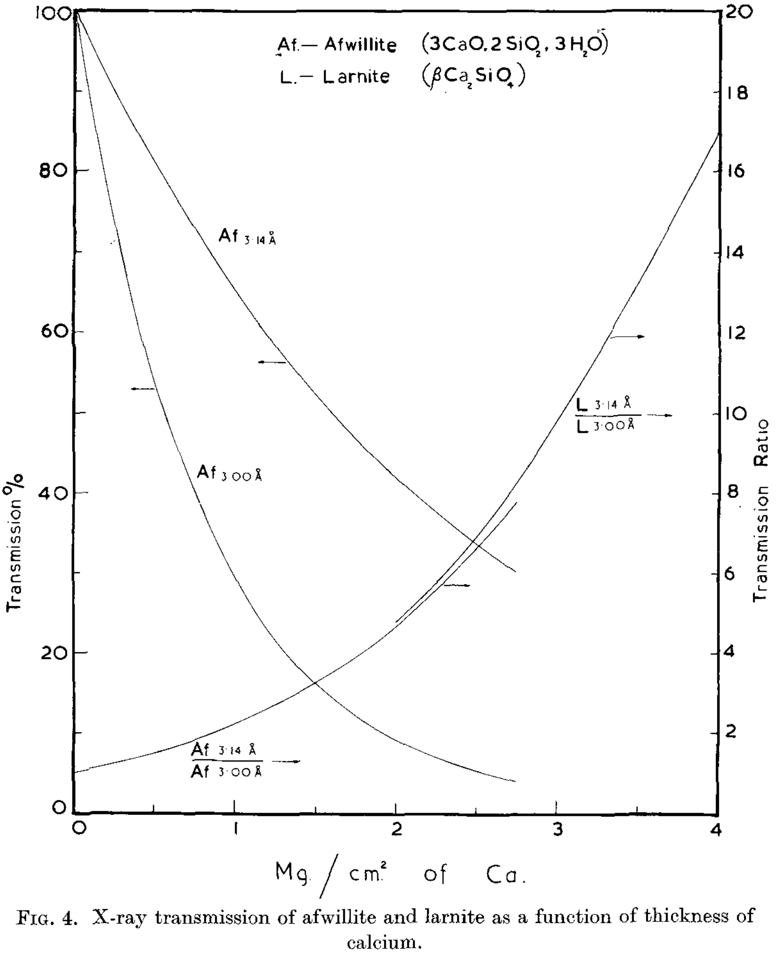

FIG. 4. X-ray transmission of afwillite and larnite as a function of thickness of calcium.

calcium silicate hydrogel corresponding in composition to the low-lime end of the above hydrogel series. The analysed specimens were taken from an environment in which the presence of circulating ground water of low pH was probable. An unpublished and more recent study of the microstructure of the low-lime hydrogel formed from bredigite, by the same author, involving low-angle scattering experiments, and a more detailed analysis of the adsorption isotherm of the low-lime hydrogel indicated that the latter has a lamellar pore structure and comprises extremely imperfect crystalline sheets possibly one unit cell or less in thickness. These imperfect sheets are irregularly stacked but the preferred orientation (already noted, McConnell, 1955, p. 675) implies that they have developed by a process of topochemical reaction from the parent dicalcium silicate structure.

The pore structure observed in the low-lime hydrogel can only reasonably be explained in terms of the former production, at higher pH values, of a defect topochemical product of higher calcium content, the additional lime being present as calcium hydroxide intimately associated with the sheet silicate structure. In order to test this hypothesis it was necessary to determine the calcium content of the natural hydrogel where the latter had been produced and maintained in contact with solutions saturated with calcium hydroxide. This condition was considered to obtain in some of the smallest infilled hydration cavities in the larnite rocks at Ballycraigy, where, as illustrated in fig. 5, the centre of the cavity has been filled with portlandite and afwillite and the complete absence of carbonate implies that the cavity has, in effect, been sealed off from circulating ground water.

The equilibrium conditions illustrated by these cavities are of interest. The hydrogel formed by a process of topochemical reaction from larnite appears to represent a metastable equilibrium assemblage. The existence of afwillite and portlandite within the cavity represents crystallization of a stable equilibrium assemblage. It would appear that at the temperatures and pressure involved in the natural hydration process no dicalcium silicate hydrate phase is stable.

The results of the absorption microanalyses within the grid square outlined in fig. 5 are set out in table I. The values obtained for the larnite are consistent and provide immediate information on the thickness of the thin section. The last value for larnite was obtained at a point on the side of the cavity opposite that at which the other measurements were made. It indicates that although the section varies in thickness by about 10 % over the width of the cavity, any systematic change within the grid square will be negligible. The figures for the calcium content of the hydrogel present in the same grid square are based on the calculated ratio curve for afwillite illustrated in fig. 4.

