

METHODS IN GEOCHEMISTRY

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CHAPTER I

INTRODUCTION

A. A. SMALES and L. R. WAGER

'The primary purpose of geochemistry is on the one hand to determine quantitatively the composition of the earth and its parts, and on the other to discover the laws which control the distribution of the individual elements. To solve these problems the geochemist requires a comprehensive collection of analytical data on terrestrial material, such as rocks, waters and the atmosphere; he also uses analyses of meteorites. . . .' In this way one of the greatest geochemists, V. M. Goldschmidt, described the scope of the subject.

Apart from questions of crystal structure, usually dealt with by X-ray or neutron diffraction, which are not discussed in this book, the problems involve the analytical determination of all the elements of the Periodic Table and often also the abundance of the isotopes of the elements.

Ideally the geochemist should be trained in geology and in chemistry, with some emphasis in the latter case on analytical chemistry. In practice this wide training is not always possible and the alternative is that those hoping to play a part in this exciting field should at least know in a general way the various links in the chain between the original site of the sample and the final data on it. It is a long way from the geologist's hammer to the mass spectrometer and the nuclear reactor which are now sometimes the tools the analyst uses.

The data obtained must be accurate and significant. To carry out a correct and reliable analysis may be a very difficult and time-consuming operation and it is not so easy as sometimes supposed. It is of little use spending weeks or months of careful laboratory work on a sample which is not representative, cannot be related to anything significant, or has been contaminated in collecting or preparing it. An early chapter therefore deals with the collection and preliminary treatment of the sample.

Considered from the analytical viewpoint, the problems can be roughly subdivided and each subdivision approximately coupled

with the analytical techniques required to deal with it. But it must be emphasized that there is often an almost embarrassingly wide choice of techniques for any given problem, and the selection of the best technique calls for the exercise of judgement based on experience. In special cases, it is well worth while to have determinations by more than one technique. This has proved to be of particular value in obtaining reliable data on the so-called 'standard samples' of rocks and most illuminating with regard to the significance which can be attached to some analytical figures.

The methods of analysis for the main constituents of rocks, minerals, etc., as used, for instance, to provide the information in Clarke's classic *Data of Geochemistry*, were almost entirely based on gravimetric, volumetric and absorptiometric techniques. There are several authoritative books on methods of this kind and no attempt to duplicate them is made here. In chapter three, Dr. Vincent has, however, selected for comment certain recent advances in this branch of analysis and has included a discussion of flame photometry which has become an important adjunct.

General survey of the amounts of minor elements was, until quite recently, almost wholly the province of emission spectroscopy, and the tremendous surge forward in the accumulation of data, using this technique, by Goldschmidt and others in the 1930s, is recognized by all geochemists. Again, only the general basis and recent developments are dealt with in the chapter by Professor Ahrens and Dr. Taylor. A competitor has recently re-entered this field in the shape of X-ray fluorescence spectroscopy. This method was also used in the 1930s, but has only blossomed into a rapid and reliable method with the development of highly efficient electronic counting equipment. Perhaps at the present stage it would be fairer to call it a potential competitor, but it is a method so full of promise that it has been dealt with in some detail by Mr. Shalgosky in chapter five.

Where very high sensitivity is required in the estimation of individual trace elements, the usual approach hitherto has been to combine some sort of chemical pre-concentration with emission spectrography. In the last few years, however, two additional methods of remarkable sensitivity have become available.

The first of these, the mass spectrometer isotope dilution method, owes much in its application to geochemical analysis, to the development of thermal ionization source mass spectrometers and to the availability of separated isotopes of a wide range of elements. It is described by Dr. Webster, following a

discussion of the basic techniques of mass spectrometry and the determination of isotope abundances, by Dr. Mayne.

The other comparatively recent development in analytical technique is that of radioactivation analysis. An introduction to the topic, giving general background in instrumentation and radiochemical operations by Mr. Moorbath, is followed in the next chapter by a full description of radioactivation analysis in relation to geochemistry by Mr. Mapper.

