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EDITED BY
A. C. D. NEWMAN



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CHEMISTRY OF CLAYS
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Preface

The monograph series published by the Mineralogical Society has until now been concerned mainly with the application of techniques like X-ray diffraction, thermal analysis, infrared spectroscopy and electron optical methods to the identification and study of clay minerals. Inevitably much information about the chemical constitution was contained within these volumes and was essential to them. However, it seemed that there was also a need for a monograph that contained all this information in one volume and also covered some wider aspects of clay chemistry such as their colloid behaviour and surface chemistry, their reactions with organic substances and to heating, and the chemical conditions necessary for their formation.

These were the views of the Committee of the Clay Minerals Group of the Mineralogical Society that initiated over fifteen years ago the production of a monograph on the chemistry of clays. It is perhaps unfortunate that owing to a succession of unforeseen circumstances, its publication has been delayed until now. Sadly two of the original contributors have died in the intervening period: W. T. Granquist in 1974, and the death of G. W. Brindley, for long associated with clay minerals and with the monograph series, in 1983, is still fresh in our memories. Despite these regrets about the long gestation of this monograph, a bonus is that many advances in knowledge from recent studies have been included now that were missing from earlier drafts, and it is hoped that in its present form, the monograph will be a valid source of information about clays for many years to come.

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A. C. D. NEWMAN

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Chapter 1

The Chemical Constitution of Clays

A. C. D. NEWMAN and G. BROWN

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1.1 INTRODUCTION

Chemical analysis was an early and essential step in establishing the nature of minerals but the chemical composition of silicates is so complex that a satisfactory systematic classification was not formulated until the spacial arrangement of the atoms was revealed by X-ray diffraction studies. This application of X-ray diffraction led to an enormous increase in our knowledge of the nature of clay minerals and has helped us to understand how important chemical composition is in determining their structure and properties. As a consequence, establishing the chemical constitution of a clay mineral remains as important today as ever it was in its mineralogical description. We now know that relatively small differences in the chemical composition of clays can greatly influence their chemical and physical properties and measuring these differences may be quite demanding on analytical techniques.

In this chapter, as an introduction to the monograph, we survey the chemical constitution of the various types of layer silicates and clay minerals in particular. The non-silicate clays, the oxides of Fe, Al, Mn and Ti are reviewed in Chapter 2.

Clay minerals are essentially hydrous aluminosilicates but magnesium and iron substitute aluminium in varying degrees, and alkali and alkaline earth elements can also be essential constituents. Hydrogen is usually present as hydroxyl in the structure and as water both within the structure and sorbed on the surface. These substitutions cause wide diversity in chemical composition within the broad general class of phyllosilicates or layer silicates to which the clay minerals belong.

Within this class, phyllosilicate minerals are subdivided, by international agreement (Bailey 1980a), into a number of groups and subgroups according to their structure and chemical constitution. Structural details of the phyllosilicates are described by Bailey (1980b), but here we

are concerned with expressing the chemical composition of the clay minerals on a structural basis, and the simplest way to do this is in terms of their structural formulae. Therefore, after a brief summary of methods used to analyse clays and to calculate structural formulae from the analysis, we describe the variations in the chemical constitution of the clay minerals by their groups and subgroups. However, it is becoming increasingly evident that a number of clay minerals do not have exactly the ideal anion framework listed, and several instances of this (e.g. antigorite, Section 1.14.2) will be noted.

1.2 ELEMENTAL ANALYSIS OF CLAYS

In general the techniques used in rock and silicate analysis may be used with only minor modifications for clays; indeed, because of the small particle size, the preparation of a matrix for analysis (solution, glass, pressed pellet, etc.) may be easier with clays than with coarser grained samples. However when the aim of the chemical analysis is to calculate a structural formula and to determine the distribution of cations in several structural sites, good accuracy is required and only certain analytical methods are capable of the standard necessary.