A preliminary calculation indicated that the calcium content of the analysed low-lime hydrogel should be of the order of 0·9–1·0 mg./cm.^{2} in a section 20 μ thick. These limits were defined by the variable density of the low-lime hydrogels studied. Considerably higher values for the calcium content were obtained for the hydrogel within the figured grid square as indicated in table I. These recorded values are consistent with a $CaO:SiO_2$ ratio for the gel of the order of 1·5. Table I illustrates one difficulty in the determination of the calcium content of the hydrogel.

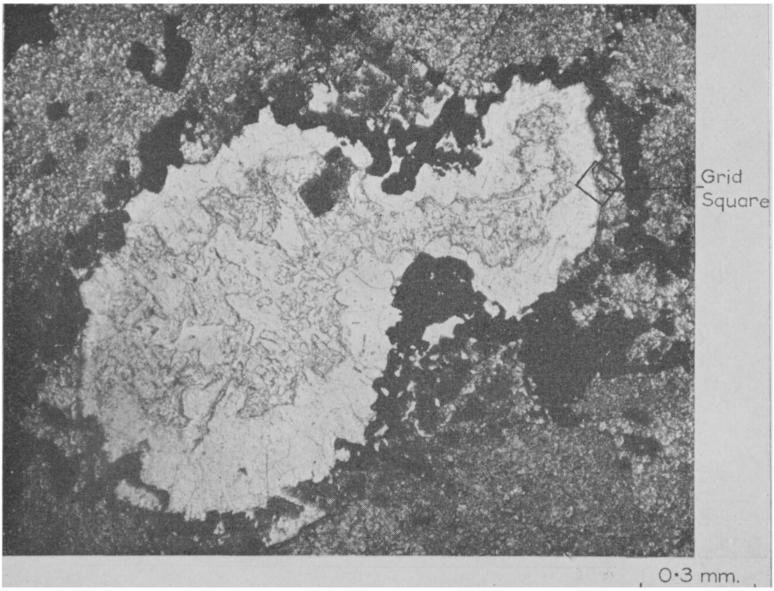

FIG. 5. A small infilled cavity in larnite-spinel rock from Ballycraigy, Co. Antrim, showing calcium silicate hydrogel, afwillite, and portlandite.

Since the gel is extremely brittle, irregularities in its surfaces and the presence of cracks imply that the calcium contents determined must be regarded as minimum values. In table I the values of calcium content that are low have been marked with an asterisk. The corresponding areas were shown to correspond with the position of a crack in the thin section by taking a high resolution microradiograph of the area. This source of error is unlikely to be of importance in carefully ground thin sections of normal minerals.

The interest of the present determination lies in the recognition of a primary stage in the topochemical hydration reaction of natural β-Ca_2SiO_4 involving a defect phase of high lime content. Further study of the precise mechanism of this hydration reaction is of importance in that the mechanism can with reasonable certainty be applied to the

TABLE I.

	A.	B.	C.
Larnite	9·61	2·97	—
Larnite	9·43	2·94	—
Larnite	9·82	3·00	—
Larnite	9·53	2·96	—
Larnite	9·36	2·93	—
Hydrogel	3·57	1·62	1·66
Hydrogel	3·89	1·75	1·79
Hydrogel	3·31	1·46	1·50
Hydrogel	3·74	1·61	1·65
Hydrogel	3·17	1·41	1·47*
Hydrogel	2·10	0·90	0·92*
Larnite	10·60	3·12	—

A. Corrected ratio of transmissions.

B. Calcium content expressed as mg./cm.^{2} in the thin section studied.

C. Calcium content of the hydrogel stated in mg./cm.^{2} in a thin section of thickness 20μ. (The thickness of the section studied was found to be 19·6μ from the average of determinations made on the larnite present.)

* In these determinations the low values were correlated with the presence of a crack in the thin section.

hydration of cement clinker particles of β-Ca_2SiO_4. The extremely slow rate of hydration has so far prevented study of this process on grains of β-Ca_2SiO_4 in the laboratory. A more detailed account of the microstructure of the hydrogels formed and the mechanism of the topochemical hydration reaction will be presented elsewhere.

References.

COSSLETT (V. E.) and NIXON (W. C.), 1953. Brit. Journ. Appl. Phys., vol. 24, p. 616.

ENGSTRÖM (A.), 1946. Acta Radiol., Suppl. 63.

LINDSTRÖM (B.), 1955. Ibid., Suppl. 125.

LONG (J. V. P.), 1958. Journ. Sci. Instr., vol. 35, p. 323.

—— and COSSLETT, (V. E.), 1957. 'X-ray Microscopy and Microradiography', Academic Press, N.Y., p. 435.

MCCONNELL (J. D. C.), 1955. Min. Mag., vol. 30, p. 672.