Although techniques have been broadly listed as applying to certain types of geochemical requirements, it must be remembered that there is no clear demarcation. Equally there are other techniques which are sporadically used but nevertheless are of considerable value; polarography is one of these which is dealt with in a separate chapter by Mr. Moorbath.

In almost all the high sensitivity techniques chemical separations are involved. These are so many and varied that a whole book could be written on them. We have nevertheless felt it important to have a final chapter by Dr. Cornish giving a basic account of three of the more important separation methods, particularly useful for, but not necessarily restricted to, the isolation of trace elements from their major partners and from each other. This chapter, in conjunction with that on radiochemical methods, should perhaps stimulate the design of special variants to meet specific analytic requirements.

This book is the result of a collaborative effort between geologists and chemists, each with a real interest in geochemistry and, fortunately, situated geographically almost in juxtaposition. It is our hope that chemists working in the borderline field of geochemistry will find the more geological parts of the book of value and that geologists wishing to know how analytical data are obtained, or planning to obtain them themselves, will find it of value in estimating the significance of data or in selecting methods. Finally we hope that students in the later stages of geological, geochemical and analytical chemistry courses will be able to get an overall picture of the many new analytical methods which, in good hands, are rapidly increasing the amounts of fundamental information about the composition of the earth as a whole and of its major parts.

CHAPTER II

COLLECTION AND PREPARATION OF MATERIAL FOR ANALYSIS

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The geochemist is concerned with the study of the materials making up the earth and also, because of similarities in the methods of investigation, with meteorites. From the point of view of collection, the materials for geochemical study may be divided into: (1) rocks, veinstones and individual minerals; (2) unconsolidated sediments and soils; (3) natural waters; (4) atmospheric, volcanic and other natural gases; and (5) vegetable and animal material. Some degree of detail is given here about the methods of collection and preparation for analysis of rocks and

minerals, but for the rest only a general indication can profitably be given as many *ad hoc* methods have to be devised to suit specific investigations.

2.1 COLLECTION AND SAMPLING TECHNIQUES

'The geologist should see that a fairly representative sample is provided, else the chemist's work, however careful, may count for little.' (Hillebrand *et al.*, reference 20, p. 809.)

In the majority of cases the geochemical investigations will come after a fairly detailed field study, in which case the distribution and relationships of the materials and the degree of variation within each type will be known. The collection of specimens should, if possible, be undertaken by a field scientist who should, at the same time, be conversant with the geochemical study envisaged. Indeed, it is well for the field man to be accompanied by the geochemist, as routine field work and specimen collection may omit precautions desirable in detailed collecting for geochemical study. For example, unless collected with the geochemical investigation in mind, the specimens may not be adequately representative of the material, or they may not be of sufficient bulk to provide a fair sample for analysis. The initial collecting should be sufficient in quantity, not only to provide material for bulk analysis but, in many cases, for separate analysis of the different constituents. It is always better to collect at one time all the material that may be required than to return a second time and hope to be able to collect, again, exactly the same type of material from exactly the same locality. Finally, it is desirable that after the geochemical work has been completed, there should be left over, for future reference, a representative sample of the material investigated.

2.1.1 Rocks, Veinstones and Minerals

The collection of a representative sample is usually dependent upon the geologist's intimate knowledge of the rocks and their relationships. Few geologists use any standard sampling methods (*cf.* Ingerson²²) but vary their practice according to the nature of the outcrop. In the simplest case of an extensive mass of homogeneous rock, one fresh piece large enough for several types of analysis would be sufficient. The desirable amount is much larger than the usual geological hand specimen which is only $20 \times 15 \times 10$ cm. It is always best to have plenty of both the uncrushed and

crushed rock in reserve; if it should happen that the material proves especially interesting there will often be a demand for samples, for comparison purposes, from other investigators.