The chemical elements in the matrix can be determined by chemical analysis, by analysis based on the physical properties of the elements, or by judicious combination of both. Gravimetric and volumetric chemical determinations were the basis of the "classical" schemes (Washington 1918, Hillebrand 1919) of analysis, but with the development of commercial instruments capable of precise measurements, physical methods now often replace the traditional chemical ones. Although it is probably misleading to quote "best" methods, each element has a chemical and physical individuality that can be used to advantage in analysis. For example, the older chemical methods for determining the alkali metals are now superseded by flame emission or absorption methods, but only the heavier metals in the group, K, Rb and Cs, are advantageously determined by X-ray spectroscopy. The final choice of the method to be used depends upon the concentration of element in the sample, the accuracy required, the instruments and time available, and to some extent the individual ability of the analyst, although to obtain accurate analyses, much skill and care is necessary no matter which methods are used.

It is not possible within the space of the present chapter to give detailed analytical procedures; moreover the techniques of classical chemical analysis are described in many texts, and recent publications are available for the modern instrumental methods. The book by Maxwell (1968) is comprehensive; that by Jeffery (1970) has a bias towards colorimetric methods and describes procedures for many minor constituents as well as the major elements, whereas Volborth (1969) emphasizes the value of traditional methods when used with modern methods of separation, and also includes a useful introduction to neutron activation analysis, currently the most satisfactory method of determining oxygen, the neglected element in silicate analysis.

1.2.1 Chemical analysis schemes

In most traditional silicate analysis, the aim was to account for the total composition of the sample so that when each elemental determination was expressed as the percentage of oxide present, the sum totalled close to 100%. It was generally found that to achieve this total it was necessary at the very least to make the following determinations: Si, Al, Fe^{3+} , Fe^{2+} , Ti, Mn, Mg, Ca, Na, K, P and water evolved below 105°C (H_2O^-) and between 105 and 1000°C (H_2O^+).

For some minerals, additional determinations (e.g. of F, Li and less common elements) were needed to complete the total satisfactorily.

In the *classical analysis scheme*, most of the determinations were done on solutions prepared after fusing the sample with Na_2CO_3 , using predominantly gravimetric and volumetric procedures. Further samples were required for determining F, H_2O , alkali metals and Fe^{2+} . The methods were accurate when done by experienced analysts but were slow, so that the introduction of *rapid analysis schemes*, based mainly on colorimetric determinations, was widely adopted in the 1960s. At the same time, however, instrumental methods of analysis were developing rapidly and a survey of clay mineral literature for the period 1982–1984 revealed that few analyses are now done by chemical methods. The determination of F, H_2O^+ and H_2O^- , and Fe^{2+} , however, is still done chemically, unless the instrumental methods for them are available. The following sections outline the main features of these determinations.

1.2.1.1 Determination of Fe^{2+}

Schafer (1966) and Hey (1982) have reviewed the many methods proposed for determining Fe^{2+} in silicates. They are grouped according to the initial decomposition stage: (a) acid decomposition in a sealed tube; (b) acid decomposition in an inert atmosphere; (c) acid decomposition in the presence of an oxidant; (d) fusion in a sealed tube. Method (d) is useful for resistant minerals; method (c) is attractive in principle but in practice some additional decomposition of the oxidant usually seems to occur during the mineral dissolution, causing large blanks. The method most widely used is decomposition with acid, usually hydrofluoric acid, air being excluded by boiling the reactants in a closed vessel or by displacement with nitrogen or carbon dioxide. Aerial oxidation of Fe^{2+} is accelerated in the presence of fluoride, so that it is usual to complex fluoride immediately after the decomposition by adding boric acid. Dichromate solution is then added and the excess reagent titrated with standard Fe^{2+} solution using diphenylamine sulphonate indicator. References for this and other methods of determining Fe^{2+} in the digest solutions are given in the articles cited above.

With the increasing availability of the instrument, $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios are sometimes determined by Mossbauer spectrometry (Goodman 1981), and this technique also offers the possibility of determining whether Fe is present in octahedral or tetrahedral sites.

1.2.1.2 Determination of hydrogen

Hydrogen is present in clays as water and as structural hydroxyl groups, and also combined with organic compounds and ammonium cations if these are present. Molecular hydrogen may be evolved when minerals are heated, particularly in a non-oxidizing environment, but this is formed by a reaction between ferrous iron and structural hydroxyl; the percentage of hydrogen gas in clay minerals is normally very small. The major problem in determining hydrogen in clay minerals is in distinguishing between the several categories of hydrogen that make up the total.