In collecting fresh material from hard rock masses it is often necessary to use a large sledge hammer weighing, say, 15 lb. Where collection by hammering proves difficult, specimens may be obtained by blasting with explosives.

The amount of material to be collected as a representative sample will vary according to the nature of the problem and the accessibility of material. An indication of the ideal amounts required, supposing the rock body to be homogeneous and the rock grains approximately equi-dimensional, is given in Table I.

TABLE I

Grain size	Textural term	Sample weight, g
3 cm	Pegmatitic	5,000
1-3 cm	Coarse grained	2,000
1-10 mm	Medium grained	1,000
0-1 mm	Fine grained	500

after Mercy²⁰

If the rock is uneven in grain size, e.g. porphyritic, then it would be safest to consider the size of the largest grains, in using the table. Should the rock be heterogeneous, and the aim be to obtain average material, then much larger samples must be used. Pitcher and Sinha,⁴² for example, demonstrated the need for a bulk sample of 750 g of a heterogeneous fine-grained rock, to constitute a representative sample.

Sometimes a composite sample is made up of many specimens of about equal size; this has little merit for scientific investigations as opposed to economic, because the analysis does not represent any single sample which can be preserved for future investigation. As an ideal, Shaw and Bankier⁴³ recommended that to obtain the average composition of a rock several separate samples should be analysed and the results averaged. One reason for this is that the range in composition is as useful as the average value, or, in statistical terms, the standard deviation is as valuable as the mean. In practice, however, this ideal is seldom realized because of the labour and time it involves, and one analysis of material which is as representative as possible is usually sufficient.

If a composite rock mass is divisible into various homogeneous

units and if the area of the mass can be divided by a grid-system into sampling units, then a sampling technique on a statistical basis such as outlined below (page 8) can be used. However, for igneous and metamorphic rocks true random collection is usually impracticable and specimens are collected from a single point, along a traverse, or within an area or volume using traverses in two or three dimensions.

Average material of a single rock face can be obtained by channel-sampling, a common practice in mining. The surface is first cleaned to remove vegetation, soil, or weathered rind, after which the location of the desired channel is marked by two parallel chalk lines, usually between three and six in. apart depending upon the nature of the rock or of the ore body. The channel is cut out either with a prospector's pick, with a hammer and chisel, with a machine drill or by heat cracking. By using a block of wood, cut to the appropriate dimensions and fitted periodically into the channel, a standard width and depth can be approximately achieved.

Drilling, which provides a core, is a valuable means of obtaining a set of samples equivalent to an accurate traverse collection or channel sampling. The core is best split longitudinally, one half being used for analysis and the other kept for future reference. It is fortunate that there is an increasing tendency for drilling concerns to preserve carefully the whole length of a drill core rather than selected portions, thus providing a valuable source of material for fundamental investigations. A diamond-drill core if available will obviously be preferable to the sludge obtained from churn-drilling, although this sometimes provides useful material.

The collection of large-size minerals is clearly a different problem from that of collecting average rock. Usually a distinct crystal or a group of crystals are collected and sampling difficulties hardly exist.

2.1.2 Unconsolidated Sediments

The less consolidated materials, usually occurring near the surface, can be collected more easily than the solid rocks. For example, collection from a vertical exposure of incoherent sand can be effected by drawing a geological hammer from the top of the bed downwards and collecting the dislodged sand in a canvas bag held at the bottom of the face. Plastic rocks such as clays, on the other hand, have to be cut out with a knife (Milner³¹).

To obtain shallow sub-surface samples of soft rocks such as clay, sand, silt and marl, Milner (reference 31, p. 17) describes a simple auger drill. It is made from a carpenter's auger attached to a length of gas pipe which is provided with a *T* piece for turning. Holes up to 20 ft in depth can be made by handturning alone, in favourable sediments. The samples obtained are those held in place in the convolutions of the bit, adhering chiefly with the aid of moisture; collection of loose, dry sand is therefore aided by a slight water-flush.

Sampling procedures have been particularly developed for soils, and the methods can generally be applied to the other materials described in this section. Workers in this field have emphasized that the accuracy of a soil analysis is dependent to a greater extent upon the soundness of the initial sampling process than on the sub-sampling and analysis (Cline⁵).

The soil may be considered a population of sampling units that vary among themselves both horizontally and vertically. The selection of sampling units depends upon the objective, but for obtaining an unbiased estimate of the mean, incomplete randomization by means of a grid superimposed at random is satisfactory. As suggested by Snedecov⁴⁷ it is often safer to instruct non-technically trained men to sample by a grid than to sample 'at random', while Cline (reference 5, p. 279) emphasizes that walking 'at random' over an area when selecting sampling units is far from complete randomization and is subject to strong personal bias. When using a grid, however, special precautions must be taken to avoid superimposing the grid parallel to some systematic variation in the soil.

It is important to remember in soil analysis that the chemical properties of soils vary not only horizontally and vertically, but also with time. Cline (reference 5, p. 280), for example, records unpublished data showing wide seasonal fluctuation of interchangeable potassium as determined by rapid chemical methods, and insists that samples which are to be compared should be taken at the same season, and that the possible effects of varying weather conditions or crops be considered.

The collection of sediments from the sea floor requires special devices selected according to the character of the deposit and the depth of water (Sverdrup, Johnson and Fleming⁵⁰). Dredges, snapper samplers and coring tubes are the main devices used, the two former being used mainly where the sea floor is covered with rock fragments. The momentum-type coring instrument sinking under its own weight may take cores up to about 5 m in length

in soft sediments at depths of up to 2,000 m, while a corer devised by Piggott⁴⁰, which is driven into the sediment by an explosive charge, is useful at depths greater than 4,000 m. Long cores of up to 65 ft have been obtained with Kullenberg's piston corer (Pettersson, reference 39, p. 34).

The bottom sample collected in a coring tube will be compacted, the amount varying between about 25 and 50 per cent, and this may have a marked effect upon the sample's stratification (Emery and Dietz¹⁰). Distortion of the core due to friction with the sides of the tube is considerable in some corers. Volchok and Kulp (reference 51, p. 236), in assessing the accuracy of dating deep sea sediments by the ionium method, considered the errors resulting from core-sampling but concluded that these were much less important than the errors of radium measurements. A common source of error is loss of rather fluid surface material from the top of the core during handling. The bottom samples may be conveniently preserved in Mason jars fitted with rubber washers, no additional water or preservative being added. However, if a subsequent mechanical size operation is contemplated it is advisable to keep the specimen in sea-water.

2.1.3 Natural Waters

Included under this heading are waters collected from such diverse sources as the oceans, fjords, rivers, lakes, springs, reservoirs, artesian basins, oilfield brines, rain, snow, ice, geysers and fumarole condensates.

Water sampling at the deeper levels of the oceans requires the use of vessels which can be closed by remote control at any desired depth, and which usually carry also a reversing thermometer to record the temperature at that depth. The chief devices are described by Sverdrup, Johnson and Fleming (reference 50, p. 352), and include particularly the Nansen bottle (capacity 1,200 ml). The bottles must be of non-corrosive material and are usually made of brass, plated inside with tin or silver, coated with a special lacquer, or lined with glass.

The sea-water collected in these special bottles is usually transferred immediately to either 35-l. glass bottles or 5-l. polyethylene flasks, but in some cases it may be evaporated on board ship and preserved as a wet salt in a plastic tube. In a study of the relative abundance of the boron isotopes in sea-water, Parwel, Ubisch and Wickman (reference 38, p. 187) were provided with both sea-water

and wet salt specimens, the former being evaporated to the desired volume.