Total hydrogen is determined by heating the mineral in an oxidizing atmosphere and weighing the water evolved. Modifications of the Penfield method (Shapiro and Brannock 1955; Wilson 1962) are quite often used and are quick, but the relatively low temperatures attainable in a gas flame may be insufficient to ensure complete dehydroxylation; the results from these methods can at best be regarded as approximate. More accurate is the closed-circuit circulation system devised by Jeffery and Wilson (1960), in which water collection is more efficient and closer temperature control is possible. Temperatures above 900°C are required to drive off all structural hydrogen from magnesium chlorites, serpentines and vermiculites; phlogopites may

be heated at 1000 °C for several hours with very little decomposition. At these high temperatures other constituents such as fluorine compounds are volatile and retained in the absorption tube (El-Attar *et al.* 1972), so that in the determination of total water in refractory minerals there can be a balance between positive and negative errors. Sodium tungstate is often recommended as a flux to facilitate decomposition but as the evolution of non-aqueous volatiles is also accelerated, “retainers” must be included as well: Groves (1937) suggests covering the sample with freshly ignited quicklime to absorb fluorine. Because of the relative volatility of lead fluoride, the use of litharge in the flux seems undesirable.

If the hydrogen determination is required for recalculating the chemical composition of a mineral as a structural formula, the surface-adsorbed and hydration water must be determined separately so that the structural hydrogen may be found by difference from the total hydrogen. In the traditional analysis scheme, the hygroscopic moisture is frequently determined by oven drying in a weighing bottle at 105 or 110 °C; the weight loss after cooling is termed $H_2O - 105$ or H_2O^- , and the difference between this weight and the total water, H_2O^+ .

With clay minerals this procedure is unsatisfactory for two reasons. First, many clays are exceedingly hygroscopic after drying and resorb water so quickly that an accurate dried weight cannot be obtained in this way; one of the gas circulation methods proposed by Jeffery and Wilson (1960) should be used instead. A very convenient method of determining hygroscopic and structural water on the same sample, termed “thermohygroscopy” by Creer *et al.* (1971), measures evolved water continuously as a function of temperature.

The second more fundamental objection to any procedure is that the evolution of hydration water from many clay minerals is far from complete at 110 °C. For example, Fripiat *et al.* (1960) showed that water was still present in montmorillonites and vermiculites at 300 °C, and a vermiculite derived from a phlogopite containing 6% F retained molecular water up to nearly 600 °C (Newman 1967). In these investigations, the infrared adsorption in the region 1650 cm^{-1} , attributed to the angular deformation vibration of molecular water, was used as an indicator of water present; structural hydrogen in the form of hydroxyl does not absorb in this spectral region. Therefore infrared absorption can be used to determine the minimum temperature necessary to release all molecular water, and water evolved in heating beyond this temperature, measured by adsorption in a desiccant tube, is structural hydrogen. With some minerals, however, the dehydration and dehydroxylation temperature ranges overlap, and for these a satisfactory separation of hydration water and structural hydrogen cannot at present be achieved by thermal analysis.

1.3.1.3 Determination of fluorine

Most methods of determining fluorine are subject to interference from elements common in silicates, so that after decomposition by fusion, a separation of fluorine from these constituents is necessary. Often this was done by distillation from concentrated acid at 140–160 °C (Willard and Winter 1933); accurate control of the conditions is essential (Ingamells 1962) but recovery of fluorine is sometimes incomplete (Peck and Smith 1964; Evans and Sergeant 1967) and the analysis is time consuming. Hydrolysis at 600–800 °C by moist carrier gas in the presence of a catalytic flux (“pyrohydrolysis”; Nardozzi and Lewis 1961) is an attractive alternative because preliminary fusion is unnecessary and the separation is complete in 15–30 minutes (Newman 1968; Jeffery 1970; Clements *et al.* 1971). For best decomposition of the silicate and evolution of HF, a mixed flux of vanadium pentoxide, bismuth trioxide and tungstic oxide has been recommended. The hydrolysate is collected in dilute alkali and fluoride determined by titration or by a colorimetric method; these are described in the references quoted.