Collection from shallow bodies of water is usually done simply by filling polyethylene or glass bottles. In the investigation of oxygen isotope ratios Dansgaard⁷ advised, in order to avoid ^{18}O enrichment due to evaporation, that fresh water should be collected from large reservoirs, where it is being constantly replenished, or from rivers in preference to lakes. Krauskopf (reference 26, p. 11), in studying the concentrations of 13 rare metals in sea-water, could not use the samples obtained from a 26 m depth in Oslo fjord for lead determinations because it had been pumped through lead pipes. Apart from errors through addition to the sample of elements sought, there may also be loss to the walls of the pipes or containing vessel. Krauskopf (reference 26, p. 11) ran a series of experiments on water acidified with HNO_3 immediately after collection, in order to prevent adsorption of ions or organic matter on the glass walls of the containing vessel. Comparison, however, with results from sea-water which had stood in a soft glass container for several weeks showed no significant differences, and hence the sea-water was used directly for most experiments.

The collection of rain-water is described in some detail by Gorham (reference 15, p. 231) in a recent study of the acidity and salinity of rain.

2.1.4 Natural Gases

Under this heading are included only gases which are collected from natural occurrences in the gaseous state; thus gases extracted in the laboratory from rocks and minerals are only mentioned briefly in the final paragraph.

Atmospheric samples at ground level can be easily collected by pumping air directly into the analytical apparatus, providing local contamination can be neglected.

In collecting atmospheric carbon dioxide, Craig (reference 6, p. 71) found that to collect by absorbing the gas in solutions of $\text{Ba}(\text{OH})_2$ resulted in some isotopic fractionation. This was avoided if collection was carried out by running air slowly from outside the laboratory through a glass trap cooled in liquid nitrogen.

The collection of air from high altitudes by aeroplane, balloon or rocket is carried out by using evacuated glass bulbs or large evacuated steel cylinders with automatic stopcocks. The use of a simple evacuated vessel as a collecting chamber at high altitudes

means that the amount of material collected is greatly limited by the size of the vessel which the balloon or rocket can carry. Simon⁴⁶ has described a method by which a vessel is sent up cooled by liquid hydrogen, capable of condensing at one-tenth of an atmosphere pressure about 10,000 times as much material as it could otherwise take up. By this means a sample of 50 l. was collected, for example, from a height of 6,000 m.

The collection of volcanic gases from an active vent has been described by Day and Shepherd,⁸ Jaggar²³ and Shepherd.^{44, 45} These workers collected and analysed gases from Kilauea, an active vent on Hawaii, by driving a specially designed evacuated tube (with a tip which is easily broken) into vents which are safely accessible and have a gas flow strong enough to maintain a steady flame outside the orifice. The problems involved in collection and avoiding contamination are discussed by Shepherd.⁴⁴ The gases from hot springs and geysers are probably best collected by a simple method, using a glass funnel, described by Craig (reference 6, p. 56) for the Yellowstone National Park, U.S.A. Magmatic gases are often obtained from rocks, by heating them under reduced pressure. The early development of this technique was by Shepherd.⁴⁴ Many investigators consider that these provide a more significant sample than can be collected at a volcanic vent.

2.1.5 Vegetable and Animal Material

In the collection and sampling of modern organic material, in contrast with that which occurs in fossilized or reconstituted form such as oil and coal, a knowledge of the anatomy and physiology of the specimens is desirable in view of the tendency in living organisms for elements and isotopes to suffer fractionation in different parts of the organism.

The methods of sampling in biogeochemistry have been considered by Warren, Delevault and Fortescue.⁵² They have demonstrated the importance of always sampling the same part of the plant when comparisons are to be made, such as in geochemical prospecting. In a study of the variation of the stable carbon isotopes of terrestrial plants, Craig⁶ took into consideration such factors as geographical and geological environment, variation with date of sample collection (covering a period of 58 years), variation within different parts of the same plant, etc.

2.2 CRUSHING FOR BULK ANALYSIS

Solid materials are usually analysed as a small sample of fine powder which must be representative of the original specimen. The preparation of this powder requires special methods of size reduction to reduce to a minimum errors introduced by loss of rock dust, contamination in crushing or sieving and inaccurate sample-splitting.