Methods have been described for determining fluorine without distillation (Huang and Johns 1967; Ingram 1970); as these require a preliminary fusion they appear to offer little advantage over pyrohydrolysis. Ingram determined fluorine electrometrically with the fluoride-selective Eu^{2+} -lanthanum fluoride electrode (Lingane 1967); the excellence of this electrode suggests that it could be used to best advantage in determining F in the condensate from pyrohydrolysis.

1.2.2 Instrumental methods of analysis

Measurement of the electromagnetic radiation absorbed or emitted when atoms or molecules undergo a transition from one energy state to another forms the basis of spectroscopic methods of elemental analysis. Transitions in the valence shell electrons involve light in the visible and ultraviolet regions of the electromagnetic spectrum, whereas radiation of X-ray frequencies is absorbed or emitted during transitions between energy states of the inner shell electrons. Spectroscopic methods are grouped according to the spectral region studied and the method of excitation, and also by whether the absorption or emission of radiation is measured.

1.2.2.1 Arc-spark spectroscopy

In arc excitation the elements in a solid matrix are vaporized and excited by the heating effect of the discharge; the lines emitted arise principally from neutral atoms. By contrast, an a.c. spark excites predominantly ionic spectra; because of its lesser heating effect the direct analysis of solutions is possible. Complex spectra are excited by both methods so that a monochromator with medium to large dispersion is required to isolate spectral lines for measurement. Modern instruments have multichannel direct-reading spectrometers, which measure the intensity of lines electronically, using an internal standard to compensate for source fluctuations.

1.2.2.2 Flame spectrophotometry

The sample, in solution form, is nebulized into the oxidant gas stream of a flame and because of the relatively low temperatures, the atomic and molecular spectra excited are comparatively simple so that less sophisticated dispersive devices are required to isolate the spectra lines for measurement. The methods are versatile and modern instruments have excellent precision. Nitrous-oxide-supported flames greatly extend the range of analyses possible and most elements of the periodic table can now be determined by flame methods; there remain practical difficulties in the determination of H, C, N, O and F, sensitivity for a few elements is relatively poor (e.g. Ce, Th, U), and although flame methods are available for Ce, Br, I, P and S, these have not been applied in silicate analysis. There remain sixty or more elements for which methods are readily available and comprehensive analysis schemes have been devised to take advantage of this versatility by combining a single decomposition of the sample with flame spectrophotometric analysis of the solution produced (Medlin *et al.* 1969; Boar and Ingram 1970).

Two main types of measurement are made in flame spectrophotometry. In *atomic emission* methods, the analyte atoms are excited by collision with flame gas molecules and a portion of the radiation emitted when excited atoms are deactivated is measured; the intensity of radiation is proportional to the concentration of excited atoms, the number of which is a small fraction (usually much less than one-hundredth) of the total number of atoms in the flame. Band

emission from molecular species in the flame may also be used analytically, for instance, in the methods for the non-metals mentioned above.

In *atomic absorption*, the analyte atoms are excited by an external light source and the fraction of radiation absorbed is measured. In practice this measurement is best made with radiation from a sharp line source containing the element being determined; the incident radiation is modulated and the measurement system ideally detects only modulated radiation, rejecting unmodulated direct emission from the flame. In this way, the inherently narrow line width of atomic lines is used to enhance the effective resolution of the spectrophotometer and to eliminate spectral interferences (for example, the measurement of small amounts of Mg at 2852.1 Å in the presence of Na, emitting at 2852.8 Å). Under ideal conditions, the absorbance ($= \log I_0/I$) is proportional to the concentration of atoms in the flame; in practice, calibration lines are sometimes curved. Its chief disadvantage is that normally only one element is measured at a time.

A full discussion of the relative merits of the methods is beyond the scope of this chapter. Winefordner *et al.* (1970) have critically reviewed the analytical possibility of flame techniques and list detection limits for 68 elements. Dean (1960) discusses the general principles of flame emission methods, though some of the applications he lists are now superseded. Texts by Slavin (1968), Ramirez-Munoz (1968) and Rubeska and Moldan (1969) deal specifically with atomic absorption; Dean and Rains (1969) consider fundamental topics of general importance in all three methods and the text edited by Mavrodineanu (1970) contains articles of particular value for the practical use of all these techniques.

1.2.2.3 Non-flame atom cells

Atomization by injection of aerosol into a flame is so inefficient (1–15% for the premix burners necessary for precise measurements by atomic absorption) that very large improvements in sensitivity are possible with more efficient atomization. Vapour phase analysis by atomic absorption will determine 10^{-8} to 10^{-9} g Hg; this technique is vital in pollution studies but unlikely to be needed in silicate analysis. More generally useful to the silicate analyst is the production of atoms by heating solid or dried solutions in a graphite tube or on a graphite rod to temperatures in the range 2000–3000 °C. Advantages are the very small sample required and limits of detection 10^{-3} lower than are possible in flame cells. Disadvantages are that many interferences have been reported and good precision is difficult to achieve.

1.2.2.4 Plasma excitation

Plasma sources maintained by inductively coupled radio frequency heating are excellent media for exciting atomic spectra (Greenfield *et al.* 1964). In modern equipment, an aerosol of the solution to be analysed is fed into the centre of an argon plasma and the atomic emission focused into a multichannel spectrometer. This records the integrated intensity of 25 to 40 spectral lines simultaneously; for best accuracy, an internal standard may be included in the analyte solution (Thompson and Walsh 1983). As the plasma generates temperatures in the region 6000–10 000 K, interelement compounds are decomposed and there are no interelement interferences. Spectral lines overlap can however occur owing to the large number of lines excited, and these are allowed for in the computation using a dedicated microcomputer. The system is being used successfully in silicate analysis (Walsh 1980; Walsh and Howie 1980); clearly the multielement analysis facility has much advantage in rapidity, and good precision and accuracy are claimed. In a comparative study, Hannaker *et al.* (1984) found that there was close agreement between ICP and XRF for many elements in a wide concentration range.

1.2.2.5 X-ray emission spectrometry

In X-ray emission spectrometry the X-ray spectra of the elements in the sample to be analysed are excited either by electrons, as in the electron microprobe, or by X-rays in X-ray fluorescence spectrometry. Analysis is possible for elements from fluorine upwards in the periodic table using fluorescent X-rays. The spectra are analysed either by diffraction from large single crystals or in non-dispersive systems by solid state detectors in combination with multichannel analysers.

The electron microprobe is used to determine the elemental composition of very small volumes, a few cubic micrometres, in the surface of sections of rocks and minerals. Long (1977) has given an excellent review of the method and its application to mineralogical problems, and Sweatman and Long (1969) have carefully investigated factors affecting the accuracy of analyses. Weaver (1968) used the electron microprobe to study the distribution of impurities in kaolins. Although the method cannot be used to study compositional variations across small clay mineral flakes, it provides useful information about the chemical composition of impurities.

Analytical electron microscopy (Duncomb 1962; Cooke and Duncomb 1968) provides an even more powerful tool for studies of clay minerals and clay materials. This technique enables the correlation of features observed in the transmission electron microscope having a point to point resolution of less than 10 Å, electron diffraction data for areas less than 1 µm in diameter and chemical analysis from areas 1000 to 2000 Å in diameter. The method requires thin specimens, typically 1000 Å or less for silicates and requires analysed specimens for calibration (Lorimer *et al.* 1973; Cliff and Lorimer 1975; Lorimer and Cliff 1976). In this application the energy-dispersive technique has advantage over wavelength-dispersive systems because intensities of all the elements are measured simultaneously and are therefore independent of probe current.

The method has been used to compare the composition of different kaolinite flakes as small as 0.2 to 0.3 µm in diameter by Jepson and Rowse (1975) (i.e. particles with mass of the order of 10^{-13} g) with a coefficient of variation of about 3% for silicon and aluminium (see Section 1.4.1). Hayashi *et al.* (1978) made semi-quantitative analyses of asbestos fibres and clay minerals using analytical electron microscopy and Tazaki (1982) was able to show that spherical and crinkly forms of halloysite contained more iron than tubular forms. The same techniques enabled Veblen (1983a) to establish the compositional differences between the finely lamellar components of wonesite that had been detected by high resolution electron microscopy.