Before crushing, the specimen should be examined to see that it is not contaminated with smears of steel from a hammer, paint from labels, etc. It is desirable, also, to examine the material with a pocket-lens, or as a thin section under the petrographic microscope, to estimate the general mineral composition.

2.2.1 Crushing

The methods discussed in this section are small-scale ones for use in the laboratory. In the mineral dressing plants of mines, large-scale machinery is used such as jaw crushers, roll crushers, rod mills, ball mills, vibrating sizing screens and rotary sample splitters. Some of these machines have been adapted to the laboratory, thus making sample reduction a more automatic process.

Before crushing to prepare a rock powder for analysis, it may be necessary first to scrub the rock under running water, rinse in distilled water and carefully dry at room temperature, but if it is clean this stage should obviously be omitted. In crushing to prepare a sand for mineral separation (see page 19) preliminary cleaning is less essential.

Small pieces (1–2 cm diameter) are then obtained from the specimen, either by flaking off chips with a geological hammer, or breaking the specimen by hammering it on a small steel anvil. Alternatively, the rock may be broken between two steel jaws in a manually operated rock-splitting machine, such as the one shown in Fig. 1. Whichever method is used, the pieces selected for further crushing must be free from steel smears.

The small pieces of rock are usually then crushed in a hand percussion mortar of the type shown in Fig. 2. The block, cylinder and pestle are made of surface-hardened steel. The mortar will reduce pieces of 1–2 cm diameter directly to – 100 mesh, although some laboratories transfer 12 mesh material from the steel mortar to the automatic agate pestle and mortar for reduction to – 100 mesh. The pestle should not be struck with more than about six

light blows with the hammer, rotating it after each blow, before the material is emptied into a sieve. If struck skilfully there will be little or no steel contamination. The use of the eccentric head to the pestle tends to reduce matting of the fragments into a resistant cake.

An alternative method is to reduce the pieces of 1–2 cm diameter to –200 mesh with a manually operated hydraulic rock-crusher followed by a mechanically driven roller-crusher. In the hydraulic rock-crusher (Fig. 1) the jaws used for breaking the rock into 1–2 cm diameter pieces are replaced by two steel blocks (shown in position), crushing taking place between flat steel surfaces. From this crusher, a coarse grit (*ca.* 1 mm diameter) is obtained, and can be transferred directly to the roller-crusher.

The roller-crusher (Fig. 3) reduces the material from about 2 mm diameter to –200 mesh. This machine was designed in the Department of Geology, University of Manchester, specifically for rapid reduction of small pieces of rock to a powder, for silicate analysis, with the minimum of metallic contamination. The steel rollers are mounted slightly eccentrically, so that on rotation the gap between them alternately increases, allowing powder to fill it, and then decreases, crushing the packed powder. The left-hand set of rollers, carrying grooves parallel to their length, take the coarse pieces down to about 80 mesh, while the right-hand set take this sand down to a powder, at –200 mesh, suitable for most types of analysis. The distance between the rollers is adjustable and is progressively narrowed as the material becomes finer in grain size.

The above methods of crushing are used satisfactorily at Oxford, but other laboratories employ different methods. For example, Fairbairn's laboratory (Fairbairn¹¹) reduces rock samples to a sand by employing a hydraulic-type chisel, laboratory jaw breaker and a disc grinder, in that order.

Any grinding action is more liable to produce steel contamination than straight crushing, and in certain investigations the degree of contamination should be measured. Hard steels are susceptible to abrasion by minerals softer than quartz, while quartz itself will become darkened by metallic contamination when a grinding motion is substituted for a crushing motion. This effect is described by Hillebrand *et al.* (reference 20, p. 810) who recommend that a crushed, non-metallic test sample be ground to a very fine powder in the presence of water. The steel film, if present, will then rise as a visible scum to the surface and can be removed with a magnet. In other cases a spectrographic test may be made.

Whatever method is employed in crushing, powder-loss must