The most common analysis method using X-ray spectra of the elements is X-ray fluorescence spectrometry. Bulk samples may be analysed in the form of solids, pressed powders or liquids. When standards and unknowns differ little in composition direct comparison of intensities often gives acceptable results. Because matrix composition affects the intensity of the fluorescent X-rays, intensities are not directly proportional to amount when the composition of the standards is not close to that of the unknowns. For accurate analysis of samples with a range of compositions, corrections have to be made that take account of the effect of differences in composition on intensities. Methods for rocks and minerals for both major and minor elements have been reviewed by Norrish and Chappell (1977).

1.2.3 Matrix preparation

In the classical analysis scheme the mineral was fused with Na_2CO_3 and the glass dissolved in water. This obviously prevented the determination of sodium and a separate sample was required for the Lawrence Smith procedure. In the rapid schemes using flame photometric

determination of the alkali metals, the silica was volatilized by digestion with HF and a less volatile acid such as HClO_4 or HNO_3 , and the residue dissolved in dilute acid. Both schemes thus needed two digestions, and furthermore, some minerals resist decomposition by HF/ HClO_4 . To overcome these limitations, new decomposition methods were developed, based either on high-pressure HF decomposition or fusion with lithium metaborate.

Langmyhr and Sveen (1965) studied the decomposition of silicates by HF and concluded that a very wide range of minerals was decomposed if the vessel was pressurized so that the HF could be heated above its boiling point at atmospheric pressure. Decomposition vessels made from PTFE are now commercially available (Bernas 1968; Paus 1971) and analysis schemes have been based on the solutions obtained (Bernas 1968; Langmyhr and Paus 1968, 1969, 1970). Si is retained within the solution if the bomb is cooled before opening, and after addition of boric acid to complex fluoride, the solution may be analysed by colorimetric or flame emission and atomic absorption methods.

A more widely applied decomposition method is fusion with lithium metaborate (LiBO_2) followed by acid dissolution. Although first developed as a flux for colorimetric and spectrographic determinations (Ingamells 1966; Suhr and Ingamells 1966), it has been found to be an excellent technique for bringing silicates into solution (Ingamells 1970) prior to atomic absorption analysis (Medlin *et al.* 1969; Yule and Swanson 1969; Van Loon and Parissis 1969; Boar and Ingram 1970) or plasma emission methods (Hannaker *et al.* 1984).

1.2.4 Purity of samples

Clay minerals are seldom, if ever, monomineralic and before attempting to analyse a sample or use it for research, it is advisable to examine it by X-ray diffraction for the presence of other phases. If these are found, or the presence of X-ray amorphous substances is suspected, the clay can be purified by one or a combination of the following techniques.

1.2.4.1 Size fractionation

The aim is to prepare a stable dispersion of the clay sample that can be separated in different fractions by centrifugation. Soluble salts, e.g. gypsum, must first be dissolved by washing with water and the recommended treatment for dissolving CaCO_3 is heating with acetic acid buffered to pH 5 by the addition of sodium acetate. This reagent has the added advantage that when Na replaces Ca, Al and other flocculating cations on the clay surface, a stable dispersion is formed when the buffer is removed by washing. It is also recommended that organic matter removed by peroxidation with H_2O_2 is done in the same buffer, otherwise the excessive acidification that sometimes results may alter or even destroy the clay mineral present. Some manufacturers stabilize hydrogen peroxide with phosphoric acid and such reagents should *not* be used to peroxidize clays. It may also be necessary to remove free iron oxides by selective dissolution (see below, Section 1.2.4.4) as these can have a cementing or flocculating action on the clay. The principles and practice of fractional sedimentation are described in detail by Jackson (1956).

1.2.4.2 Magnetic separations

Clays frequently contain relatively small quantities of iron oxides which may adversely affect properties like colour and also make it impossible to calculate a structural formula for the layer silicate mineral fraction. The separation of iron oxides from aluminosilicates in soil clays is possible in a high field gradient magnetic separator (Schulze and Dixon 1979; Hughes 1982) and